



Science of Synthesis

Houben-Weyl Methods of Molecular Transformations

Sample Contributions

<i>Category</i>	1	Organometallics
<i>Volume</i>	2	Compounds of Groups 7–3
<i>Product Class</i>	2.6	Organometallic Complexes of Chromium, Molybdenum, and Tungsten without Carbonyl Ligands
<i>Written by</i>		R. Poli and K. M. Smith
<i>Category</i>	2	Hetarenes and Related Ring Systems
<i>Volume</i>	14	Six-Membered Hetarenes with One Chalcogen
<i>Product Class</i>	14.11	Selenopyranones and Benzoselenopyranones
<i>Written by</i>		P. J. Murphy

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Product Class 6: Organometallic Complexes of Chromium, Molybdenum, and Tungsten without Carbonyl Ligands

R. Poli and K. M. Smith

General Introduction

Almost all of the complexes described in this product class are air- and/or moisture-sensitive, both as solids and in solution. Prior to use all solvents should be dried and distilled under nitrogen or argon, and the compounds should be synthesized, handled, and stored under an inert atmosphere using Schlenk or glovebox techniques. The bonds between group 6 metals and carbon are often readily hydrolyzed, with the notable exception of several alkylchromium(III) species. In general, these compounds are less sensitive to oxygen when the metals are formally in the +6 oxidation state, and are thus incapable of being oxidized further, although the extreme atmospheric sensitivity of molybdenum(VI) ring-closing metathesis catalysts (Section 2.6.1.5.3) provides a striking exception to this trend.^[1]

Due in part to their hydrolytic instability, the toxicity of the organometallic complexes described in this product class have generally not been investigated. A prominent exception is dichlorobis(cyclopentadienyl)molybdenum(IV), which has been studied as an antitumor agent.^[2,3] Purely inorganic compounds of chromium(VI) are well-established carcinogens, in contrast to the relatively low toxicity characteristic of chromium(III) species. While chromium(III) compounds are not readily transported through cell walls, the negative charge and tetrahedral structure of the chromate dianion makes it analogous to the phosphate and sulfate ions, and so chromium(VI) is brought into the cell via nonspecific anion transport channels. Chromium(VI) is then reduced to chromium(III) inside the cell, leading to the DNA lesions responsible for the carcinogenic activity.^[4] In the absence of more detailed toxicity studies for organometallic group 6 complexes, care should be taken when handling all the compounds in this product class.

Product Subclass 1: Metal–Carbene Complexes

While group 6 complexes containing carbonyl ligands (Fischer-type) are most common for chromium, those without carbonyl ligands (Schrock-type, also called alkylidene complexes) are more typical of molybdenum and tungsten. Although a few chromium examples are known,^[5] our attention will be almost completely devoted to molybdenum and tungsten systems. These complexes are generally found in high oxidation states (≥ 4) and supported by electronegative, π -donor ligands (alkoxo, amido, imido). These ligands have the possibility of stabilizing low-coordination environments by π -donation in excess of the valence requirement (e.g., $\sigma + 2\pi$ M=O or M=NR for oxo and imido derivatives), resulting in tetrahedral species. Often, however, these complexes allow expansion of the coordination sphere by formation of dimers (e.g., halide bridged) or by addition of a two-electron donor with formation of five-coordinate and occasionally six-coordinate species, the formation of which is more likely for tungsten than for molybdenum and when the metal bears electron-withdrawing ligands.^[6]

Group 6 metal–carbene complexes are most stable when devoid of β -hydrogen atoms on the carbene ligand, the latter leading to decomposition by 1,2-H migration and formation of alkene derivatives.^[7] The carbene ligand usually bears hydrogen or alkyl substitu-

ents, and is normally considered as a dinegative ($=CR^1R^2$)²⁻ ligand for the purpose of formal oxidation state assignment. Like all other Schrock-type carbene complexes, those of group 6 metals present marked nucleophilic reactivity and undergo Wittig chemistry with X=Y molecules, the thermodynamics favoring the M=X and R₂C=Y combination where X is harder than Y.^[8] This reaction, however, does not represent particular advantages over classical Wittig reagents for organic synthesis, a major use being the metal removal at the end of organic transformations carried out on carbene complexes (e.g., alkene metathesis, see Section 2.6.1.5).

Synthesis of Product Subclass 1

2.6.1.1

Method 1:

By α -Hydrogen Elimination from Alkyl Complexes

High oxidation state dialkyl complexes may undergo transfer of an α -hydrogen atom from one alkyl ligand to the second one under suitable conditions, with formation of a carbene product and elimination of alkane. The reaction is favored by an increase of steric bulk in the metal coordination sphere. This has been achieved in a number of ways, as outlined in the following variations.

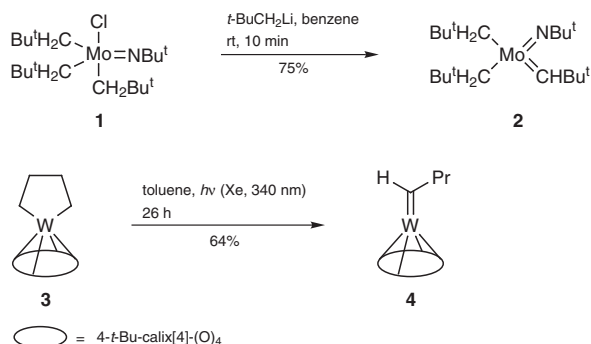
2.6.1.1.1

Variation 1:

Alkylation of Chloride Precursors

The replacement of a halide with a bulky alkyl group is often sufficient to induce the alkane elimination process. Thus, while the complex *tert*-butylimidochlorotris(2,2-dimethylpropyl)molybdenum(VI) (**1**) does not spontaneously undergo the α -hydrogen elimination process, substitution of the chloride ligand with a fourth 2,2-dimethylpropyl ligand directly affords the carbene product **2** (Scheme 1).^[9] For the analogous tungsten system, tetraalkylimido intermediates, e.g. phenylimidotetrakis[(trimethylsilyl)methyl]tungsten(VI), have been isolated, and their slow first-order elimination to the alkylidene product has been investigated.^[10] Other alkane eliminations from stable dialkyl derivatives may be induced by simple irradiation,^[11,12] e.g. the transformation of **3** into **4**.^[13]

Scheme 1 α -Hydrogen Elimination Induced by Alkylation^[9,13]



{4-*tert*-Butylcalix[4]-(O)₄}butylidenetungsten(VI) (**4**):^[13]

A soln of W(cyclo-C₄H₈){4-*t*-Bu-calix[4]-(O)₄} (8.45 g, 8.77 mmol) in toluene (200 mL) was irradiated with a Xe lamp (540 W·m⁻² at 340 nm) for 26 h. Volatiles were removed in vacuo, pentane (60 mL) was added to the residue, and pale brown **4** was collected and dried in vacuo; yield: 5.62 g (64%); ¹H NMR (benzene-*d*₆, δ): 10.0 [t, ³J = 7.5 Hz, 1H, WC(Pr)H], 5.47 [m, 2H, WC(H)CH₂CH₂CH₃], 1.69 [m, 2H, WC(H)CH₂CH₂CH₃], 1.15 [t, ³J = 7.2 Hz, 3H, WC(H)-

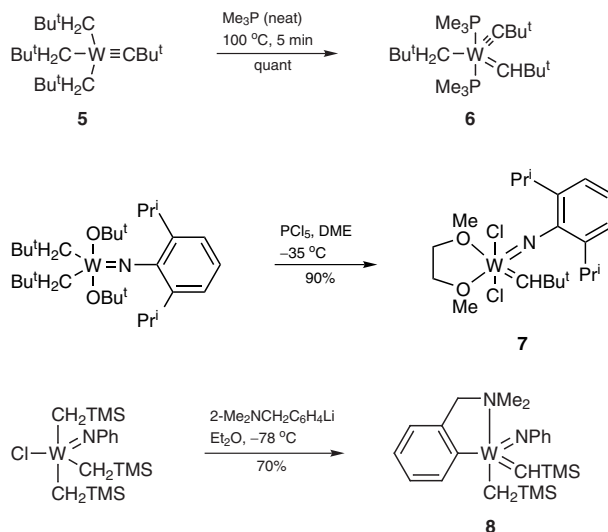
$\text{CH}_2\text{CH}_2\text{CH}_3$]; ^{13}C NMR (benzene- d_6 , δ): 272 [d, $\text{WC}(\text{Pr})\text{H}$, $^1J_{\text{CW}} = 180$ Hz, $^1J_{\text{CH}} = 142$ Hz], 41.6 ($\text{WCCH}_2\text{CH}_2\text{CH}_3$), 29.5 ($\text{WCCH}_2\text{CH}_2\text{CH}_3$), 14.5 ($\text{WCCH}_2\text{CH}_2\text{CH}_3$).

2.6.1.1.2 Variation 2: Ligand Addition

When di- or polyalkyl complexes do not spontaneously give rise to α -hydrogen elimination, this process may often be accomplished by addition of two-electron ligands (e.g., phosphines).^[14,15] Thus, the tris(2,2-dimethylpropyl)(2,2-dimethylpropylidyne)tungsten complex **5** transforms into the (2,2-dimethylpropyl)(2,2-dimethylpropylidene)(2,2-dimethylpropylidyne) product **6** upon addition of trimethylphosphine (Scheme 2). The conditions required to induce this process depend on the system, from -78 °C for dibromotetrakis[(trimethylsilyl)methyl]dimolybdenum(III)($\text{Mo}\equiv\text{Mo}$)^[15] to room temperature for cyclopentadienylbis(2,2-dimethylpropyl)nitrosylmolybdenum(II).^[16]

In the synthesis of compound **7**, substitution of two alkoxide ligands with the less sterically encumbering (and also poorer π -donor) chlorides opens up the coordination sphere to the coordination of a bidentate 1,2-dimethoxyethane molecule, inducing carbene formation. The dialkoxo precursor, albeit five coordinate, does not spontaneously undergo the alkane elimination process.^[17] The increase of the coordination sphere can also be achieved by replacement of a monodentate ligand (e.g., chloride) with a polyfunctional ligand, e.g. hydrotris(pyrazolyl)borate^[18] or 2-[(dimethylamino)methyl]phenyl (see synthesis of **8**) (Scheme 2).^[19] This strategy has also been utilized in other cases via replacement of a bulky alkyl with chloride by protonation with $\text{LH}^+ \text{Cl}^-$ in the presence of excess ligand L.^[10]

Scheme 2 α -Hydrogen Elimination Induced by Ligand Addition^[14,17,19]



Dichloro[(2,6-diisopropylphenyl)imido](1,2-dimethoxyethane-*O,O'*)(2,2-dimethylpropylidene)tungsten(VI) (**7**); Typical Procedure:^[17]

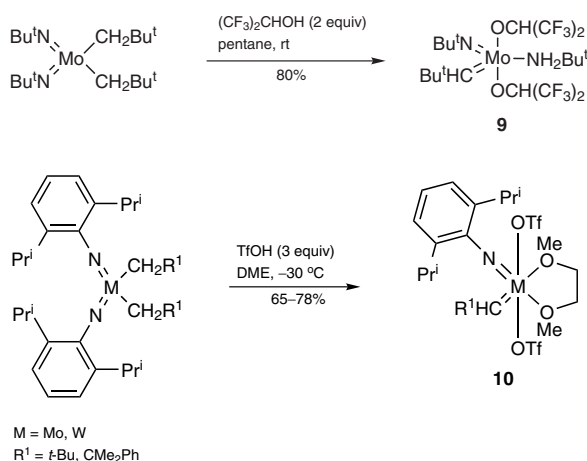
Finely ground PCl_5 (2.25 g, 10.8 mmol) was added to a chilled (-35 °C) soln of $[\text{W}(\text{CH}_2t\text{-Bu})_2(\text{Ot-Bu})_2](=\text{NC}_6\text{H}_3-2,6\text{-iPr}_2)$ (7.0 g, 10.8 mmol) in DME (120 mL). The mixture was warmed to rt and stirred for an additional 1 h after all the solids had disappeared. The mixture was then concentrated in vacuo until an orange powder formed. This material was washed with cold pentane to give the product as a yellow-orange powder. This synthesis can fail virtually completely if the DME is not scrupulously dried and the PCl_5 not

rigorously purified; yield: 5.75 g (90%); $^1\text{H NMR}$ (benzene- d_6 , δ): 9.97 (s, $J_{\text{HW}} = 7.3$ Hz, CHt-Bu); $^{13}\text{C NMR}$ (benzene- d_6 , δ): 283.8 (d, $\text{W}=\text{C}$, $J_{\text{CH}} = 114$ Hz, $J_{\text{CW}} = 163$ Hz).

2.6.1.1.3 Variation 3: Replacement of an Oxo or Imido Ligand

Replacement of an oxo^[20–22] or imido^[23] ligand with two singly bonded heteroelement ligands has often proven to be an efficient method for inducing the α -elimination process from dialkyl compounds. Examples of syntheses of these types are shown in Scheme 3. The interaction between a dialkoxodialkyloxo complex of tungsten(VI) and a Lewis acid (AX_n , viz. aluminum trichloride, tin(IV) chloride, magnesium bromide, etc.) proceeds via an isolable adduct containing the $\text{W}=\text{O}-\text{AX}_n$ moiety when conducted in hexane, which then yields the dialkoxodihalocarbene product.^[24] Although this procedure is not general, subsequent ligand exchange or stoichiometric alkene metathesis (see Section 2.6.1.2) allows the preparation of a much broader series of derivatives.^[21,22] Lewis base adducts such as compound **9** easily undergo exchange of the Lewis base, or can be converted into the base-free material. The reaction yielding **10** is the most convenient entry into the catalytically active dialkoxo(alkylidene)imido complexes of molybdenum and tungsten, since the trifluoromethanesulfonate ligands can be easily replaced with a variety of alkoxide groups, and the dialkyldiimido precursor complex is readily available in two high-yield steps from commercially available dichlorodioxotungsten(VI) or ammonium dimolybdate.^[17,25]

Scheme 3 α -Hydrogen Elimination Induced by Substitution of Oxo or Imido Ligands^[8,17,23,29]



[(2,6-Diisopropylphenyl)imido](1,2-dimethoxyethane-*O,O'*)(2,2-dimethylpropylidene)-bis(trifluoromethanesulfonato-*O*)molybdenum(VI) (10**, M = Mo; R¹ = *t*-Bu);**

Typical Procedure:^[8]

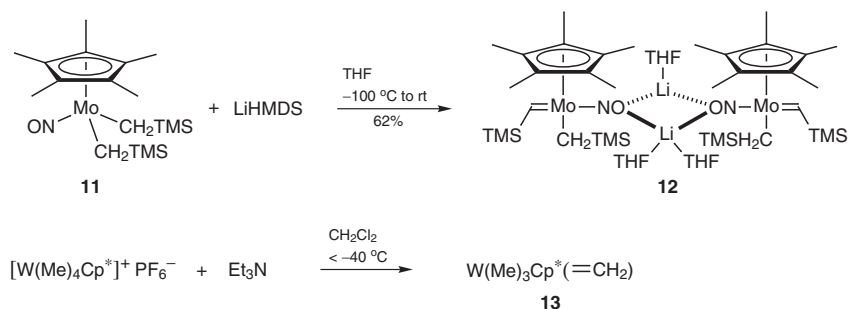
A prechilled soln of TfOH (3.15 mL, 35.5 mmol, 3 equiv) in DME (20 mL) was added in a dropwise manner to an orange soln of $\text{Mo}(\text{CH}_2\text{t-Bu})_2(=\text{NC}_6\text{H}_3-2,6\text{-iPr}_2)_2$ (7.00 g, 11.8 mmol) in DME (200 mL) at -30°C over a period of 10 min. [It is important in this step that the soln be homogeneous and cold. It is best to grind the crystals of the molybdenum starting complex to a fine powder to aid dissolution; the addition of some pentane (15–30 mL) may facilitate this step.] The soln was allowed to warm up to rt and stirred for 3 h. During this period the color changed from orange to dark yellow. The solvent was evaporated in vacuo to yield a yellow solid, which was then extracted with cold toluene (100–150 mL). The

extract was filtered through a bed of Celite and the toluene removed from the filtrate in vacuo to give the product as yellow flakes. The product should be checked by NMR for contamination by anilinium trifluoromethanesulfonate, which is slightly soluble in toluene; yield: 5.9 g (65%); ^1H NMR (benzene- d_6 , δ): 14.29 (s, *CH*-Bu); ^{13}C NMR (benzene- d_6 , δ): 331.9 (d, Mo=C, $^1J_{\text{CH}} = 121$ Hz).

2.6.1.1.4 Variation 4: Deprotonation with an External Base

Deprotonation of alkyl ligands at the α -position is another potentially general method for forming carbene complexes from alkyl compounds that are either electronically unsaturated or possess labile ligands. However, this method is little documented for group 6 metals as well as for metals of other groups. The neutral dialkyl compound **11** reacts with a range of lithium reagents to yield the dimeric, anionic alkyl–alkylidene complex **12**, as shown in Scheme 4.^[26] Methylidene product **13** is only stable at low temperature, decomposing upon warming in a nonselective manner to yield alkylidene-bridged dinuclear products.^[27]

Scheme 4 Deprotonation of Alkyl Complexes^[26,27]



Bis{nitrosyl(η^5 -pentamethylcyclopentadienyl)}[(trimethylsilyl)methyl][(trimethylsilyl)-methylidene]molybdenum(II) (Dilithium)tris(tetrahydrofuran) (**12**):^[26]

[Mo(CH₂TMS)₂Cp*(NO)] (200 mg, 0.46 mmol) and LiHMDS (90 mg, 0.46 mmol) were intimately mixed and cooled to -100°C in a small flask. THF was slowly poured down the sides of the flask and allowed to freeze onto the solid mixture. Over the course of 4 h, a color change from purple to red occurred; the final mixture was taken to dryness in vacuo. The remaining red solid was extracted into pentane (2 mL), and the extracts were filtered through Celite. Slow evaporation of the pentane filtrate resulted in the deposition of pale red crystals, which were recrystallized (pentane) to obtain pale yellow crystals of **12**; yield: 143 mg (62%).

2.6.1.2 Method 2: By Stoichiometric Alkene Metathesis

The addition of an alkene to a carbene complex may lead to a metathesis reaction with exchange of the carbene ligand with one of the two halves of the alkene. The reaction proceeds via formation of an alkene–carbene complex, which rearranges via a metallacyclobutane intermediate.^[28] This reaction is synthetically useful when a terminal alkene is used and vacuum evaporation of the more volatile alkene product (typically 3,3-dimethylbut-1-ene) is possible to displace the equilibrium.^[22] An excess of the alkene reagent is also used to ensure a favorable equilibrium position (see Scheme 5). The properties of the an-

cillary alkoxide ligands can influence whether this reaction results in metathesis or the formation of stable tungstacyclobutane derivatives (see Section 2.6.5).^[17,29]

Scheme 5 Stoichiometric Alkene Metathesis^[8,17,22]



M(L) _n	R ¹	R ²	Conditions	Yield (%) of [M(=CR ¹ R ²)(L) _n]	Ref
[WBr ₂ (OCH ₂ <i>t</i> -Bu) ₂]		(CH ₂) ₄	CH ₂ Cl ₂ , rt, 4 h	87	[22]
[Mo(=NC ₆ H ₃ -2,6- <i>i</i> Pr ₂)[OCMe(CF ₃) ₂] ₂]	H	TMS	pentane, -30 °C, 2.5 h	74	[8]
[W(OR ³) ₂ (=NC ₆ H ₃ -2,6- <i>i</i> Pr ₂)] ^a	H	Si(OMe) ₃	pentane, rt, 30 min to 2.5 h	50–78	[17]

^a R³ = 2,6-*i*Pr₂C₆H₃, CMe₂(CF₃), CMe(CF₃)₂.

Dibromo(cyclopentylidene)bis(2,2-dimethylpropan-1-olato)tungsten(VI);

Typical Procedure:^[30]

Methylenecyclopentane (0.36 mL, 3.42 mmol) was added to an orange soln of [WBr₂(=CH*t*-Bu)(OCH₂*t*-Bu)₂] (0.127 g, 0.215 mmol) in CH₂Cl₂ (10 mL). After 4 h, the volatiles of the red mixture were removed in vacuo, and the orange residue was washed twice with pentane to give the product as an orange powder; yield: 110 mg (87%); ¹³C NMR (CD₂Cl₂, δ, gated decoupled): 47.1 (t, ¹J_{CH} = 134 Hz, W=CCH₂), 28.2 (t, ¹J_{CH} = 131 Hz, W=CCH₂CH₂); the W=C signal could not be observed.

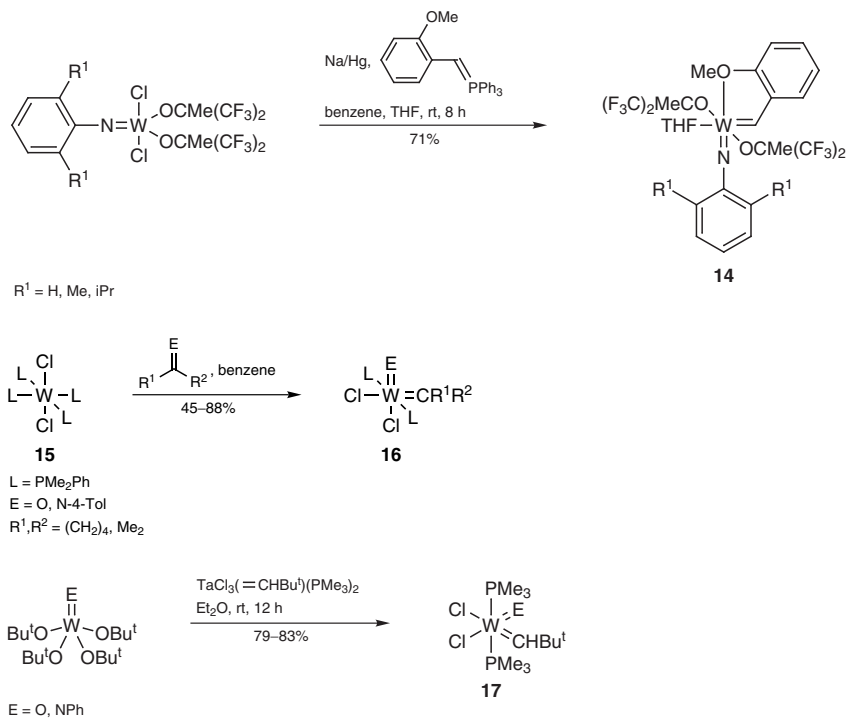
2.6.1.3

Method 3:

By Carbene Transfer

The carbene ligand may be either directly added to the metal center or exchanged for two X groups. The first strategy requires preparation of the metal in a reactive, reduced form. For the preparation of compound **14** (Scheme 6), this is achieved by sodium reduction of the dichloro precursor complex.^[31] The phosphorane carbene transfer agent is readily accessible with a variety of carbene functionalities and the triphenylphosphine byproduct does not coordinate with the metal center, allowing its easy removal by scavenging with copper(I) chloride. For the tungsten(II) system **15** (L = tertiary phosphine), even ketones and imines are sufficiently good carbene transfer reagents, providing alkylideneoxo and alkylideneimido tungsten(VI) products **16**, respectively, in remarkable four-electron oxidative addition reactions.^[32] For ketones different than cyclopentanone, stable and unreactive bis(η²-ketone) adducts are obtained by use of an excess of the ketone, but the use of one equivalent still leads to the alkylideneoxo product.

The exchange strategy involves the use of reactive tantalum alkylidene complexes, resulting in the replacement of alkoxo ligands. This method, which is also accompanied by the scrambling of other ligands, applies equally well to the synthesis of the oxo and imido tungsten products **17**,^[33] but is limited by the availability of the tantalum alkylidene reagent and has not been reported for molybdenum.

Scheme 6 Carbene Transfer^[31–33]

(2,6-Dimethylphenylimido)bis(1,1,1,3,3,3-hexafluoro-2-methylpropan-2-olato)(2-methoxybenzylidene-κC)(tetrahydrofuran)tungsten(VI) (14, R¹ = Me); Typical Procedure:^[31]

The compounds $[\text{WCl}_2\{\text{OCMe}(\text{CF}_3)_2\}_2(=\text{NC}_6\text{H}_3\text{-2,6-Me}_2)(\text{THF})]$ (16.0 g, 19.8 mmol) and $\text{Ph}_3\text{P}=\text{CH}(\text{C}_6\text{H}_4\text{-2-OMe})$ (7.78 g, 20.3 mmol) were dissolved in a mixture of benzene and THF (160 mL and 2.5 mL, respectively) and the resulting soln was added to 1% Na/Hg (3.59 g of Na, 7.90 equiv). After being stirred for 8 h at rt, the mixture was allowed to settle, and the orange-brown supernatant was added via a cannula to CuCl (2.07 g, 20.9 mmol). The residual Na/Hg was washed with Et₂O (120 mL), and the combined benzene/Et₂O soln was stirred with CuCl for 12 h before removal of the solvent in vacuo. The brown solid was then extracted with Et₂O (260 mL). After addition of THF (2 mL) to the extract and filtering, the soln was slowly cooled to -50°C to yield the product as an olive-yellow powder; yield: 12.0 g (71%); ¹H NMR (benzene-*d*₆, δ): 10.81 (s, W=CHAr).

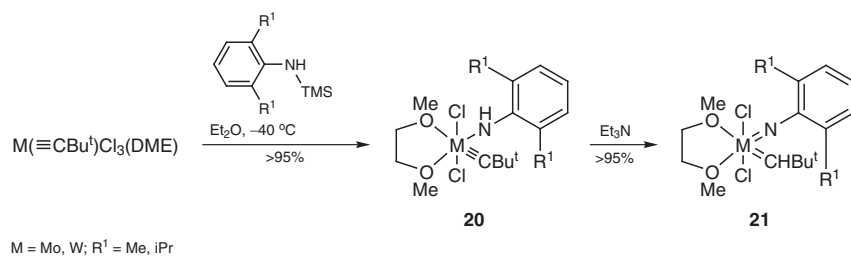
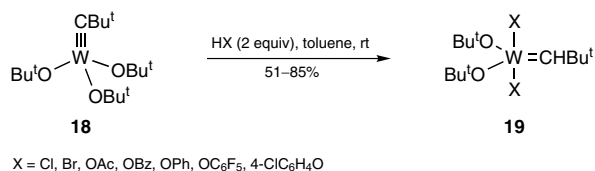
**2.6.1.4 Method 4:
From Carbyne Complexes**

Addition of a proton to a carbyne ligand may transform it into a carbene. The proton can be provided by an external source or by transfer from another ligand. Examples of the first kind are provided by the addition of acids to complex **18** (see Scheme 7).^[7] The use of pyridinium salts yields more stable pyridine adducts. This reaction can be reversed by the addition of a strong base (see Section 2.6.2). When an acid containing a noncoordinating anion is used, e.g. trifluoromethanesulfonic acid, cationic derivatives may be obtained.^[34] Depending on the nature of the coligands, the proton may preferentially add to another position in the molecule (see Section 2.6.2).

Internal proton transfer is observed for amido ligands. The reaction between the 1,2-dimethoxyethane adduct of trichloro(carbyne)molybdenum or -tungsten complexes and (trimethylsilyl)arylamines produces the stable intermediates **20**. The latter, however, re-

arrange by a base-catalyzed proton transfer to the final carbene–imido products **21**.^[8,17,29] These proton-transfer processes occur much more slowly or not at all for the dialkoxo analogues, although the anticipated proton-transfer products are stable systems. A mechanism of reversible amine-assisted dehydrohalogenation has been proposed for this transformation. This synthetic route is inconvenient for the molybdenum system, mainly because of difficulties in the preparation of the precursors to the trichlorocarbene complex of molybdenum. The tungsten analogue is more easily prepared (see Section 2.6.2).^[29] However, even the tungsten product is more conveniently prepared by another procedure [α -H elimination from a bis(2,2-dimethylpropyl) precursor, Section 2.6.1.1].^[17]

Scheme 7 Protonation of Carbyne Complexes^[7,8,17]



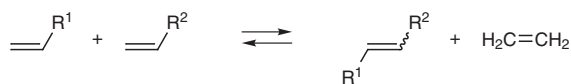
Di-tert-butoxodichloro(2,2-dimethylpropylidene)(pyridine)tungsten(VI); Typical Procedure:^[7]

The alkylidyne complex [W(≡Ct-Bu)(Ot-Bu)₃] (1.00 g, 2.12 mmol) was added at rt as a solid to a CH₂Cl₂ soln (25 mL) of pyridine hydrochloride (4.2 mmol). After 10 min the solvent was removed in vacuo and the residue was recrystallized (pentane) to yield the product as orange crystals; yield: 0.92 g (79%); ¹H NMR (benzene-*d*₆, δ): 10.76 (s, CHt-Bu); ¹³C{¹H} NMR (benzene-*d*₆, δ): 302.3 (CHt-Bu).

Applications of Product Subclass 1 in Organic Synthesis

2.6.1.5 Method 5: Alkene Metathesis

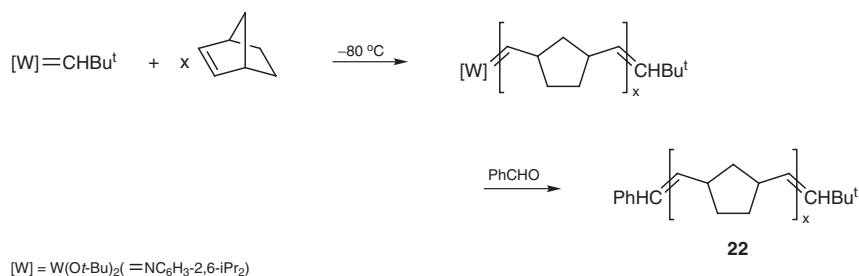
High-valent molybdenum–carbene complexes bearing electronegative ancillary ligands are efficient catalysts for alkene metathesis reactions (Scheme 8).^[20,35] This reaction proceeds via [2+2] cycloaddition and formation of metallacyclobutane intermediates, some of which have been isolated under controlled conditions (see Section 2.6.5.3).^[36] In order to make the reaction synthetically useful, it is necessary to have a driving force and high selectivities, and to suppress the self-metathesis if a cross-metathesis (e.g., R¹ ≠ R²) is desired. The driving force may be provided by conjugation or by formation of polymeric materials. Selective processes often result from the removal of a volatile byproduct, such as ethene.

Scheme 8 Alkene Metathesis

2.6.1.5.1

**Variation 1:
Ring-Opening Metathesis Polymerization (ROMP)**

The living polymerization of strained cyclic alkenes such as norbornenes and substituted norbornadienes is catalyzed by molybdenum and tungsten carbene complexes (Scheme 9).^[35] The living nature of this process allows control of the chain length and the preparation of block copolymers, which may also have a high level of tacticity.^[37] A Wittig-like capping reaction with aldehydes can be used to cleave the metal fragment off the living polymer. Essentially monodisperse products **22** with x up to 500 have been obtained from norbornene by using di-*tert*-butoxo[(2,6-diisopropylphenyl)imido](2,2-dimethylpropylidene)tungsten(VI) as a ROMP initiator.^[38] The catalyst does not attack the less reactive double bonds in the polymeric product. The use of 7,8-bis(trifluoromethyl)tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene as monomer gives oligomers from which polyenes with up to 15 conjugated double bonds have been obtained via a retro-Diels–Alder ejection of an arene upon thermolysis.^[39] Other substrates suitable for the ROMP process are substituted cyclooctatetraenes, leading to functionalized and soluble polyacetylenes of low polydispersities.^[40]

Scheme 9 Ring-Opening Metathesis Polymerization of Norbornene^[35]
1,4-Dihydro-1,4-methanonaphthalene, Homopolymer ($x = 100$); Typical Procedure:^[41]

A soln of 1,4-dihydro-1,4-methanonaphthalene (291 mg, 2.05 mmol) in toluene (3.0 mL) was added dropwise to a rapidly stirred soln of [Mo(=CH*t*-Bu)(O*t*-Bu)₂(=NC₆H₃-2,6-*i*Pr₂)] (10 mg, 0.020 mmol) in toluene (3.0 mL) and the soln was stirred for 20 min. The polymerization was quenched by addition of pivalaldehyde (25 μ L). After 20 min, the soln was added to hexane (250 mL), and the precipitated polymer was isolated by centrifugation, washed with hexane, and placed under vacuum overnight; yield: 280 mg (94%).

2.6.1.5.2

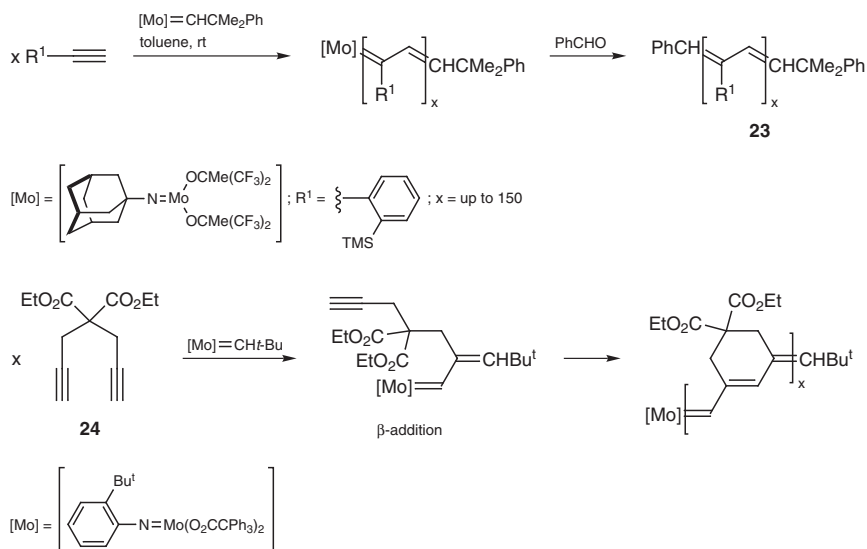
**Variation 2:
Alkyne Polymerization**

Terminal alkynes have yielded polyenes **23** with up to 150 conjugated double bonds under molybdenum–carbene catalysis (Scheme 10).^[42] The nature (in particular the size) of the ancillary ligands is important in controlling the selective α -addition. Acetylene itself produces insoluble and air-sensitive polymers that are difficult to characterize. Cyclopolymerization of dipropargyl derivatives such as **24** have been shown to yield polyenes of low polydispersity containing only six-membered rings, following a selective β -addition

for references see p 112

of the first triple bond.^[43] The nature of the coordination sphere on the carbene initiator is of capital importance, as polymers containing both five- and six-membered rings that are a consequence of an initial α - or β -addition, respectively, have been obtained with other initiators.^[44]

Scheme 10 Alkyne Polymerization^[42,43]



2,2-Diprop-2-ynylmalonic Acid, Diethyl Ester, Homopolymer (x = 20);

Typical Procedure:^[43]

Polymerization stock solutions of diethyl 2,2-diprop-2-ynylmalonate (**24**; 0.406 M) and $[\text{Mo}(\text{=CH}t\text{-Bu})(\text{O}_2\text{CCPh}_3)_2](\text{=NC}_6\text{H}_4\text{-}t\text{-Bu})$ (0.00676 M) in toluene that had been distilled over sodium benzophenone ketyl, stored over molecular sieves (4 Å), and passed through alumina, were prepared. To the catalyst stock soln (3.007 mL), toluene (3 mL) was added and the monomer stock soln (1.0 mL) was squirted in. Within 30 s the mixture turned deep red. After 6 h, benzaldehyde (16 μL) was added. After stirring for a further 3 h, the soln was concentrated in vacuo to about 1.5 mL. The polymer was precipitated in pentane (60 mL), collected on a frit, and dried in vacuo to yield a red, powdery material. All operations were carried out under a nitrogen atmosphere and the polymers were only briefly exposed to air for sample preparation for GC analysis; yield: 90 mg (91%); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 170.7 (CO_2Et), 54.5 ($\text{C}_{\text{quaternary}}$).

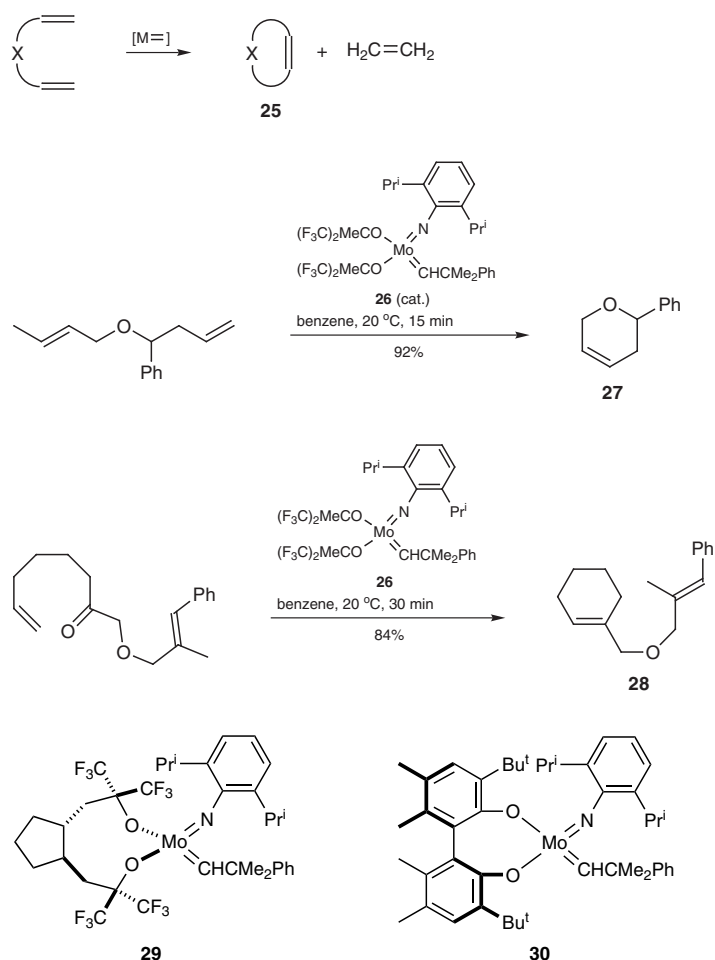
2.6.1.5.3

Variation 3: Ring-Closing Metathesis

Ring-closing metathesis (Scheme 11) affords cyclic products **25** in competition with intermolecular metathesis processes to form polymeric materials.^[45] The reaction is also complicated by the possibility of ROMP (Section 2.6.1.5.1). Which products are obtained is the result of an interplay of thermodynamic and kinetic parameters. Entropy (the generation of two molecules from one) and evaporative subtraction of the volatile acyclic alkene from solution provide the necessary driving force for the desired cyclization. The ring-closing metathesis procedure can be applied to the construction of macrocyclic natural products, although mixtures of *E*- and *Z*-isomers are often obtained in these cases (see also Section 2.6.2.7).^[46] The most widely used group 6 catalyst for this process is **26**, although ruthenium-based catalysts are generally preferred owing to their greater func-

tional group tolerance and relatively low sensitivity to air, moisture, or solvent impurities.^[47] The process has proven particularly useful for the formation of cyclic ethers, e.g. **27**.^[48] A number of functional groups, including tertiary alcohols, do not interfere with the course of the reaction. Amine and amide functional groups can be tolerated if they cannot form unreactive chelated adducts for steric reasons.^[49] A variant of this method follows the initial ring-closing metathesis step with a carbonyl alkenation process, e.g. the synthesis of **28**,^[50] which is, however, stoichiometric in metal because of the formation of a catalytically inactive metal–oxo byproduct. The success of this strategy rests on the fact that compound **26** metathesizes alkenes more rapidly than it alkenates ketones. Chiral analogues of **26** have been prepared using C_2 symmetric diol ligands, and these complexes, **29**^[51] and **30**,^[52] have been used to perform the asymmetric ring-closing metathesis of dienes^[52–54] and the synthesis of chiral furans via enantioselective desymmetrization reactions.^[55]

Scheme 11 Cycloalkenes by Ring-Closing Metathesis of Dienes^[48,50]



1-[(2-Methyl-3-phenylallyl)oxy]methylcyclohex-1-ene (28); Typical Procedure:^[50]

1-[(2-Methyl-3-phenylallyl)oxy]oct-7-en-2-one (35 mg, 0.13 mmol) was added to a homogeneous yellow soln of catalyst **26** (100 mg, 0.13 mmol) in anhyd benzene (12 mL) under argon. The resulting mixture was stirred at 20 °C for 30 min, at which time TLC showed the reaction to be complete. The mixture was quenched by exposure to air, concentrated, and

for references see p 112

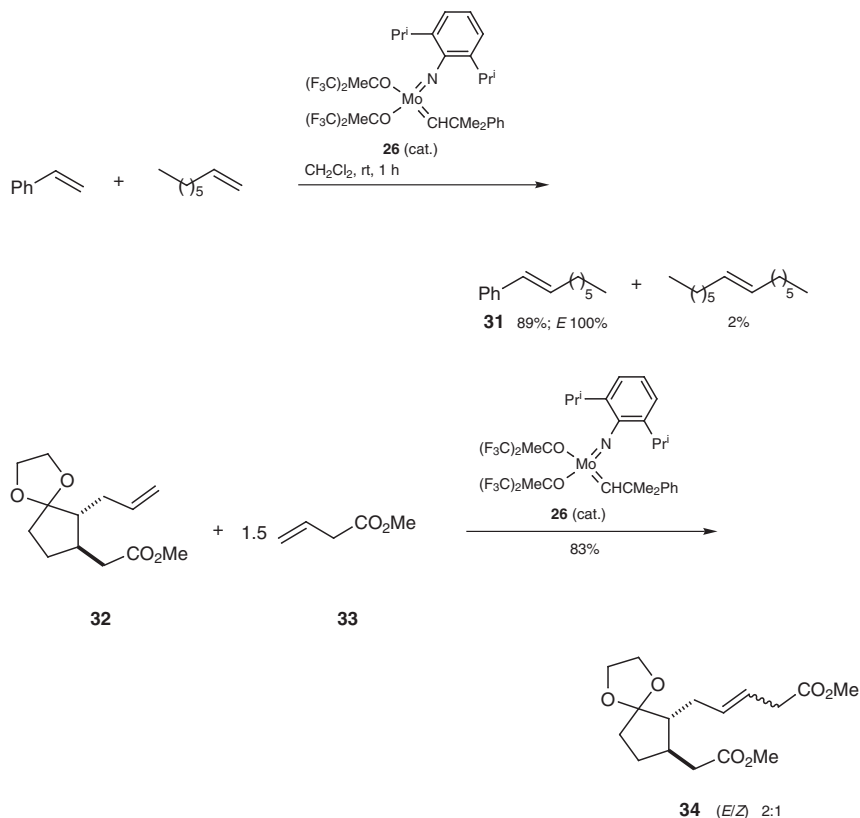
purified by flash chromatography (0–7% EtOAc/hexane) to yield the substituted cyclohexene as a colorless oil; yield: 27 mg (84%); $^1\text{H NMR}$ (benzene- d_6 , δ): 5.72 (br s, CHCH_2), 2.05–1.45 (m, 8H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$).

2.6.1.5.4 Variation 4: Other Selective Metathesis Processes

These processes are usually restrained to monosubstituted alkenes, yielding ethene as the byproduct. Fairly selective cross-coupling processes have been reported from a combination of an electron-poor alkene, especially one containing a π -substituent (e.g., styrenes, acrylonitrile),^[56,57] and a more nucleophilic one containing a small, electron-rich, nonconjugated substituent (see, for example, the synthesis of **31** in Scheme 12),^[56] or with allylsilanes.^[58] The electron-poor alkene self-metathesizes only slowly and, in addition, inhibits the self-metathesis of the nucleophilic alkene. Greater than 95% *trans* selectivity is observed in the reactions with styrene substrates,^[56] while the *cis*-product is highly favored for cross-metatheses with acrylonitrile.^[57]

The formation of the homo dimer may also be significantly slowed down by steric bulk. For example, compounds **32** and **33** yield the cross-coupling product **34** without any self-metathesis of **32** and with only 26% yield of the **33** homo dimer.^[59] The *E/Z* selectivities, however, are usually low for nonconjugated alkene products.

Scheme 12 Cross-Coupling Alkene Metathesis^[56,59]



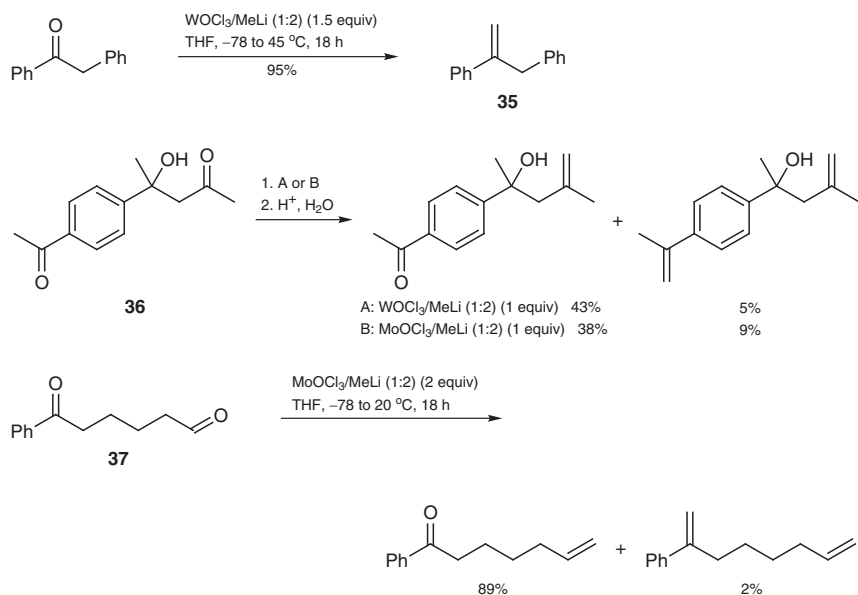
(E)-1-Phenyloct-1-ene (31); Typical Procedure:^[56]

To a mixture containing styrene (208 mg, 2 mmol) and oct-1-ene (112 mg, 1 mmol) in CH_2Cl_2 (2 mL) was added $[\text{Mo}(=\text{CHCMe}_2\text{Ph})\{\text{OCMe}(\text{CF}_3)_2\}_2(=\text{NC}_6\text{H}_3\text{2,6-iPr}_2)]$ (7.7 mg, 1 mol%). The resulting mixture was stirred at rt for 1 h, then passed through a pad of silica gel and rinsed with CH_2Cl_2 . The solvent was removed under reduced pressure, and the crude residue was chromatographed on silica gel to give **31** as a colorless oil; yield: 166 mg (89%). A similar reaction run with styrene (9.29 g, 89.2 mmol), oct-1-ene (5 g, 44.6 mmol), and catalyst (342 mg, 1 mol%) in CH_2Cl_2 (60 mL) afforded **31**; yield: 7.9 g (94%). $^1\text{H NMR}$ (CDCl_3 , δ): 2.16 (q, $J = 6.8$ Hz, 2H, allylic CH_2), 6.20 (dt, $J = 15.5$ and 6.8 Hz, 1H, $\text{PhCH}=\text{CH}$), 6.33 (d, $J = 15.5$ Hz, 1H, $\text{PhCH}=\text{CH}$).

**2.6.1.6 Method 6:
Carbonylmethylation**

The reaction of methylolithium or trimethylaluminum with molybdenum(V), molybdenum(VI), tungsten(V), and tungsten(VI) chlorides in tetrahydrofuran or diethyl ether at low temperatures produces complexes that liberate methane and convert into thermolabile μ -methylene complexes upon warming. The exact nature of these reagents has not been determined, but their subsequent addition to aldehydes and ketones results in their methylation at the carbonyl function. The low basicity of these compounds proves advantageous in carbonylmethylation of base-sensitive substrates, such as readily enolizable ketones as in the synthesis of **35** (Scheme 13).^[60] By comparison, methylidene-triphenylphosphorane ($\text{Ph}_3\text{P}=\text{CH}_2$) provides only a 16% yield of **35**. The base-sensitive ketone **36** is cleaved via a retro-aldol process by methylidene-triphenylphosphorane as well as weakly basic chromium reagents. In contrast, molybdenum(V) and tungsten(V) reagents are capable of methylating **36** with high regioselectivities.^[61] The activity of these reagents is restricted only to a surprisingly small degree by alcohol and water, thus permitting carbonylmethylation in aqueous or alcoholic media with useful applications to hydrophilic substances.

The molybdenum reagents in particular display high aldehyde selectivities, paralleling those observed for alkylchromium(III) reagents in carbonylalkylation (Section 2.6.4.5). This is illustrated in Scheme 13 by the carbonylmethylation of **37**.^[61,62] Basic groups such as hydroxy, alkoxy, dimethylamino, or alkylsulfanyl, in α - or β -positions relative to a carbonyl group, exercise an accelerating effect. This neighboring effect permits the selective monomethylation of diketones such as **36**, the selectivity depending on the solvent in the order dichloromethane < tetrahydrofuran < 1,2-dimethoxyethane. 1,3-Diketones and 1,3,5-triketones can be selectively monomethylated. In the case of triketones, a peripheral oxo group is methylated. Ketones react faster than enones. The reagents obtained from trichlorooxomolybdenum(V), tetrachlorooxomolybdenum(VI), or decachlorodimolybdenum(V) in tetrahydrofuran do not alter a number of functional groups that are attacked by other methylating agents. These include acyl chlorides, anhydrides, esters, amides, diaryl-substituted 1,2-diketones, nitro aromatics, alkenes, and dienes, as well as the individual compounds diphenylketene, benzonitrile, diphenylacetylene, chlorobenzene, benzyl chloride, and dichloromethane.^[60] The corresponding tungsten compounds have not been well investigated. The reason for this lack of reactivity is in some cases due to the formation of stable reagent–substrate complexes, from which the substrate is released unchanged on addition of water. Functional groups that, on the other hand, interfere with the carbonylmethylation reaction are azomethines, epoxides, and nitroso aromatics. A comparison of these molybdenum and tungsten reagents with other carbonylmethylating agents in various applications is available.^[60]

Scheme 13 Carbonylmethylenation^[60–62]**Carbonylmethylenation of 4-(4-acetylphenyl)-4-hydroxypentan-2-one (36);****Typical Procedure:**^[61]

To a red-brown suspension obtained by methylation of $\text{MoOCl}_3(\text{THF})_2$ (1.57 g, 4.3 mmol) with MeLi (8.7 mmol) in THF (30 mL) at -70°C was added dropwise a soln of 4-(4-acetylphenyl)-4-hydroxypentan-2-one (**36**; 0.48 g, 2.16 mmol) in THF (2 mL). The mixture was further stirred at -70°C for 4 h, followed by warming to rt over 12 h. This was hydrolyzed with sat. aq NaHCO_3 (10 mL). After separation of the two phases and Et_2O extraction of the aqueous phase, the combined organic fractions were dried (Na_2SO_4), and the solvent was removed by rotary evaporation. Flash chromatography (3 cm \times 16 cm, silica gel, CH_2Cl_2 /acetone 40:1) afforded 2-(4-isopropenylphenyl)-4-methylpent-4-en-2-ol {fraction 1; yield: 0.04 g (9%); IR $\tilde{\nu}_{\text{max}}$: 3500 cm^{-1} (br, OH); $^1\text{H NMR}$ (CDCl_3 , δ): 4.77 [m, 1H, $\text{CH}_2\text{C}(\text{CHH})\text{CH}_3$], 4.91 [m, 1H, $\text{CH}_2\text{C}(\text{CHH})\text{CH}_3$], 5.09 [m, 1H, aryl- $\text{C}(\text{CHH})\text{CH}_3$], 5.40 [m, 1H, aryl- $\text{C}(\text{CHH})\text{CH}_3$] as a colorless oil, 2-(4-acetylphenyl)-4-methylpent-4-en-1-ol [fraction 2; yield: 0.18 g (38%); IR $\tilde{\nu}_{\text{max}}$: 3420 cm^{-1} (br, OH); $^1\text{H NMR}$ (CDCl_3 , δ): 4.75 (m, 1H, $\text{C}=\text{CHH}$), 4.91 (m, 1H, $\text{C}=\text{CHH}$) as a yellow oil, and unreacted 4-(4-acetylphenyl)-4-hydroxypentan-2-one [fraction 3; yield: 0.08 g (17%)].

2.6.2

**Product Subclass 2:
Metal–Carbyne Complexes**

As for the case of carbene complexes, carbonyl-free carbyne (Schrock-type alkylidyne) complexes are most common for high oxidation state (≥ 4) molybdenum and tungsten systems,^[63] although chromium examples are known.^[64] For the purpose of formal oxidation state assignment, the carbyne ligand is considered as RC^{3-} . The majority of d^0 complexes possess the formula $\text{M}(\equiv\text{CR})\text{X}_3$, but many adducts with neutral two-electron donor ligands L, $\text{M}(\equiv\text{CR})\text{X}_3\text{L}_n$ ($n = 1$ or 2), are also known. Derivatives with more electronegative X groups (e.g., fluorinated alkoxides) form base adducts more readily. The most common supporting ligands (X) are bulky alkyl ligands, alkoxides, and halides, but derivatives with amides, and alkyl- and arylthiolates are also known. Typical ligands (L) are amines, ethers, and phosphines. In lower formal oxidation states (+4 and +5), phosphines and halides or cyclopentadienyl coligands are usually found. The halide derivatives are the most versa-

tile for further transformations by ligand exchange. Exchange of the carbyne and an alkyl ligand by intramolecular scrambling of the α -H atoms is possible.^[65,66] Since the carbyne function is polarized as $M(\delta^+) \equiv C(\delta^-)$, these compounds are susceptible to electrophilic attack at the carbyne ligand (e.g., protonation) and nucleophilic attack at the metal center (e.g., ligand addition). The addition of acids (HX) converts carbyne complexes into carbene complexes (see Section 2.6.1.4),^[7] although, in many cases, the reagents attack other ancillary ligands and the carbyne function remains intact. Examples are the reactions of trialkyl derivatives with hydrochloric acid, ammonium chloride, or carboxylic acids.^[67–69]

Synthesis of Product Subclass 2

2.6.2.1

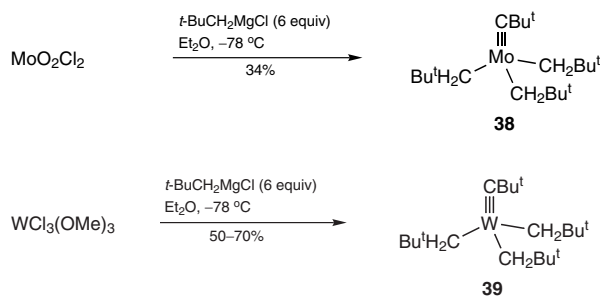
Method 1:

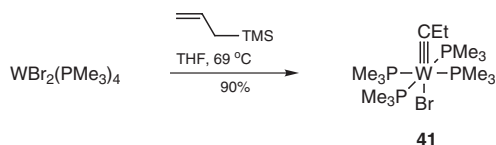
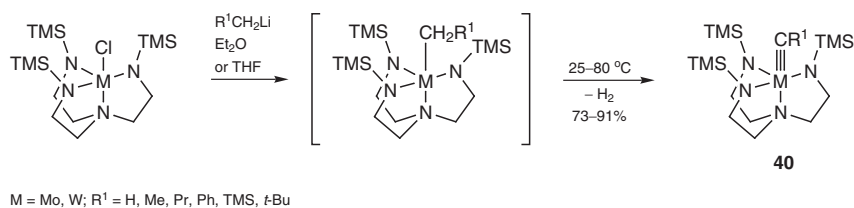
By α, α -Hydrogen Elimination from Alkyl Complexes

The increase of steric bulk in a high oxidation state complex containing alkyl ligands, or the in situ generation of encumbered complexes of this type by transmetalation reactions (see Section 2.6.1.1), induces α, α -hydrogen elimination processes with formation of carbyne products. The alkylation reaction works better from oxo or alkoxo derivatives than from the corresponding chlorides, because these are less susceptible to competing reductive processes.^[70] This reaction appears to be the preferred entry into 2,2-dimethylpropylidyne derivatives of molybdenum(VI) and tungsten(VI) through formation of the tris(2,2-dimethylpropyl) derivatives **38** and **39** (see Scheme 14). Other 2,2-dimethylpropylidyne derivatives are then readily obtained by treating **38** and **39** with sufficiently strong acids, e.g. hydrochloric or carboxylic acid, or by further ligand exchange from the trichloride derivatives. This process is presumed to take place stepwise, via intermediate carbene complexes (see Section 2.6.1.4), even when these are not observed. Some carbyne products have been obtained by alkane elimination from carbene complexes,^[15] although this strategy does not appear to have general synthetic utility.

A particular case of α, α -hydrogen elimination from an alkyl ligand leads to the formation of complex **40**.^[71] The two hydrogen atoms are eliminated as dihydrogen rather than being transferred to alkyl ligands. Thus, the reaction involves a formal metal oxidation and is so far limited to the system shown. The process is much faster for tungsten than for molybdenum, this being ascribed to a more favorable pre-equilibrium yielding the alkylidene–hydride intermediate. While the alkyl precursors can be isolated for molybdenum, they may only be obtained in situ for tungsten by transmetalation from the corresponding chloride. Other related rearrangements for cycloalkyl derivatives, leading to carbyne products in some cases, have also been observed for this system (see Section 2.6.2.5).^[72] The synthesis of **41**^[73] may be mechanistically related to the synthesis of **40**, the dihydrogen byproduct being transferred to the vinyl group.

Scheme 14 α, α -Hydrogen Elimination Processes^[67,68]





Tris(2,2-dimethylpropyl)(2,2-dimethylpropylidene)tungsten(VI) (39):^[68]

A soln of $\text{WCl}_3(\text{OMe})_3$ (19.1 g, 50 mmol) in a mixture of THF and Et_2O was added very slowly to 1 M *t*- BuCH_2MgCl (0.3 mol) in Et_2O at -78°C with vigorous stirring. The color of the soln gradually turned yellow-green. After the addition was complete, no significant amount of precipitate was apparent. The mixture was allowed to warm slowly from -78 to 25°C over a period of 10 h to give a red-brown soln and abundant precipitate. After filtration from Celite followed by washing of the filter cake with Et_2O , the solvent was removed in vacuo to give a thick red-brown oily liquid. Pentane (200 mL) was added to the residue, followed by another filtration and evaporation to dryness. The resulting oily red liquid was distilled at ca. $80^\circ\text{C}/0.001$ Torr through a short-path distillation apparatus; yield 55–60%. An additional 5–10% yield can usually be recovered by extracting the tarlike residue with pentane, filtering off the insolubles, removing the pentane in vacuo, and again distilling the residue as before. $^1\text{H NMR}$ (benzene- d_6 , δ): 1.66 (C*t*-Bu); $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6 , δ): 316.2 ($\text{W}\equiv\text{C}$).

Ethynylidene(*N'*-(trimethylsilyl)-*N,N*-bis(2-[(trimethylsilyl)amino- κN]ethyl)ethane-1,2-diamido- $\kappa\text{N},\kappa\text{N}$)tungsten(VI) (40, M = W; R¹ = Me); Typical Procedure:^[71]

An Et_2O (25 mL) soln of $[\text{WCl}[\text{N}(\text{CH}_2\text{CH}_2\text{NTMS})_3]]$ (0.20 g, 0.345 mmol) was treated with EtLi (0.019 g, 0.52 mmol) at 25°C . The mixture turned light yellow as gas evolved. The resulting mixture was stirred for another 3 h and then evaporated to dryness in vacuo. The yellow residue was extracted with pentane (60 mL), and the extract was filtered. The filtrate was concentrated to ca. 5 mL in vacuo and chilled at -40°C for several h to yield the product as light yellow crystals; yield: 0.16 g (81%); $^1\text{H NMR}$ (benzene- d_6 , δ): 3.73 ($\text{W}\equiv\text{CCH}_3$, $^3J_{\text{WH}} = 7.9$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6 , δ): 274.33 ($\text{W}\equiv\text{C}$).

2.6.2.2

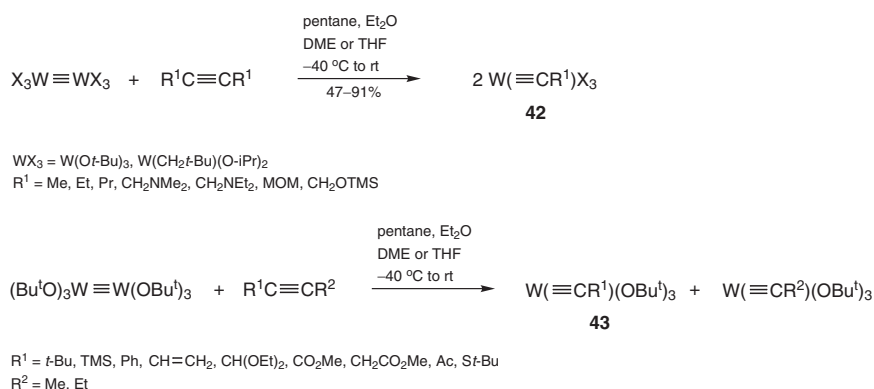
Method 2:

By Addition of Alkynes to Compounds with Metal–Metal Triple Bonds

Symmetrical alkynes provide access to carbyne complexes **42** upon reaction with symmetrical triply bonded tungsten alkoxy, aryloxy, and mixed alkyl–alkoxy complexes (Scheme 15).^[74,75] This reaction occurs readily when R¹ is a simple alkyl group but also for functionalized alkynes, more easily so in the presence of nitrogen donors (in which case the base adducts are obtained).^[74] This reaction is very sensitive to steric factors. The formation of alkyne adducts, bis-alkyne adducts, and products of C–C couplings are possible alternatives.^[75,76] Other group 6 triply bonded dimers such as hexakis(dimethylamido)- or hexaalkylditungsten(III) and molybdenum alkoxides do not cleave internal alkynes.

Unsymmetrical alkynes can often be cleaved even if one of the substituents is bulky, giving a 1:1 mixture of the two carbyne products. However, use of an excess of the alkyne increases the yield of one carbyne product, e.g. **43**, by the metathesis procedure described in Section 2.6.2.3, provided the lower-boiling alkyne is removed. Some of these reactions afford satisfactory results only in the presence of a stabilizing base, e.g. quinuclidine.^[74] Terminal alkynes react with both tungsten and molybdenum alkoxides, but the CH product is not isolable unless a stabilizing base is present.^[77] The triple bond of selected nitriles is also cleaved to afford a mixture of the carbyne and the sparingly soluble nitride products.^[78,79]

Scheme 15 Addition of an Alkyne to a Compound Containing a Metal–Metal Triple Bond ^[74,79]

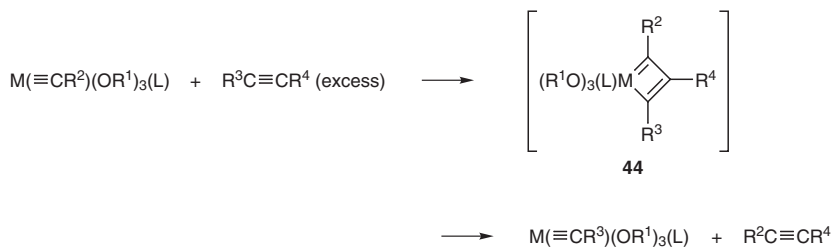


Tri-*tert*-butoxy(ethylidyne)tungsten(VI) (42, X = Ot-Bu; R¹ = Me); Typical Procedure:^[74]

But-2-yne (80.1 μL , 1.02 mmol) was added to a soln of $[W_2(Ot\text{-}Bu)_6]$ (0.75 g, 0.93 mmol) in pentane (30 mL) at -40°C . The soln was maintained at -40°C for 1 h and allowed to warm to rt. The orange color faded to light amber, and after 2 h at rt the volatile components were removed in vacuo, leaving a light brown solid. Larger scale preparations sometimes yielded a brown oil initially, but the oil always crystallized with time in vacuo or when seeded. Sublimation of the light brown residue at $25^\circ\text{C}/10^{-6}$ Torr onto a -78°C probe afforded the pure, white product; yield: 0.59 g (74%). This material is very oxygen- and moisture-sensitive and darkens slightly when removed from the probe in a drybox. It was generally prepared in pentane or THF and utilized directly for further reactions, assuming a quantitative yield. $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6 , δ): 254.3 ($W \equiv \text{CMe}$).

**2.6.2.3 Method 3:
By Stoichiometric Alkyne Metathesis**

A variety of alkoxo–carbyne complexes may be obtained from a preexisting carbyne complex and an alkyne by a metathesis process (Scheme 16). This exchange takes place via a metallacyclobutadiene intermediate **44**, which has been observed or isolated for the corresponding aryloxo and fluorinated alkoxo systems. Such intermediates have greater stability for the tungsten systems.^[67] This procedure is synthetically useful for symmetrical, unsymmetrical, and terminal alkynes. Like the reactions examined in Section 2.6.2.2, these are also sensitive to steric factors.^[67,74] Electronic factors are also important, however, fluoroalkoxo complexes reacting more readily than the corresponding alkoxo complexes without fluorine substituents. Terminal acetylenes also react with bulkier carbyne complexes, but the reaction is often complicated and other products (e.g., deprotonated metallacyclobutadiene derivatives) may be obtained, limiting the synthetic utility.^[67]

Scheme 16 Stoichiometric Alkyne Metathesis^[67,74]

M	L	R ¹	R ²	R ³	R ⁴	Conditions	Yield (%) of [M(≡CR ³)(=OR ¹) ₃ (L)]	Ref
Mo	DME	CMe(CF ₃) ₂	<i>t</i> -Bu	^a	^a	Et ₂ O, rt, 15 min	80–90	[67]
Mo	–	<i>t</i> -Bu	<i>t</i> -Bu	^b	H	Et ₂ O, rt, 30 min	quant.	[67]
W	quinoline	<i>t</i> -Bu	Me	C≡CEt	Et	pentane, rt, 2 d	64	[74]

^a R³ = R⁴ = Me, Et, Pr, Ph.

^b R³ = Pr, *i*Pr, Ph.

Addition of one equivalent of an internal alkyne, trichloro(1,2-dimethoxyethane-*O,O'*)-(2,2-dimethylpropylidyne)tungsten(VI) affords a stable tungstacyclobutadiene product, but reaction with additional alkyne yields η⁵-cyclopentadienyl products of further alkyne insertion rather than products of alkyne metathesis.^[69,80]

Butylidynetris(1,1,1-trifluoro-2-methylpropan-2-olato)molybdenum(VI);

Typical Procedure:^[67]

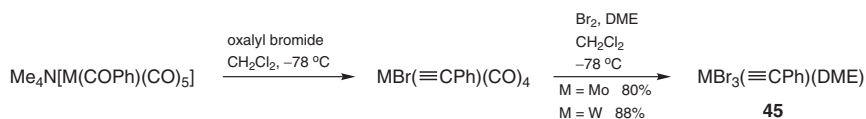
Excess PrC≡CPr (125 μL, 0.85 mmol) was added to [Mo(≡C*t*-Bu){OCMe₂(CF₃)₃}]₃ (0.09 g, 0.16 mmol) dissolved in Et₂O (3 mL). After 30 min, the solvent was removed in vacuo, leaving white needles that were pure by NMR; ¹³C{¹H} NMR (benzene-*d*₆, δ): 299.3 (Mo≡CPr).

2.6.2.4

Method 4:

By Oxidation of Fischer-Type Carbyne Complexes

The dibromine oxidation of (alkylidyne)bromotetracarbonyl complexes of molybdenum and tungsten in the presence of 1,2-dimethoxyethane (DME) provides a direct access to DME-stabilized (alkylidyne)tribromo complexes, while the corresponding chromium systems lead to complete degradation.^[81] The advantage of this procedure is the direct access to complexes with a wide variety of carbyne substituents starting from the corresponding, easily accessible Fischer-type carbyne precursor. The phenyl derivative **45**, in particular, is easily synthesized in a one-pot procedure from the precursor as shown in Scheme 17.

Scheme 17 Oxidation of Fischer-Type Carbyne Complexes^[81,82]

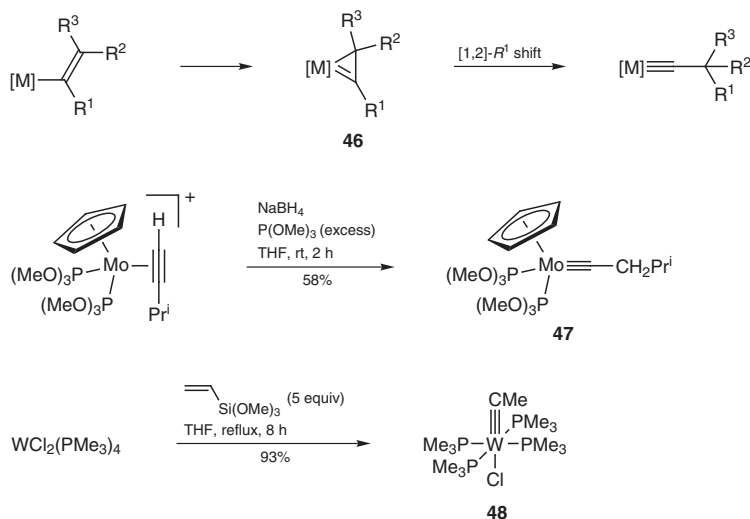
Benzylidynetribromo(1,2-dimethoxyethane-*O,O'*)tungsten(VI) (45, M = W):^[81,82]

Me₄N[W(COPh)(CO)₅] (10.00 g, 19.87 mmol) was completely dissolved in CH₂Cl₂ (300 mL) then the soln was cooled to -78 °C. Oxalyl bromide (1.87 mL, 20.0 mmol) was dissolved in CH₂Cl₂ (40 mL) and cooled to -78 °C, then quickly added against a N₂ stream to the acyl soln. This soln was left to stir at -78 °C for 15 min, then warmed in an ice bath just until a bright yellow color developed. It was immediately recooled to -78 °C; then this soln was filtered through a dry-ice jacketed frit, having a 2-cm layer of dry cellulose on it, into a cooled (-78 °C) receiving flask (500-mL Schlenk). To the soln of [WBr(≡CPh)(CO)₄] at -78 °C was added DME (10 mL). A freshly prepared 1.0 M soln of Br₂ in CH₂Cl₂ (20 mL) with an additional quantity of CH₂Cl₂ (20 mL) was cooled to -78 °C and added (poured) against a strong N₂ stream as quickly as possible. The color became red briefly then dark orange. The stirred soln was allowed to warm to rt under vacuum; much gas was evolved during the warming step. The solvent was removed in vacuo and the dark brown oily solid was washed with pentane (50 mL). The solid was then dissolved in CH₂Cl₂ (30 mL) and filtered. The volume was reduced to 15 mL and pentane (100 mL) was added gradually to precipitate the product as a green-brown solid. This precipitation process was repeated until the product in CH₂Cl₂ was emerald green. The final product was a dark green microcrystalline powder; yield: 10.49 g (88%); ¹³C{¹H} NMR (benzene-*d*₆, δ): 331.7 (W≡CPh).

2.6.2.5 Method 5: By Rearrangement of Vinyl Complexes

Vinyl complexes can, under favorable circumstances, rearrange by a [1,2]-*H* shift to carbyne complexes (Scheme 18).^[83] The reaction appears to proceed via a η²-vinyl complex **46**, which has been isolated in some cases,^[84] and thus requires an open coordination site on the metal center. The vinyl precursors are often prepared in situ by hydride addition to alkyne complexes, e.g. for the synthesis of **47** and indenyl analogues,^[84] by deprotonation of alkene complexes,^[13] or by transmetalation, as for the synthesis of **48**.^[73] The vinyl complex intermediate may not be observed in some cases. η³-Allyl complexes are possible byproducts of this reaction when the substituents R² and R³ bear α-hydrogen atoms (e.g., **47**),^[85] in which case the rearrangement to the carbyne product is favored by the presence of free ligands and higher temperatures.

Scheme 18 [1,2]-*H* Shift from Vinyl Complexes^[73,84]



η^5 -Cyclopentadienyl(3,3-dimethylbutylidyne)bis(trimethyl phosphite-P)molybdenum(IV):^[84]

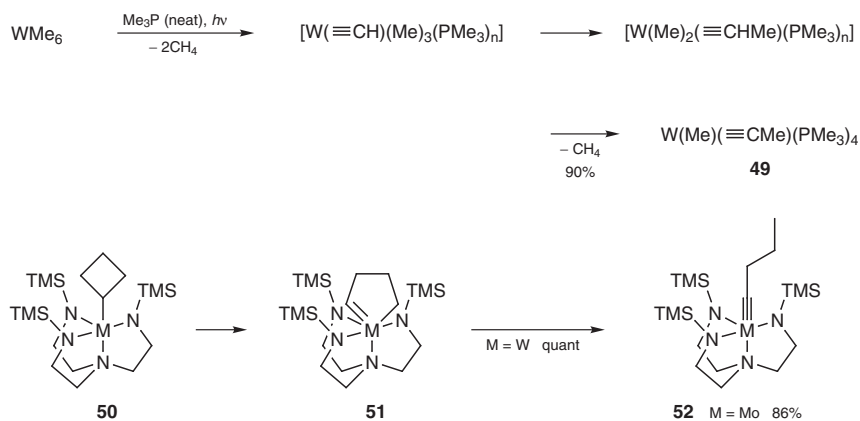
A soln of $[\text{MoCp}\{\sigma\text{-}(E)\text{-CH=CH}t\text{-Bu}\}\{\text{P}(\text{OMe})_3\}_2]$ (0.35 g, 0.5 mmol) in hexane (10 mL) contained in an evacuated sealed tube (50 mL) fitted with a Westoff stopcock was heated at 80 °C for 12 h. The mixture became bright yellow. The volatile material was removed in vacuo and the residue was dissolved in Et_2O (5 mL) and chromatographed on an alumina-packed column. Elution with hexane gave a bright yellow band, which was collected and the volume of the solvent was reduced (to 5 mL); cooling (−78 °C, 3 d) afforded the product as bright yellow crystals; yield: 0.21 g (85%); ^1H NMR (benzene- d_6 , δ): 5.2 (s, 5H, Cp), 2.2 (t, 2H, $\text{CH}_2t\text{-Bu}$, $^3J_{\text{HP}} = 4.0$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6 , δ): 299.8 (t, $\text{Mo}\equiv\text{C}$, $^2J_{\text{CP}} = 27.0$ Hz).

**2.6.2.6 Method 6:
By Other Rearrangement Processes**

The stability of the metal–alkylidyne bond, especially for tungsten, induces other remarkable rearrangements from a variety of systems. The high-yield synthesis of compound **49** upon photolysis of hexamethyltungsten(VI) in neat trimethylphosphine involves a methyl migration onto a proposed carbyne intermediate (Scheme 19).^[86]

Other rearrangement processes have been established for selected cycloalkyl complexes.^[13,72] For molybdenum complexes, the cyclobutyl complex **50** converts into the butylidyne product **52** without observation of a metallacyclopentene intermediate **51**.^[72] For tungsten complexes, on the other hand, alkylation of the chloro precursor complex with cyclobutyl lithium yields the stable complex **51** directly, which is further transformed to the carbyne product **52** upon warming (Scheme 19).^[71] Cyclopropyl derivatives undergo elimination of ethene and formation of a methylidyne product, while the cyclopentyl derivatives do not undergo the ring-opening step.

Scheme 19 Other Rearrangement Processes^[71,72,86]



Butylidyne(N' -(trimethylsilyl)- N,N -bis(2-[(trimethylsilyl)amino- κN]ethyl)ethane-1,2-diamido- $\kappa\text{N},\kappa\text{N}'$)molybdenum(VI) (52**, $\text{M} = \text{Mo}$); Typical Procedure:^[72]**

Compound **50** ($\text{M} = \text{Mo}$; 124 mg, 0.243 mmol) was dissolved in toluene (5 mL), and the soln was heated in a sealed tube to 60 °C for 2 h. The toluene was removed in vacuo, and the residue was dissolved in a minimum amount of pentane. The pentane soln was cooled to −40 °C to give brown crystals of the product after 24 h; yield: 107 mg (86%); $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6 , δ): 298.3 ($\text{Mo}\equiv\text{C}$).

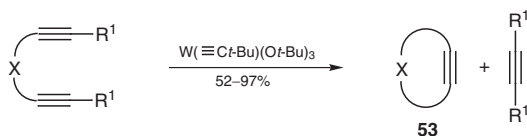
Applications of Product Subclass 2 in Organic Synthesis

The reactivity of Schrock-type carbyne complexes has to date been little exploited in organic synthetic applications in comparison with that of the corresponding carbene complexes (Section 2.6.1.5). For the most part, the interest has been limited to stoichiometric transformations to other organometallic products. Some carbyne compounds ($[M]\equiv CR$) undergo Wittig-like reactions with $X\equiv Y$ molecules, affording $[M]\equiv X$ and $RC\equiv Y$ products.^[63] As seen in Section 2.6.2.3, the addition of an alkyne ($R^2C\equiv CR^2$) to a carbyne complex ($[M]\equiv CR^1$) may afford the metathetical products ($R^2C\equiv CR^1 + [M]\equiv CR^2$). Some of these complexes catalyze the alkyne metathesis reaction.^[87]

2.6.2.7 Method 7: Alkyne Metathesis

Medium-large cycloalkynes **53** have been synthesized from diyne precursors by a ring-closing metathesis process in which a tungsten carbyne complex acts as a catalyst (Scheme 20).^[46] The cycloalkyne obtained by this methodology can be partially reduced to obtain the cycloalkene exclusively as the *Z*-isomer. The stereoselectivity of this route is particularly notable, since current molybdenum- and ruthenium-based ring-closing metathesis catalysts usually provide mixtures of *E*- and *Z*-configured cycloalkenes from diene precursors (see Section 2.6.1.5.3). The catalyst tolerates various functional groups: lactones, lactams, and silyl ethers have been obtained by this method. The catalyst is incompatible with terminal acetylenes; thus, it is necessary to use precursors with $R^1, R^2 \neq H$. The use of a high boiling point solvent (e.g., 1,2,4-trichlorobenzene) allows the removal of the alkyl byproduct ($R^1C\equiv CR^2$) under reduced pressure, with a positive effect on the conversion.

Scheme 20 Cycloalkynes by Ring-Closing Metathesis of Dienes^[46]



1,6-Dioxacyclotetradec-9-yne-2,5-dione [53, $X = (\text{CH}_2)_2\text{OC(O)(CH}_2)_4\text{C(O)O(CH}_2)_2$];

Typical Procedure:^[46]

A soln of the diyne $[\text{MeC}\equiv\text{C}(\text{CH}_2)_2\text{O}(\text{O})\text{C}(\text{CH}_2)_2]_2$ (121 mg, 0.43 mmol) and $[\text{W}(\equiv\text{Ct-Bu})(\text{Ot-Bu})_3]$ (12 mg, 6 mol%) in chlorobenzene (20 mL) was stirred under argon at 80 °C for 2 h. The solvent was removed in vacuo, and the residue purified by flash chromatography (Merck silica gel, hexane/EtOAc 4:1). This led to the recovery of some unchanged starting material (12 mg, 10%) and afforded the cycloalkyne product as colorless crystals; yield: 70 mg (73%); mp 106–107 °C; ^{13}C NMR (δ): 173.0 (alkyne).

2.6.3 Product Subclass 3: Metal- σ -Alkyl and - σ -Aryl Homoleptic Complexes

Compounds of this class are rather limited, their syntheses are generally low yielding, and have no general applications in organic synthesis. As is usually the case for any metal, the more robust complexes are those without β -hydrogens and aryl complexes. Well-characterized members of this class have the stoichiometries MR_6 , MR_4 , $[\text{MR}_6]^{3-}$, $[\text{MR}_5]^{2-}$, $[\text{MR}_4]^-$, MR_3 , and $[\text{MR}_4]^{2-}$. The MR_6 complexes are known only for tungsten and have a

for references see p 112

strong tendency to decompose by α -hydrogen elimination. The tetrahedral MR_4 complexes can only be obtained with sterically demanding ligands and are unexpectedly unreactive. While $M(III)$ complexes with three unpaired electrons are common for chromium, no unambiguous example has been reported for molybdenum or tungsten. Delicate equilibria may exist between different species as a function of the size of R, the nature of the counterion, or even the solvent. For example, orange-yellow hexaphenylchromate(III), blue-green pentaphenylchromate(III), and cherry-red tetraphenylchromate(III) have been isolated under different conditions.^[88–90] Neutral trialkylchromium(III) compounds are known only with very bulky R groups, e.g. bis(trimethylsilyl)methyl $[CH(TMS)_2]$.^[91] Unambiguous $M(II)$ complexes exist only for chromium. These are either paramagnetic ($S = 2$) and square planar tetraalkylchromate(2–) monomers or diamagnetic tetraanionic dimers. The choice of nuclearity is highly dependent on the counterion and the solvent; for example, the lithium salt of tetramethylchromate(II) adopts a monomeric or a dimeric structure depending on whether the lithium cations are surrounded by tetramethylethylenediamine or by diethyl ether molecules.^[92]

The relatively high polarity of the metal–alkyl bonds makes these derivatives rather sensitive toward proton sources including water, especially when the latter can be activated by coordination to the metal center. Thus, these compounds must generally be synthesized and handled under scrupulously dry conditions.

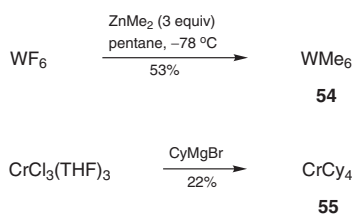
Synthesis of Product Subclass 3

2.6.3.1

Method 1: By Transmetalation

The only synthetic method that allows access to homoleptic alkyl and aryl complexes of group 6 metals is the transmetalation reaction (Scheme 21). Competitive electron-transfer processes and equilibria of association/dissociation of the alkylating reagent are often the reasons for the moderate yields usually associated with these syntheses. There is no general rule as to the best reagents and conditions to use for a specific product. Lithium and magnesium reagents are typically used, although other alkylating sources have also been employed. This is exemplified by the synthesis of hexamethyltungsten(VI) (**54**)^[93,94] and tetracyclohexylchromium(IV) (**55**).^[95] As a general rule, lithium reagents are more reactive than Grignard reagents, but have a greater tendency to engage in single-electron-transfer (SET) side reactions. The choice of solvent may also be a determinant factor. Tetrahydrofuran, diethyl ether, and toluene are the most commonly used solvents, the latter disfavoring SET processes. The group 6 metal sources are typically the halides, but the alkoxides have also been used, the latter usually reducing the SET reactivity. Many neutral metal(IV) compounds are obtained from lower oxidation state precursors in <50% yield, e.g. **55**,^[95] via a disproportionation mechanism.

Scheme 21 Homoleptic Metal Alkyl and Aryl Complexes by Transmetalation^[94,95]



Hexamethyltungsten(VI) (54):^[94]

CAUTION: Hexamethyltungsten(VI) is known to decompose explosively. Proper safety precautions should be taken during its synthesis, storage, and handling.

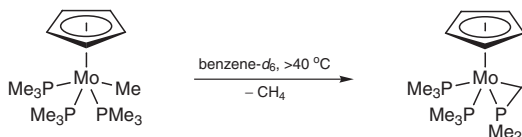
A 50-mL glass container with two openings was attached to a vacuum line, and WF_6 (1.1 g, 3.7 mmol) and pentane (10 mL) were condensed into it in vacuo and with cooling (liq N_2). A 1 M soln of ZnMe_2 in heptane (11.5 mL) was slowly added dropwise at -78°C . The mixture was stirred at -35°C for 2 d, filtered at -10°C , and concentrated in vacuo at -70°C to afford an orange soln. The yield (53%) was determined by the quantitative reaction of **54** with NO and weighing the resulting product $[\text{WMe}_4\{\text{ON}(\text{Me})\text{NO}\}_2]$.

**2.6.4 Product Subclass 4:
Metal- σ -Alkyl and - σ -Aryl Non-homoleptic Complexes**

Non-homoleptic (heteroleptic) complexes containing alkyl and aryl ligands are much more common, exist in a wider variety of formal oxidation states and coordination environments, and are more versatile in organic synthesis than the homoleptic complexes. The use of ancillary ligands with strong π -donating properties increases the relative stability of high oxidation state derivatives. Thus, M(V) and M(VI) (M = Cr, Mo) alkyl and aryl complexes exist when supported by oxo, imido, or nitrido ligands,^[96–99] whereas no homoleptic counterparts are known. Non-homoleptic tungsten(VI) complexes are more common and stable than the homoleptic ones.

Like the homoleptic complexes (Section 2.6.3), the non-homoleptic complexes tend to decompose more readily when they bear hydrogen atoms on the β -position, via the ubiquitous β -hydrogen elimination pathway. As this pathway necessitates an empty metal orbital *cis* relative to the alkyl group and a coplanar transition state, stable complexes with β -hydrogen-bearing alkyl ligands may only be obtained when one or more of the above requirements are not met.^[100] In particular, these compounds may be isolated when each valence-shell metal orbital is occupied by at least one electron and when the ligands *cis* to the alkyl group do not easily dissociate. Complexes whose alkyl substituents bear hydrogen atoms on the α -position may also decompose, this process being especially favored for high-valent molybdenum and tungsten complexes, providing good synthetic methods for carbene and carbyne complexes (see Sections 2.6.1 and 2.6.2, respectively). Other methods of decomposition are associated with intramolecular C–H bond activation of ancillary ligands, which is promoted by the metal electron richness, e.g. see Scheme 22.^[101] Finally, homolytic cleavage of the metal–alkyl bond may occur with production of radicals and reduced metal complexes. Aryl derivatives are more robust than the alkyl complexes toward this decomposition pathway.

Scheme 22 Decomposition of Alkyl Complexes by Alkane Elimination^[101]



Like the homoleptic complexes, the transmetalation reaction represents the most convenient entry to alkyl and aryl non-homoleptic complexes of group 6 metals. The metal–alkyl and metal–aryl bonds may also be formed, however, by oxidative addition reactions.

Synthesis of Product Subclass 4

2.6.4.1

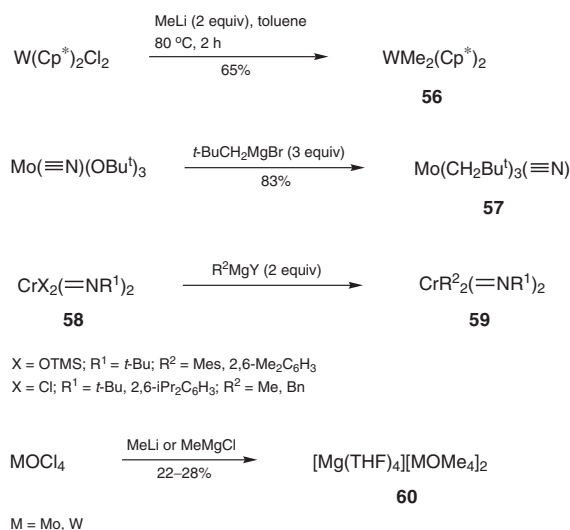
Method 1:

By Transmetalation

The ancillary ligands often provide steric and electronic protection to the transition-metal center, resulting in a greater selectivity and higher yields for the transmetalation reactions relative to those leading to the homoleptic counterparts (see Scheme 23). A typical example is the synthesis of **56**.^[102] The empiricism in the choice of alkylating/aryllating agent and conditions parallels that discussed for the homoleptic products in Section 2.6.3. In addition to lithium and magnesium reagents, the occasional use of dialkylzinc is also reported. The synthesis of compound **57** proceeds in good yields from the tri-*tert*-butoxo precursor, whereas no product is recovered when starting from the corresponding trichloride.^[103] While the bis(imido)chromium(VI) precursors **58** afford products **59**^[96,97,104] and mesitylmagnesium bromide reacts cleanly with dichlorodioxomolybdenum(VI) to afford the corresponding dimesityldioxo product, use of mesitylmagnesium bromide with dichlorodioxochromium(VI) leads to chromium(V) and chromium(III) products.^[97]

The reaction between phenylmagnesium bromide and chromium(III) chloride in diethyl ether leads to chromium(I)- π -arene complexes as final products.^[105,106] The initial reaction does, however, generate chromium(III)- σ -phenyl species, and the greater coordinating ability of tetrahydrofuran permits the isolation of triphenyltris(tetrahydrofuran)-chromium(III).^[107] In some cases, the reduction accompanying transmetalation may be synthetically useful, e.g. the synthesis of **60**.^[108]

Scheme 23 Transmetalation^[96,97,102,103,108]



Dimethylbis(η^5 -pentamethylcyclopentadienyl)tungsten(IV) (56**); Typical Procedure:**^[102] $[\text{W}(\text{Cp}^*)_2\text{Cl}_2]$ (2.0 g, 3.8 mmol) and MeLi (0.40 g, 18.2 mmol) were treated with toluene (20 mL) and heated to 80 °C for 2 h, giving a red-orange soln. The mixture was filtered and the toluene was removed under reduced pressure. The residue was extracted into pentane and cooled to -78 °C, giving orange needles of $[\text{W}(\text{Me})_2(\text{Cp}^*)_2]$; yield: 1.2 g (65%); ¹H NMR (benzene-*d*₆, δ): 1.60 (s, 30H, C₅Me₅), -0.54 (s, 6H, WMe).

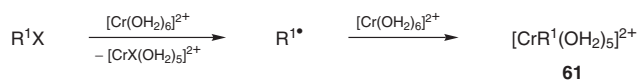
2.6.4.2 Method 2: By Oxidative Addition of Alkyl Halides

This method has mostly been used for the synthesis of chromium(III) compounds, with wide application in the Nozaki-Hiyama-Kishi reaction (Section 2.6.4.5). Other group 6 derivatives have been prepared as well.

2.6.4.2.1 Variation 1: One-Electron Oxidative Additions

Chromium(II) precursors react with alkyl halide reagents to afford a 1:1 mixture of chromium(III) halide and alkylchromium(III) products. The mechanism involves single-electron-transfer steps and radical intermediates (Scheme 24). Other radical sources may be used instead, including hydroperoxides or alkane/hydrogen peroxide mixtures under thermal, flash photolysis, or pulse radiolysis conditions.^[109] This procedure has been used to produce the alkylpentaquachromium(III) ion **61**.^[110] The latter is long-lived but cannot be isolated and must be generated in situ. Activated alkyl halides react thermally with the chromium(III) ion, while other alkyls require photolytic or radiolytic conditions. The addition of ligands such as ethylenediamine or saturated tetraaza macrocycles makes the process more favorable for both thermodynamic and kinetic reasons.

Scheme 24 One-Electron Oxidative Addition of Alkyl Halides^[110]

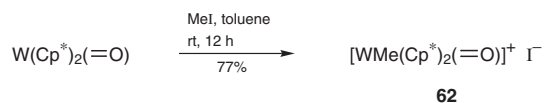


Reduction of Chloroform with Chromium(II) Perchlorate:^[111]

H₂O (1 L) was freed of oxygen and then shaken with CHCl₃ (10 mL). A 0.2 M soln of chromium(II) perchlorate (500 mL) was added in an atmosphere of N₂ and the soln allowed to stand for 2 or 3 h at rt. The grayish-red soln gave no precipitate with AgNO₃ soln at rt. A portion (100 mL) of this soln was placed on a column (15 cm × 2 cm) of Dowex 50-X4 (200–400 mesh) in the hydrogen form and the column was eluted with 1 M HClO₄ at the rate of 1–2 drops · s⁻¹. A green fraction (100 mL) was soon eluted, followed by a colorless soln (150 mL), and then by a red fraction (110 mL). The green and red fractions were identified as containing [Cr(H₂O)₅Cl]²⁺ and [Cr(H₂O)₅(CHCl₂)]²⁺, respectively, by UV-vis spectroscopy and quantitative analysis with AgClO₄ and KMnO₄.

2.6.4.2.2 Variation 2: Two-Electron Oxidative Additions

Electron-rich metal complexes containing at least one electron pair in a metal-based orbital may undergo a classical two-electron oxidative addition of alkyl halides, making a new metal-alkyl bond (Scheme 25). This synthetic strategy is thus generally limited to systems supported by electron-donating ancillary ligands. No synthetically useful examples of this type of reactivity have been described for noncarbonyl-containing group 6 organometallic species where the halide ion is incorporated in the coordination sphere of the metal. However, there are examples of two-electron oxidative addition reactions of alkyl halides where the halide remains as an outer sphere counterion, as in the preparation of **62**.^[102]

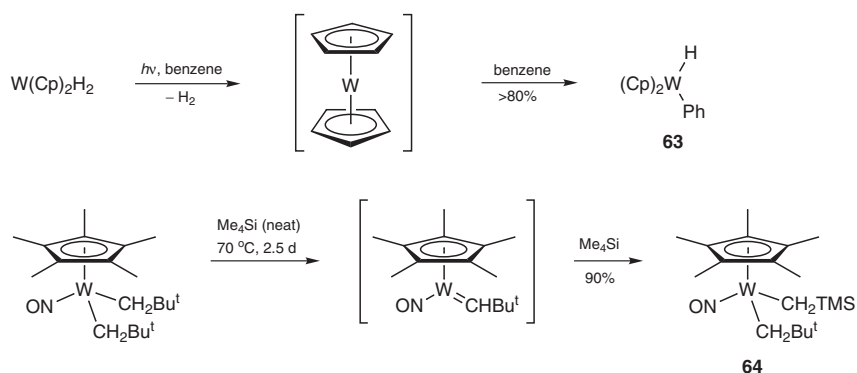
Scheme 25 Two-Electron Oxidative Addition of an Alkyl Halide^[102]**Methyloxobis(η^5 -pentamethylcyclopentadienyl)tungsten(VI) Iodide (62):^[102]**

A soln of $[\text{W}(\text{Cp}^*)_2(\text{=O})]$ (150 mg, 0.32 mmol) in toluene (3 mL) was treated with MeI (0.2 mL, 3.2 mmol) and the mixture was stirred. After ca. 5 min a yellow microcrystalline deposit started to form. The stirring was continued for 12 h. The mixture was filtered and the solid was washed with pentane (3×2 mL) and dried in vacuo to give yellow crystals of **62**; yield: 150 mg (77%); IR (Nujol) $\tilde{\nu}_{\text{max}}$: $[\text{W}(\text{=O})]$ 868 (s) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , δ): 2.13 (s, 15H, C_5Me_5), 1.07 (s, 3H, WMe).

2.6.4.3

Method 3:**By Oxidative Addition of Alkanes and Arenes**

Alkanes and arenes may be able to add oxidatively to a suitable metal complex, forming an alkyl (or aryl) hydride product (Scheme 26). Arenes are more suitable than alkanes for this methodology, for both kinetic and thermodynamic reasons. The metal complex must be quite electron-rich to accomplish this process. Sufficiently reactive metal substrates are usually generated in situ from more stable precursors by either a thermal or a photochemical dissociation or reductive elimination process. For example, the tungstenocene leading to product **63** is generated by photolytic reductive elimination of dihydrogen from bis(η^5 -cyclopentadienyl)dihydridotungsten(IV).^[112] Tungstenocene may also be generated by thermal alkane elimination from a dicyclopentadienyl-alkyl-hydride system.^[113] The product of the oxidative addition step may further evolve to afford more stable alkyl or aryl products, as is the case for the synthesis of compound **64**.

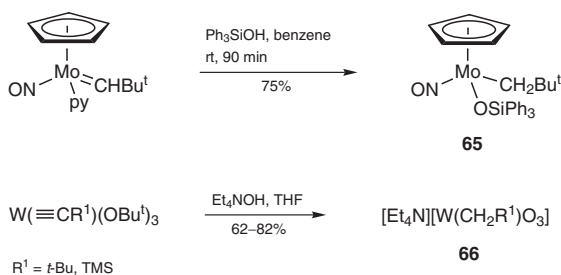
Scheme 26 Oxidative Addition of Alkanes and Arenes^[112,114]**(2,2-Dimethylpropyl)nitrosyl(η^5 -pentamethylcyclopentadienyl)[(trimethylsilyl)methyl]-tungsten(II) (64); Typical Procedure:^[114]**

In a glovebox an ampule (Teflon stopcock) was charged with $[\text{W}(\text{CH}_2t\text{-Bu})_2\text{Cp}^*(\text{NO})]$ (0.048 g, 0.098 mmol) and Me_4Si (1 mL). The resulting wine-red mixture was stirred and heated at 70 °C for 2.5 d, during which time it changed to a darker red soln. The organic volatiles were removed under reduced pressure. The remaining dark wine-red solid was redissolved in pentane and filtered through Celite. The resulting soln was stored for several days to provide **64** as maroon crystals; yield: 0.045 g (90%); $^1\text{H NMR}$ ($\text{benzene-}d_6$, δ): 1.54 (s, 15H, C_5Me_5), 1.35 (s, 9H, $t\text{-Bu}$), 0.38 (s, 9H, TMS).

2.6.4.4

**Method 4:
By Protonation of Carbene and Carbyne Ligands**

Under suitable conditions, carbene and carbyne ligands can take up protons to generate alkyl derivatives. The proton source must be of low acidity to avoid further protonolysis of the alkyl product. This methodology is of rather limited synthetic utility. Two examples are shown in Scheme 27.^[115,116] The formation of **65** involves loss of the pyridine ligand and proton transfer from the silanol to the carbene ligand, while even more extensive changes accompany the protonation of the carbyne ligand to give alkyl complex **66**. Intramolecular proton transfer from other ligands (e.g., other alkyl groups) is also possible.^[65,66]

Scheme 27 Protonation of Carbene and Carbyne Ligands^[115,116]

 η^5 -Cyclopentadienyl(2,2-dimethylpropyl)nitrosyl(triphenylsilanolato)molybdenum(II) (65**); Typical Procedure:**^[115]

In a glovebox, [Mo(=CH*t*-Bu)Cp(pyridine)(NO)] (102 mg, 0.30 mmol) and Ph₃SiOH (83 mg, 1.0 equiv) were weighed into the reaction vessel. Benzene (20 mL) was vacuum-transferred onto the solids. The mixture was then warmed to rt and stirred for 1.5 h. Over the course of the reaction a color change from amber to dark red-brown occurred. The solvent was removed from the final mixture in vacuo, and the residue was extracted with Et₂O (2 × 25 mL). The extracts were filtered through Celite and the filtrate was concentrated under reduced pressure to incipient precipitation. Well-defined red blocks formed overnight and were isolated by cannulation; yield: 121 mg (75%); IR (Nujol) $\tilde{\nu}_{\text{max}}$: (NO) 1607 (vs) cm⁻¹; ¹H NMR (benzene-*d*₆, δ): 3.79 (d, 1H, CHH, $J_{\text{HH}} = 9.9$ Hz), 0.99 (d, 1H, CHH, $J_{\text{HH}} = 9.9$ Hz).

Applications of Product Subclass 4 in Organic Synthesis

Alkylchromium(III) compounds are involved in the large-scale commercial polymerization of ethene and propene. Well-defined complexes that mimic the activity and selectivities of the commercial catalyst have been obtained.^[117] An application of group 6 alkyl and aryl complexes that has been successfully applied to organic synthesis is the addition reaction to carbonyl compounds (see Sections 2.6.4.5 and 2.6.4.6). Other chromium-based systems have been developed for single-electron-transfer chemistry,^[118] oxidation of alkanes via hydrogen atom abstraction,^[119] and asymmetric ring opening of *meso*-epoxides.^[120] Although these latter systems are of interest for synthetic organic chemistry, they do not involve the formation of direct Cr–C bonds, and consequently these applications are not treated here.^[121]

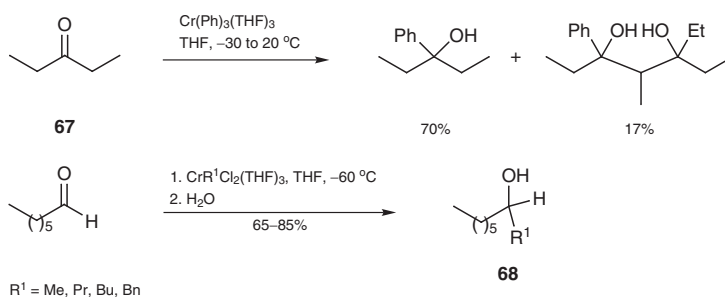
2.6.4.5 Method 5: Addition of Organochromium(III) Compounds to Carbonyl Compounds

Under certain circumstances, organochromium(III) compounds transfer their alkyl or aryl groups to aldehydes and, less frequently, to ketones. The particular selectivity and tolerance of this reaction make it particularly useful in organic synthesis. The use of these chromium reagents may be advantageous for use with acid-sensitive substrates, because of their reduced Lewis acidity relative to other transfer reagents [e.g., trichloromethyltitanium(IV) or alkyltrisisopropoxotitanium(IV)].

2.6.4.5.1 Variation 1: Reaction of Organochromium(III) Compounds Prepared from Organochromium(III) Chloride by Transmetalation

The organochromium(III) compound may be either isolated before the addition to the carbonyl compound or prepared in situ, as shown in Scheme 28. Triphenyltris(tetrahydrofuran)chromium(III) is able to react with ketones, viz. pentan-3-one (**67**) and cyclohexanone.^[122] On the other hand, chlorodialkyl and dichloroalkyl derivatives are highly aldehyde selective, while alkylpentaquachromium(III) is unreactive. The alkyl-dichlorochromium(III) reagent is particularly useful as it can be readily generated in situ by transmetalation from chromium(III) chloride and a Grignard reagent; see the formation of **68**.^[123] These reagents are able to transfer the alkyl group to the organic substrate even in an alcoholic medium or in the presence of water.^[124] Dichloro[(trimethylsilyl)methyl]-chromium(III) allows an aldehyde-selective alkenation process after acid hydrolysis.^[125] This procedure has been more recently supplanted by those described in the following variations.

Scheme 28 Reaction of Organochromium(III) Complexes with Carbonyl Compounds^[122,123]



Reaction of Triphenyltris(tetrahydrofuran)chromium(III) with Pentan-3-one (**67**):^[122]

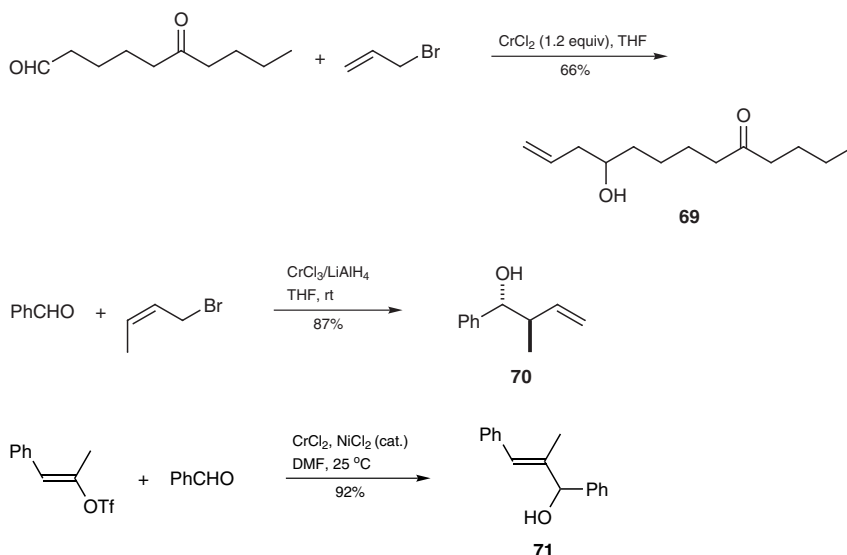
A briskly stirred suspension of $[\text{CrPh}_3(\text{THF})_3]$ [from $\text{CrCl}_3(\text{THF})_3$ (16 g, 43 mmol) suspended in THF (500 mL) and PhMgBr (129 mmol)] in THF at -30 °C was treated dropwise with freshly distilled pentan-3-one (**67**; 20 mL, 190 mmol). The mixture was then allowed to warm up to rt. After 2 h at 20 °C the solvent was removed by distillation under reduced pressure and the product hydrolyzed with H_2O and filtered, both residue and filtrate being washed with Et_2O . The dried ethereal layer was evaporated and the residue (21.2 g) separated by distillation. The volatile component, bp 57 – 62 °C/0.01 Torr (14.9 g, 90 mmol, 70% relative to PhMgBr) was shown to be 3-phenylpentan-3-ol by a direct comparison of its IR spectrum with that of an authentic specimen. The semicrystalline residue (5.87 g) was chromatographed to give traces of oily products and 3-ethyl-4-methyl-5-phenylheptane-3,5-diol; yield: 5.36 g (17% relative to PhMgBr); mp 90 – 92 °C (hexane).

2.6.4.5.2

Variation 2:**Reaction of Organochromium(III) Compounds Prepared from Chromium(II) Chloride by Oxidative Addition (The Nozaki–Hiyama–Kishi Procedure)**

This methodology was pioneered by Hiyama^[126] and refined by Kishi^[127] and Nozaki.^[128] The organochromium reagent is readily formed from chromium(II) salts upon one-electron oxidative addition (Section 2.6.4.2.1) of a wide range of substrates including allyl, propargyl, alkenyl, and aryl halides, alkenyl trifluoromethanesulfonates, and allyl sulfonates and phosphates. The most convenient chromium(II) salt is the anhydrous chloride, which can either be purchased or prepared in situ from chromium(III) chloride and various reducing agents. The performance of the chromium(II) chloride reagent in forming the Cr–C bond is enhanced by the addition of a catalytic amount of nickel(II) chloride.^[127,128]

The alkylchromium(III) species are highly aldehyde selective, e.g. the formation of **69** in Scheme 29.^[126] The most important feature, however, is the unparalleled compatibility with a wide array of functional groups in both reaction partners. In addition, the method features useful stereoselectivities. Substituted allyl reagents lead to the homoallyl alcohols. If the allyl reagent is γ -monosubstituted, the *anti*-alcohol is favored independent of whether the starting halide is *E* or *Z* configured; see the synthesis of **70** where the *anti*-product is obtained in 100% selectivity.^[129] Alkenyl halides or trifluoromethanesulfonates react with complete retention of their double-bond geometry, e.g. the synthesis of **71**.^[128] These useful features have made chromium-induced inter- or intramolecular C–C bond formations a frequent key step in the total synthesis of molecules of utmost complexity,^[130] including the total synthesis of brevetoxin B.^[131]

Scheme 29 The Nozaki–Hiyama–Kishi Reaction^[126,128,129]**3,3,6-Trimethylhepta-1,5-dien-4-ol; Typical Procedure:**^[126]

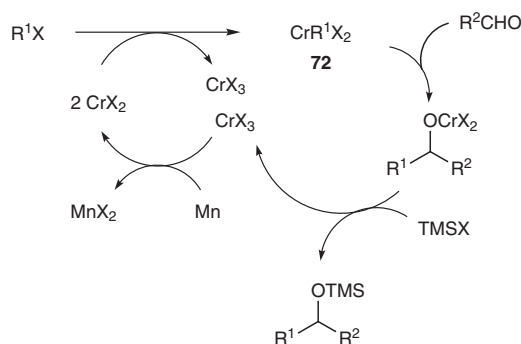
CrCl₃ (4.28 g, 27 mmol) was reduced with LiAlH₄ (513 mg, 13.5 mmol) in THF (20 mL). After stirring at rt for 10 min, 3-methylbut-2-enal (0.56 g, 6.1 mmol) and subsequently 1-bromo-3-methylbut-2-ene (2.01 g, 13.5 mmol) in THF (10 mL) were added dropwise over 20 min. Stirring for 3 h, followed by workup and distillation (97–100 °C/4 Torr, Kugelrohr), gave the product as an oil; yield: 0.90 g (88%).

for references see p 112

2.6.4.5.3

**Variation 3:
Catalytic Nozaki–Hiyama–Kishi Reaction (The Fürstner Procedure)**

The examples outlined in Section 2.6.4.5.2 are stoichiometric in chromium(II) chloride and generally employ a large excess of this reagent. As shown in Scheme 30, reaction of the organic halide with two equivalents of chromium(II) halide yields the desired organochromium species **72** and one equivalent of chromium(III) halide. The nucleophile then adds to the aldehyde with formation of a chromium alkoxide species. The high stability of the oxygen–chromium(III) bond serves as the thermodynamic sink; the alcohol product is recovered by hydrolysis in the stoichiometric process. The use of halosilane, however, forces an exchange by virtue of the higher oxophilicity of silicon, producing an additional equivalent of chromium(III) halide. At this point the reaction can be made catalytic in chromium by simply using a reagent capable of reducing chromium(III) to chromium(II), e.g. metallic manganese. This modification does not compromise the scope, practicability, efficiency, and chemo- and diastereoselectivity of the C–C bond formation.^[130,132,133] In addition, it reduces the consumption of the rather high-cost and toxic chromium reagent and paves the way for potential applications in enantioselective syntheses using chromium catalysts with chiral ancillary ligands.^[134]

Scheme 30 The Catalytic Nozaki–Hiyama–Kishi Reaction**2-Butyl-1-(4-methoxyphenyl)prop-2-en-1-ol: Typical Procedure:**^[130]

A soln of 4-methoxybenzaldehyde (340 mg, 2.5 mmol), 2-[(trifluoromethyl)sulfonyloxy]hex-1-ene (1.06 g, 4.6 mmol), and $TMSCl$ (0.75 mL, 6.0 mmol) in DMF (1.5 mL) and DME (5 mL) was dropped into a suspension of Mn powder (230 mg, 4.2 mmol), $CrCl_2$ (46 mg, 0.38 mmol), and $NiCl_2$ (10 mg, 0.07 mmol) in DME (5 mL) at $50^\circ C$. After being stirred for 5 h at that temperature, the mixture was quenched with H_2O (15 mL) and extracted with $EtOAc$ (3×50 mL), and the combined organic layers were washed with brine. Aq TBAF (75% w/w) was added, and the soln was stirred at rt until TLC showed complete desilylation of the crude product. Standard workup followed by flash chromatography (hexane/ $EtOAc$ 15:1) afforded the product as a colorless syrup; yield: 420 mg (76%).

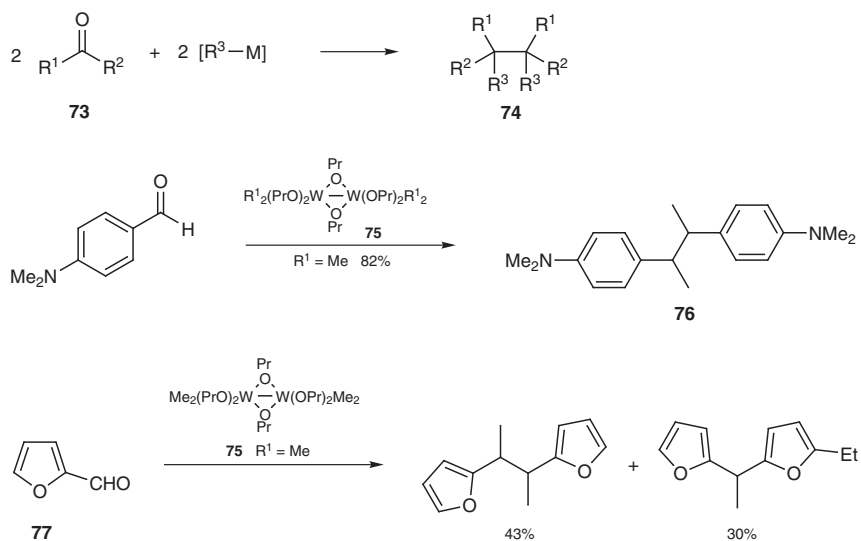
2.6.4.6

**Method 6:
Additive–Reductive Carbonyl Dimerization**

In this reaction an alkyl group R^3 is transferred from a suitable metal–alkyl complex to the electrophilic carbon of a carbonyl substrate **73** (Scheme 31), resulting in the deoxygenation and dimerization to product **74** in a single step.^[135] The substrate **73** can be an aromatic aldehyde or ketone, a conjugated enone, or a benzoic acid derivative. The alkyl transfer reagents $[R^3M]$ are tungsten(V) compounds formulated as dialkyldipropoxo(μ -propoxo)tungsten(V) dimers **75**. They are obtained in situ by alkylation of the correspond-

ing dichloro dimers with lithium or Grignard reagents and they are not isolated in view of their extreme thermolability. A large variety of alkyl groups, (trimethylsilyl)methyl, and phenyl have been used as R^3 , including ones where the β -hydrogen elimination process is possible.^[60] The procedure consists of the addition of the carbonyl substrate to **75** in tetrahydrofuran at -78°C , followed by warming to reflux and room-temperature base hydrolysis. Various substituents (e.g., methoxy, dimethylamino, fluoro, chloro, and hydroxy) on phenyl groups are tolerated (e.g., see synthesis of **76**), but the nitro and ethoxycarbonyl groups are not.^[135] For $R^3 = \text{Me}$, the carbonyl group must be conjugated with an unsaturated group, otherwise the monomeric carbinol is obtained. With $R^3 = \text{Ph}$, however, even saturated ketones yield the additive–reductive carbonyl dimerization product. Rearrangement products can also be obtained, depending on the substituents linked to the carbonyl group; see, for example, the reaction of 2-furaldehyde (**77**).^[60]

Scheme 31 Additive–Reductive Carbonyl Dimerization^[60,135]



1,2-Bis[4-(dimethylamino)phenyl]-1,2-dimethylethane (76); Typical Procedure:^[135]

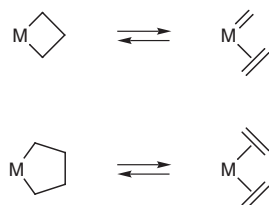
$[\text{W}_2\text{Cl}_4(\mu\text{-OPr})_4(\text{OPr})_4]$ (2.2 g, 2.50 mmol) was dissolved in THF (100 mL) at -78°C , followed by treatment with 1.5 M MeLi in Et_2O (4 equiv), resulting in a color change to dark green. After 30 min, the Gilman test indicated the absence of MeLi. To this soln was added a THF soln (25 mL) of 4-(dimethylamino)benzaldehyde (2.50 mmol). After stirring for 15 min at -78°C , the mixture was slowly warmed and refluxed for 3 h. The mixture was then hydrolyzed with 2 M NaOH (100 mL) at 20°C . Et_2O (50 mL) and petroleum ether were added and the mixture was stirred until dissolution of the amorphous hydrolysis product occurred. The organic phase was removed and the aqueous phase was extracted with Et_2O (2×100 mL). The combined organic phases were washed with H_2O and dried (Na_2SO_4). The solvents were removed by rotary evaporation, leaving a crude material which was identified (by GC in comparison with authentic samples) as a mixture of the title compound **76**; yield: 82% and 1-[4-(dimethylamino)phenyl]ethanol; yield: 4%.

2.6.5 Product Subclass 5: Metallacyclic Complexes

In many respects, the synthetic methods and reactivity of metallacyclic complexes parallel those of analogous dialkyl complexes. Metallacyclobutanes and metallacyclopentanes, on the other hand, display unique features. They may easily transform into, or be pre-

pared from, carbene–alkene and dialkene isomers, respectively (Scheme 32). The cyclic forms tend to be more stable for the heavier metal, with differences in stability of three orders of magnitude being reported for congeneric molybdenum and tungsten compounds.^[8]

Scheme 32 Transformations of Metallacyclobutanes and Metallacyclopentanes



Metallacyclobutane complexes are involved as intermediates in alkene metathesis reactions catalyzed by alkylidene complexes and their use is equivalent to that of the carbene complexes in this particular organic application (see Section 2.6.1). Chromacyclopentane complexes are invoked as intermediates in the catalytic trimerization of ethene to hex-1-ene.^[136] This catalytic process takes place with good selectivity (74%), but has not yet found application for the oligomerization of other alkenes nor for cross-oligomerization processes.

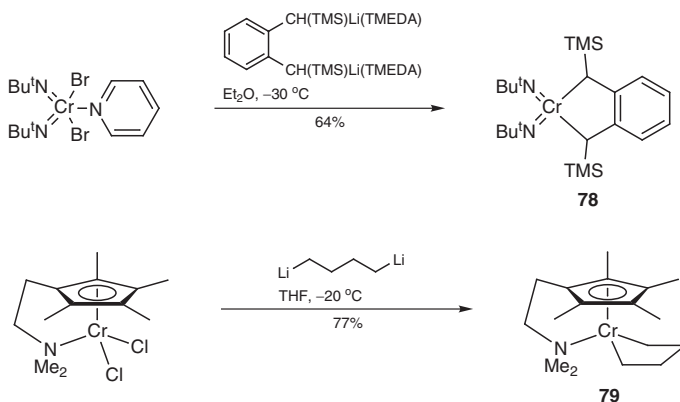
Synthesis of Product Subclass 5

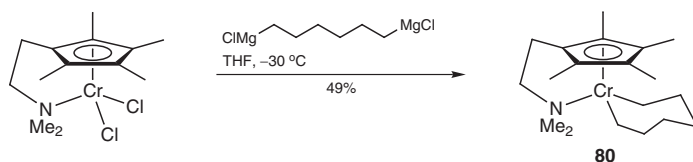
2.6.5.1

Method 1: By Transmetalation

This method is not as common as those described below for the preparation of group 6 metallacyclic derivatives. Dilithium and di-Grignard reagents have been used, as exemplified by the syntheses of **78**, **79**, and **80** (see Scheme 33).^[104,137] The synthesis of metallacycles with large ring sizes suffers from the competitive formation of oligomers and from β -hydrogen elimination processes.

Scheme 33 Metallacycles by Transmetalation^[104,137]





Butane-1,4-diyl(η^5 -pentamethylcyclopentadienyl)(trimethylphosphine)chromium(III);

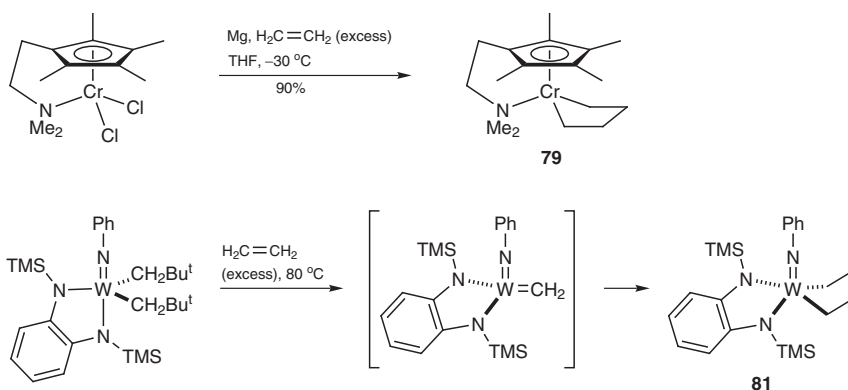
Typical Procedure:^[137]

[CrCp*Cl₂(THF)] (100 mL of a 0.085 M THF soln, 8.5 mmol) was treated with Me₃P (1 mL, 9.88 mmol) and cooled to -50 °C. 1,4-Dilithiobutane (35 mL of a 0.277 M soln in Et₂O) was added slowly and the mixture was stirred at -35 °C. The mixture was evaporated to dryness and the residue was extracted with pentane (2 × 150 mL) at -20 °C. The extract was filtered, cooled to -78 °C, and the resulting blood-red crystals isolated and dried under high vacuum; yield: 2.06 g (76%).

**2.6.5.2 Method 2:
By Reductive Coupling of Alkenes**

This method is specific for metallacyclopentanes. The alkene-coupling process is favored by metal reduction. A typical synthetic strategy is the in situ reduction of a metal halide precursor in the presence of the alkene; see, for example, the synthesis of **79** in Scheme 34.^[137] An alkylidene precursor may also lead to a metallacycle with elimination of the carbene ligand as in the synthesis of **81**, representing a deactivation pathway for alkene metathesis catalysts.^[138] The two alkenes may be generated in situ in the coordination sphere by rearrangement processes, such as intramolecular hydrogen transfer from an alkyl-*vinyl* precursor.^[139]

Scheme 34 Metallacyclopentanes by Reductive Coupling of Alkenes^[137,138]



Butane-1,4-diyl(η^5 -pentamethylcyclopentadienyl)(trimethylphosphine)chromium(III);

Typical Procedure:^[137]

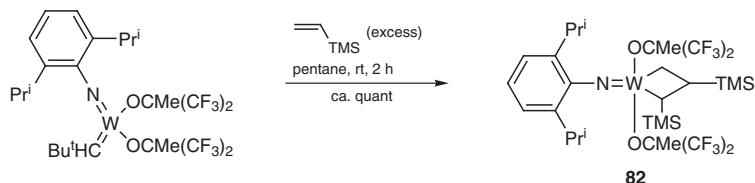
The compound described in the experimental procedure in Section 2.6.5.1 can also be prepared in 68% yield by reacting [CrCp*Cl₂(THF)] with active Mg and Me₃P in an Et₂O soln saturated with ethene at -78 to -10 °C.

2.6.5.3

**Method 3:
By Addition of Alkenes to Carbene Complexes**

This method is specific for metallacyclobutane complexes. For stability reasons this method has been mostly applied to the preparation of high oxidation state tungstacyclobutane derivatives. Given the equilibrium shown in Scheme 32, the use of excess alkene may result in further exchange processes. The preparation of **82** in Scheme 35 is a two-step process involving the elimination of 3,3-dimethylbut-1-ene.^[29]

Scheme 35 Metallacyclobutanes by Alkene Addition to Carbene Complexes^[29]


1,2-Bis(trimethylsilyl)propane-1,3-diyl(2,6-diisopropylphenylimido)bis(1,1,1,3,3,3-hexafluoro-2-methylpropan-2-olato)tungsten(VI) (82); Typical Procedure:^[29]

Trimethyl(vinyl)silane (124 μ L) was added to a soln of $[W(=CHt-Bu)(=NC_6H_3-2,6-iPr_2)(OCMe(CF_3)_2)_2]$ (212 mg) in pentane (15 mL). The solvent was removed in vacuo after 2 h to give a light yellow product that was recrystallized from pentane to give light yellow crystals. The yield of the crude product was essentially quantitative.

2.6.6

**Product Subclass 6:
Complexes with Triply Bonded Heteroelement Ligands**

The only known examples are nitride complexes, whereas terminal phosphide and arsenide complexes are known only without metal–carbon bonds. The lone pair on the nitride ligand retains sufficient Lewis basicity for coordination. Consequently, electronically unsaturated derivatives yield polymeric or oligomeric structures where nitrido groups bridge two metal centers symmetrically or asymmetrically.^[140,141] Mononuclear complexes with terminal nitrido ligands are only found when the Lewis acidity of the metal center is suppressed by π -donation from other ligands, e.g. amido ligands as in bis(diisopropylamido)[(dimethylphenylsilyl)methyl]nitridochromium(VI).^[142] In addition, oligonuclear structures where the nitrogen atom forms bonds of lower order with more metal atoms may be preferred to a triply bonded mononuclear structure.

Almost all organometallic nitride complexes have been obtained by adding the organic group(s) to inorganic substrates that already contain the $M\equiv N$ function. An example is the synthesis of compound **57** shown in Scheme 23.^[103] A large number of methods for assembling a metal–nitrogen triple bond in inorganic compounds are outlined in a review.^[143] Some of these methods are also of potential applicability to organometallic substrates and are, therefore, briefly mentioned here (Scheme 36).

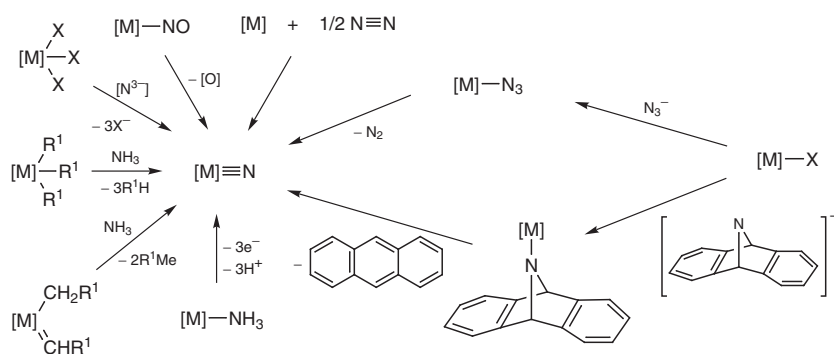
The exchange of three halides with a nitride can be accomplished by use of the $[Hg_2N]^+$ ion, tris(trimethylsilyl)amine, or ammonia, with elimination of mercury(II) salts, trimethylsilyl halide, or hydrogen halide, respectively. In the latter case, excess ammonia is needed to neutralize the acid. The ammonolysis of trialkyl or alkyl–carbene complexes has been used successfully to prepare organometallic nitride complexes of group 4 and 5 metals (see Sections 2.8–2.11) and could potentially be used for group 6 metals as well. Ammonolysis of a carbyne complex would appear to have the same potential.

Nitride complexes are also obtained by exchange of a halide with groups capable of readily eliminating a stable byproduct while leaving a nitrogen atom bonded to the met-

al, with concomitant metal oxidation. Azide is the ubiquitous ligand with these characteristics, leading to the expulsion of dinitrogen. It can be administered either as a hydrophilic alkali metal salt or as the lipophilic trimethylsilyl derivative. The reaction between trichloro(η^5 -pentamethylcyclopentadienyl)molybdenum(IV) dimer and trimethylsilyl azide generates dichloro(η^5 -pentamethylcyclopentadienyl)nitridomolybdenum(VI) which, however, further evolves to more complex products.^[140] An alternative to the azide reagent is the deprotonated 9,10-dihydro-9,10-epiminoanthracene,^[144] leading to the elimination of anthracene.

Other nitride compounds have been obtained by oxidation of coordinated ammonia ligands. The deoxygenation of a nitrosyl ligand is of potentially wide applicability. The oxygen-abstracting agent is an oxophilic metal complex such as trimesityl(tetrahydrofuran)vanadium(III).^[145] Nitride compounds are also the byproducts of the addition of nitriles to triply bonded molybdenum and tungsten compounds (see Section 2.6.2.2). The splitting of the dinitrogen triple bond by a metal complex is a more recent achievement^[146] but is so far limited to a sterically protected triamidomolybdenum system.^[147] Other methods include the use of nitrogen trichloride, trithiazyl chloride, or aryl azide reagents.^[143,148] Splitting of nitrous oxide (N_2O) provides mixtures of nitrido and nitrosyl products.^[148]

Scheme 36 Methods for Assembling the $M\equiv N$ Function in Inorganic Compounds of Group 6 Metals



Phosphide and arsenide complexes have also been synthesized for the first time in non-organometallic complexes.^[149,150] Organometallic derivatives have yet to be reported.

2.6.7 Product Subclass 7: Complexes with Doubly Bonded Heteroelement Ligands

The vast majority of examples in this subclass are oxo and imido derivatives. A fair number of sulfido derivatives are also known, whereas selenido and tellurido derivatives and compounds containing a double bond to phosphorus (phosphinidene complexes) are fewer. The relative small number of derivatives with phosphorus and the chalcogenides may be attributed to the weakness of the π -interaction. The bonds between the aforementioned groups and a transition metal are considered double according to valency; however, these bonds are often relatively short and strong in electronically unsaturated systems, especially for oxo and imido ligands, because of the participation of an additional ligand lone pair to the bonding.

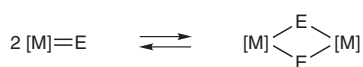
In many cases a mononuclear structure with a terminal, doubly bonded heteroelement ligand may be unfavorable with respect to the alternative dinuclear structure where the ligand adopts a bridging, singly bonded conformation (Scheme 37). Facile interconversion of the two forms may occur, leading to analogous synthetic strategies and reactivity.

for references see p 112

For this reason, bridged dinuclear compounds are also included in this section, although emphasis is placed on the terminally bonded derivatives. The mononuclear structure is favored by a sterically encumbering coordination sphere, whereas electronic configurations that allow the formation of metal–metal bonds lead preferentially to dinuclear structures. First-row heteroelement-containing ligands (oxo, imido) are found terminally bonded more frequently than their heavier congeners because of their superior π -bonding ability.

As seen for the triply bonded heteroelement derivatives, the most common synthetic method for the present subclass consists of the introduction of the organic fragment into an inorganic substrate that already contains the desired doubly bonded heteroelement ligand. This is especially true for the oxo compounds, as metal oxides or oxometalate precursors are readily available and inexpensive starting materials. The methods discussed in this section are those leading to the assembly of the metal–heteroatom double bond starting from substrates that already contain hydrocarbyl ligands.

Scheme 37 Monomer–Dimer Dichotomy for Doubly Bonded Heteroelement Ligands



Synthesis of Product Subclass 7

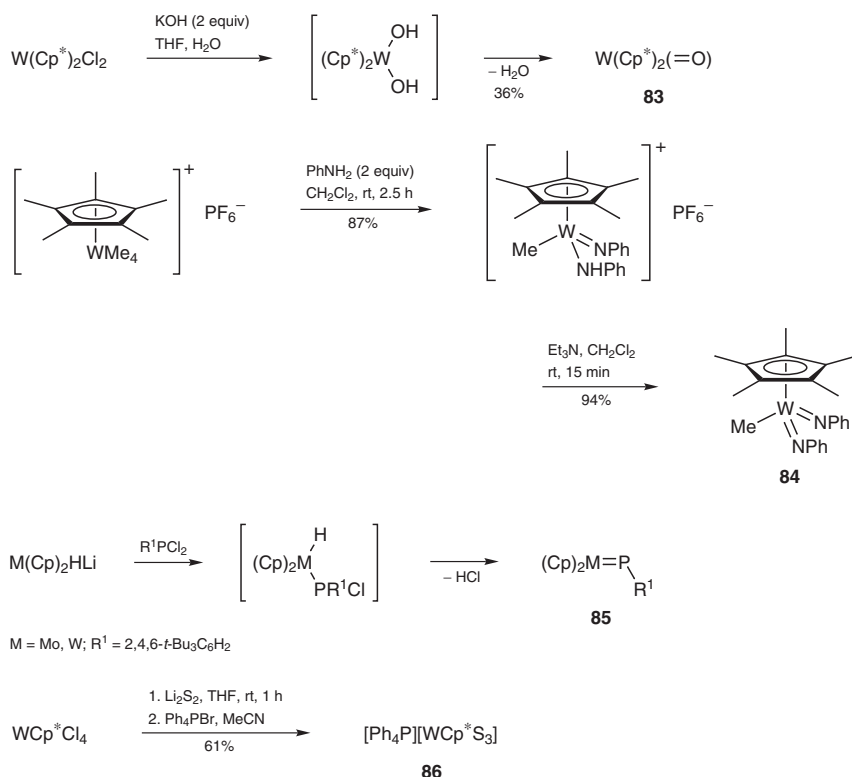
2.6.7.1

**Method 1:
From Complexes Containing Singly Bonded Heteroelement Ligands**

Singly bonded heteroelement ligands that contain a hydrogen substituent may be deprotonated by either an internal or an external base and transformed into doubly bonded ligands. In many cases the singly bonded hydrogen-bearing ligand is formed in situ by ligand exchange from a halide or alkoxide precursor. This is the case for the reaction between dichlorobis(η^5 -pentamethylcyclopentadienyl)tungsten(IV) and potassium hydroxide, leading to the oxo derivative **83** by spontaneous elimination of water; see Scheme 38.^[102] In this case the proton scavenger is a coordinated base (OH) and the conjugate acid is expelled. In high oxidation state systems, halides may be sufficiently good bases leading to the expulsion of the hydrogen halide, as in the hydrolysis of tetrabromo(η^5 -cyclopentadienyl)molybdenum(V).^[151] An intramolecular hydrogen transfer to a carbyne ligand furnishes the oxo–alkyl derivative **66** (Scheme 27).

For the synthesis of **84**, aminolysis of tungsten–methyl bonds yields an imido and an amido ligand in a first step. An external base, however, is necessary to produce the second imido ligand, as neither the residual methyl ligand nor excess aniline is sufficiently basic to carry out the last deprotonation.^[152] Imido derivatives have also been obtained from trimethylsilylamido derivatives, the elimination of the trimethylsilyl group (a proton equivalent) being favored by the presence of chloro, alkoxo, or oxo ligands. An external base may also serve as a catalyst for the intramolecular proton transfer to another ligand, as shown in the triethylamine-catalyzed isomerization of the amido–carbyne complexes **20** to the imido–carbene complexes **21** (Scheme 7).^[8,17,29]

A reverse strategy involves rearrangement from a precursor complex that contains the proton on the metal center and the base on the heteroatom ligand, as in the synthesis of the phosphinidene complex **85**.^[153] Ligand exchange from halide precursors with lithium disulfide has provided access to sulfido derivatives, occasionally involving metal oxidation, as in the formation of (η^5 -pentamethylcyclopentadienyl)trisulfidotungstate(VI) **86**.^[154] The same transformation can also be performed, although in lower yield, using hydrogen sulfide in the presence of triethylamine.^[155]

Scheme 38 Syntheses from Complexes Containing Singly Bonded Heteroelement Ligands^[102,152–154]***tert*-Butylammonium Trioxo(η⁵-pentamethylcyclopentadienyl)tungstate(VI)**^[155]

An excess of *t*-BuNH₂ (0.08 mL, 0.76 mmol) and H₂O (0.04 mL, 2.2 mmol) was added to a CH₂Cl₂ soln (25 mL) of [WCp*Cl(=O)₂] (140 mg, 0.36 mmol). The soln was stirred for 1 h, dried (MgSO₄), and filtered through a pad of Celite. The solvent volume was reduced to 2–3 mL and hexane was added to induce precipitation of [WCp*(=O)₃][*t*-BuNH₃], which was isolated; yield: 137 mg (86%).

2.6.7.2

Method 2:**From Other Complexes Containing Doubly Bonded Heteroelement Ligands**

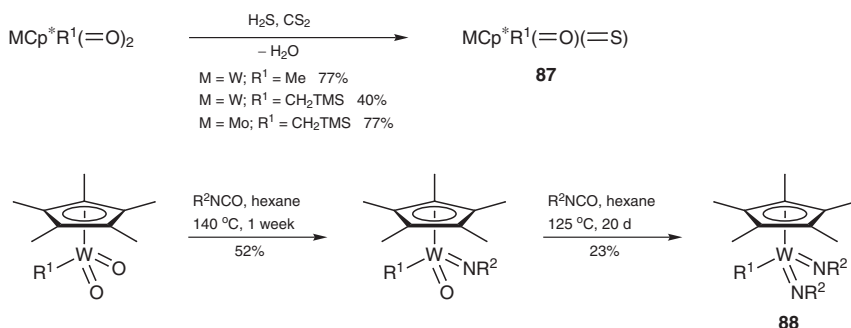
Compounds containing a metal–heteroatom double bond may be obtained from analogous derivatives by exchanging the heteroelement ligand. This strategy is especially useful for preparing imido and sulfido derivatives from more easily available oxo compounds. In most cases, this method is used for the preparation of inorganic materials that are subsequently converted into organometallic compounds via metathetical reactions (see Section 2.6.1.5).^[25] The new function (X) can be administered as either the diprotic acid (H₂X) or the cumulene (O=C=X).

The use of the acid presents potential problems in the presence of sensitive hydrocarbyl ligands. For particular systems, especially high oxidation state molybdenum and tungsten compounds, the metal–carbon bonds are sufficiently covalent and resist protonolysis. This is illustrated in the oxygen/sulfur exchange leading to products **87** in Scheme 39.^[156] The relative strengths of the metal–heteroelement double bonds are against the exchange of oxygen by sulfur, whereas the weaker acidity of water vs hydrogen sulfide favors the exchange. Concerning the oxo/imido exchange, the acidity criteri-

on favors the conversion of imido ligands into oxo ligands, especially when the amine by-product is further consumed by protonation in an acidic medium.^[152] The synthetically more useful reverse exchange is favored by trapping water with the chlorotrimethylsilane/triethylamine combination, leading to hexamethyldisiloxane and triethylammonium chloride.^[25] This reaction could in fact involve the in situ conversion of the primary amine into a bis(trimethylsilyl)amine which subsequently carries out the exchange process. The direct use of a trimethylsilyl-substituted amine has also led to satisfactory results.^[157]

The use of cumulenes has practical synthetic use only for the conversion of oxo into imido derivatives by the use of isocyanates. Formation of carbon dioxide provides the necessary driving force to the reaction. An example is the synthesis of compound **88**, where the incompleteness of the second step limits the yield.^[158] A problem of this synthesis is the potential cycloaddition of the imido product with excess isocyanate, leading to metalated ureas.

Scheme 39 Syntheses from Other Complexes Containing Doubly Bonded Heteroelement Ligands^[156,158]

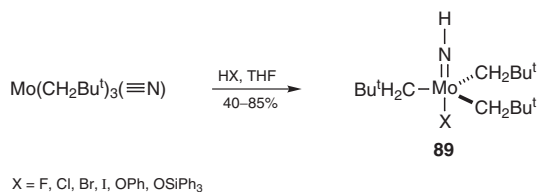


Oxo(η^5 -pentamethylcyclopentadienyl)sulfido[(trimethylsilyl)methyl]molybdenum(VI) (87**, M = Mo; R¹ = CH₂TMS); Typical Procedure:**^[156]

A soln of [Mo(CH₂TMS)Cp^{*}(=O)₂] (25 mg, 0.071 mmol) in CS₂ (10 mL) saturated with H₂S was incubated at rt for 3 d, during which time the color of the soln changed from tinted yellow to red. The solvent was removed with a stream of N₂. The red residue was spotted on a 0.25-mm-thick silica gel TLC plate and then developed with Et₂O. The red band was collected to give [Mo(CH₂TMS)Cp^{*}(=O)(=S)]; yield: 20.2 mg (77%). X-ray crystallographic quality, dark red crystals were grown from a saturated soln in hexane at -20 °C.

2.6.7.3 Method 3: From Complexes Containing Triply Bonded Heteroelement Ligands

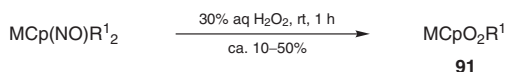
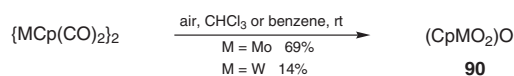
This method is restricted to the transformation of terminal nitrides to imide compounds. A rare example of the application of this method to organometallic substrates is the protonation of tris(2,2-dimethylpropyl)nitridomolybdenum(VI) to afford the imido complexes **89** (Scheme 40).^[1103,159]

Scheme 40 Synthesis from a Complex Containing a Triply Bonded Heteroelement Ligand^[159]**Tris(2,2-dimethylpropyl)imido(triphenylsilanolato)molybdenum(VI) (89, X = OSiPh₃);****Typical Procedure:**^[159]

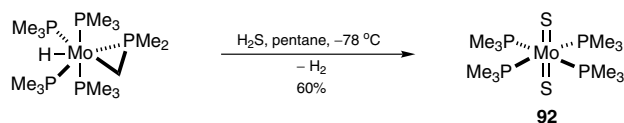
[Mo(CH₂*t*-Bu)₃(≡N)] (1.0 mmol) and triphenylsilanol (1.0 mmol) were placed in a Schlenk tube under argon and dissolved in THF (30 mL). The mixture was stirred at 60 °C for 48 h. Removal of the solvent under reduced pressure and extraction of the residue with hexane (5 mL) afforded [Mo(CH₂*t*-Bu)₃(=NH)(OSiPh₃)] as a white powder. Recrystallization from hexane at 0 °C gave white crystals; yield: 240 mg (40%); IR (Nujol) $\tilde{\nu}_{\text{max}}$: (N–H) 3371 cm⁻¹.

**2.6.7.4 Method 4:
By Oxidative Processes**

The most useful oxidizing agents for the preparation of organometallic oxo compounds have been nitrogen oxides such as trimethylamine oxide, nitrous oxide, and nitric oxide, allowing the preparation of compounds that cannot be accessed by other methods, although the oxidations are often accompanied by the formation of other products.^[160] For selected systems, oxidation of a low-valent precursor with the heteroelement itself in its natural state (e.g., O₂, S₈) is sufficiently clean to be synthetically useful for the preparation of oxo and sulfido complexes. This is especially true for η⁵-cyclopentadienyl and η⁵-penta-methylcyclopentadienyl systems. The synthesis of **90** (Scheme 41), involving exhaustive decarbonylation, represents a typical example.^[161] Photochemical activation of the carbonyl precursor is necessary in some cases.^[162] Occasionally, elemental oxygen can be replaced by hydrogen peroxide, as, for example, in the synthesis of **91**, but this requires the use of a strict stoichiometric ratio to avoid further conversion into peroxy analogues.^[163] Hydrogen sulfide also leads to oxidation, with expulsion of dihydrogen, in the synthesis of compound **92**.^[164] The synthetic utility of the oxidation with a diazene to yield a bis(imido) product has only been illustrated for inorganic target systems.^[165]

Scheme 41 Oxidative Processes^[161,163,164]

R¹ = Me, CH₂TMS; M = Mo, W



Chlorodioxo(η^5 -pentamethylcyclopentadienyl)molybdenum(VI):^[162]

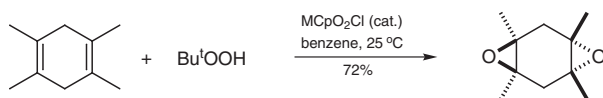
In a drybox, a 100-mL glass ampule (Teflon stopcock) was charged with a soln of $[\text{MoCp}^*\text{Cl}(\text{CO})_3]$ (0.980 g, 2.79 mmol) in toluene (50 mL). O_2 was bubbled through the soln via a 24-gauge syringe needle at a rate of approximately $2 \text{ bubbles} \cdot \text{s}^{-1}$ while the soln was irradiated with a 450-W medium-pressure Hg immersion lamp at 5°C . The reaction was monitored by IR spectroscopy and was stopped after 90 min when the absorbances due to the carbonyl ligands of the starting material at $1700\text{--}2000 \text{ cm}^{-1}$ had disappeared. During the reaction the soln turned from a red-orange to an amber shade with some blue solids precipitated on the walls of the reaction vessel. The toluene was removed under vacuum, leaving a brown solid. The solid was taken up in toluene in the drybox and the resulting soln filtered through a medium-porosity sintered-glass frit to remove insoluble blue impurities. Recrystallization (toluene/hexane) afforded $[\text{MoCp}^*\text{Cl}(\text{=O})_2]$ as a yellow solid; yield: 0.508 g (61%); IR (benzene- d_6) $\tilde{\nu}_{\text{max}}$: (Mo=O) 920 (s), 890 (s) cm^{-1} ; $^1\text{H NMR}$ (benzene- d_6 , δ): 1.63 (s, C_5Me_5).

 η^5 -Cyclopentadienyldioxo[(trimethylsilyl)methyl]tungsten (91, $\text{R}^1 = \text{CH}_2\text{TMS}$; $\text{M} = \text{W}$);**Typical Procedure:**^[163]

To a stirred, purple soln of $[\text{W}(\text{CH}_2\text{TMS})_2\text{Cp}(\text{NO})]$ (1.20 g, 2.65 mmol) in Et_2O (50 mL) was added a 30% by weight aq soln of H_2O_2 (0.22 mL, 2.8 mmol of H_2O_2). The initial purple color of the mixture faded over the course of 1 h to pale yellow. An IR spectrum of the final yellow soln was devoid of absorptions due to the nitrosyl reactant. Volatiles were removed from the final mixture under reduced pressure to obtain a sticky yellow solid which was dried at $20^\circ\text{C}/0.005 \text{ Torr}$ for 2 h. Recrystallization of the resulting pale yellow solid from $\text{Et}_2\text{O}/\text{hexanes}$ (1:1) at -20°C afforded $[\text{W}(\text{CH}_2\text{TMS})\text{Cp}(\text{=O})_2]$ as a white microcrystalline solid; yield: 0.50 g (51%); IR (benzene- d_6) $\tilde{\nu}_{\text{max}}$: (W=O) 948 (s), 907 (s) cm^{-1} ; $^1\text{H NMR}$ (benzene- d_6 , δ): 5.69 (s, 5H, Cp), 0.88 (s, 2H, CH_2), 0.28 (s, 9H, TMS).

Applications of Product Subclass 7 in Organic Synthesis**2.6.7.5****Method 5:****Catalytic Epoxidation of Alkenes**

High oxidation state molybdenum oxo complexes are well-established catalysts for the epoxidation of alkenes by alkyl hydroperoxides, such as in the production of 2-methyloxirane (Halcon process). Chlorodioxo(η^5 -pentamethylcyclopentadienyl)molybdenum(VI) provides an organometallic example of a catalytically active system. The epoxidation reaction is stereoselective, as shown by the selective formation of *trans*- and *cis*-1,2-diphenyloxirane from the respective *E*- and *Z*-alkenes, and can be applied to highly substituted alkenes; see Scheme 42.^[162] Studies on this system have shown that the degradation of the catalyst involves oxidative poisoning to an unreactive peroxy complex.^[162]

Scheme 42 Catalytic Epoxidation of Alkenes^[162]**1,2-Epoxyoctane; Typical Procedure:**^[162]

In a drybox, a soln of $[\text{MoCp}^*\text{ClO}_2]$ (0.101 g, 0.338 mmol) in benzene (5 mL) was placed into a 50-mL bomb. Cyclooctene (1.77 mL, 13.6 mmol) was added via a syringe. Outside the drybox, 3 M *t*-BuOOH in 2,2,4-trimethylpentane (11.3 mL, 34 mmol) was added. The bomb was heated to 60°C for 3 h. The soln was then diluted to a total volume of 150 mL with benzene. The organic layer was washed with H_2O ($6 \times 100 \text{ mL}$) to remove excess hydroper-

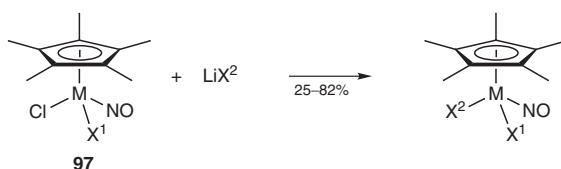
1-[(Diphenylphosphino-κP)methyl]-N-[[[(diphenylphosphino-κP)methyl]dimethylsilyl]-1,1-dimethylsilanamido-κ,N](phenylsulfido)methylchromium(III) (96):^[170]

To a red-brown soln of $[\text{CrMe}\{\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2\}]$ (0.16 g, 0.27 mmol) in toluene (10 mL) cooled to 0 °C was added a soln of PhSSPh (0.03 g, 0.14 mmol) in toluene (5 mL). Immediately, the soln changed to a dark purple color. After the mixture was stirred for 1 h at 0 °C, the soln was warmed to rt and the solvent was removed almost to dryness. The residue was quickly dissolved in hexane (1 mL) and filtered through Celite, and the solvent was removed in vacuo. Recrystallization from hexanes/toluene (1 mL: 3 drops) in a -40 °C freezer yielded a thick oil, which upon agitation gave **96** as purple crystals; yield: 0.12 g (66%).

**2.6.8.2 Method 2:
By Transmetalation**

Compounds that already contain a single bond between the metal and a heteroatom ligand may exchange the latter upon treatment with a suitable salt of the desired new ligand. The ubiquitous substrates are the halides, especially the chlorides which are easily accessible by oxidative procedures (Section 2.6.8.1 above) or from inorganic halide precursors. One example is the synthesis of **20** in Scheme 7. Like the alkylating agents discussed previously (Sections 2.6.3.1 and 2.6.4.1), some salts are potential reducing agents, especially alkyl and aryl sulfides, phosphides, and amides. The reaction of precursor **97** (Scheme 44) with a variety of lithium salts always affords the metathesis product in good yield when $\text{X}^1 =$ alkoxy or amido.^[171,172] When $\text{X}^1 =$ chloro, 5% of reduction is afforded by the 4-tolylamide salt with the molybdenum system, while the diphenylphosphido reagent yields exclusively reduction products for both molybdenum and tungsten.^[173]

Scheme 44 Transmetalation^[171–173]



M = Mo, W; $\text{X}^1 = \text{Cl}, \text{NHtBu}, \text{OtBu}$; $\text{X}^2 = \text{NHtBu}, \text{OtBu}, \text{PPh}_2$

Bis(2,6-diisopropylphenolato)(2,6-diisopropylphenylimido)(2,2-dimethylpropylidene)-tungsten; Typical Procedure:^[17]

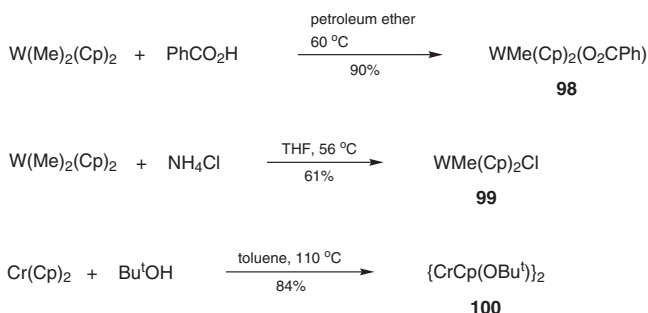
The lithium salt of 2,6-diisopropylphenoxide (1.60 g, 6.19 mmol) was added to $[\text{W}(=\text{CHtBu})\text{Cl}_2(=\text{NC}_6\text{H}_3-2,6\text{-iPr}_2)(\text{DME})]$ (1.82 g, 3.09 mmol) in Et₂O (50 mL) at -40 °C. The soln was warmed to 25 °C and stirred for 45 min. The mixture was filtered, and the filtrates were concentrated to afford an orange solid. Recrystallization of this material from a minimum of pentane afforded the product as a bright yellow solid in two crops; yield: 1.74 g (72%).

**2.6.8.3 Method 3:
From σ-Alkyl Complexes**

Protonolysis of the typically polar bond between a group 6 metal and a hydrocarbyl ligand is usually considered to be an unwanted decomposition reaction. When metal–heteroatom bonds are desired, however, selective alkane-elimination reactions can sometimes offer significant advantages, such as ready availability and stability of the protonated source of the desired ligand (such as carboxylic acids, alcohols, or amines) and the absence of inorganic salts as byproducts (the resulting alkane is normally easily removed

in vacuo). The synthesis of **84** proceeds via the protonolysis of the tungsten–methyl bond with aniline to form an arylamide ligand (Scheme 38),^[152] and Scheme 45 illustrates related examples involving benzoic acid and ammonium chloride (**98** and **99**, respectively).^[174,175] Hydrocarbyl groups other than σ -alkyls may also be used as precursors for this reaction, as demonstrated by the reaction of chromocene with *tert*-butyl alcohol to give **100**.^[176]

Scheme 45 Syntheses from σ -Alkyl Complexes^[174–176]



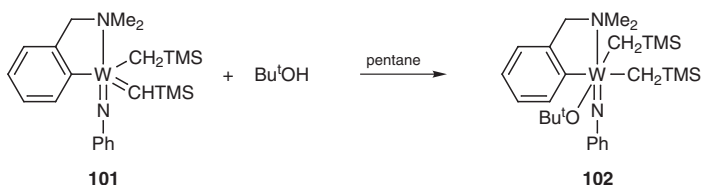
(Benzoato-O)bis(η^5 -cyclopentadienyl)methyltungsten(IV) (98**); Typical Procedure:**^[174]

The compound $[\text{W}(\text{Me})_2(\text{Cp})_2]$ (0.52 g, 1.52 mmol) in petroleum ether (bp 100–120 °C, 25 mL) was treated with benzoic acid (0.19 g, 1.51 mmol) and the mixture was warmed to 60 °C. Methane was evolved and the soln turned red. After 1 h the soln was filtered and slowly concentrated under reduced pressure. Red-brown crystals separated which were collected by filtration, washed with petroleum ether (2 \times 15 mL), and finally recrystallized (petroleum ether/Et₂O 2:1); yield: 0.61 g (90%).

2.6.8.4 Method 4: From Carbene or Carbyne Complexes

Addition of the conjugate acid of the desired ligand to a metal–carbene or –carbyne compound results in protonation of the hydrocarbyl ligand (see also Sections 2.6.1.4 and 2.6.4.4), transforming it into an alkyl or carbene ligand with formation of a new metal–heteroatom bond. Examples are the preparations of compound **19** (Scheme 7) and compound **65** (Scheme 27). The reaction of the carbene substrate **101** with *tert*-butyl alcohol produces product **102** (Scheme 46) which, upon heating, eliminates alkane and affords a new carbene compound in an overall process which resembles the protonolysis of an alkyl complex (Section 2.6.8.3).^[19] The same reaction of **101** with triphenylsilanol at low temperatures leads to the protonolysis product directly.

Scheme 46 Synthesis from a Carbene Complex^[19]



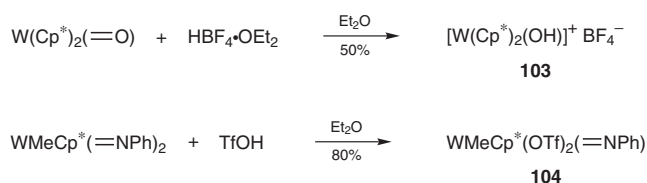
η^5 -Cyclopentadienyl(2,2-dimethylpropyl)nitrosyl(triphenylsilanolato)molybdenum(II) (65); Typical Procedure:^[115]

See Section 2.6.4.4.

**2.6.8.5 Method 5:
From Complexes Containing Doubly Bonded Heteroelement Ligands**

Like the synthesis of alkyl compounds by selective protonation of carbene groups (Section 2.6.8.4), ligands with metal–heteroatom single bonds may be obtained from oxo or imido complexes via a single-proton-transfer reaction, as illustrated for **103** in Scheme 47. Alternatively, the metal–heteroatom bond may be protonated twice, with the external acid (HX) providing the M–X bond of the final product, as in the synthesis of **104**. The replacement of an oxo or imido ligand with two singly bonded ligands may induce other modifications in the molecule, notably α -hydrogen elimination from an alkyl group, transforming it into a carbene ligand (see Section 2.6.1.1.3).

Scheme 47 Syntheses from Complexes Containing Doubly Bonded Heteroelement Ligands^[102,152]



Hydroxobis(pentamethylcyclopentadienyl)tungsten(IV) Tetrafluoroborate (103):^[102]

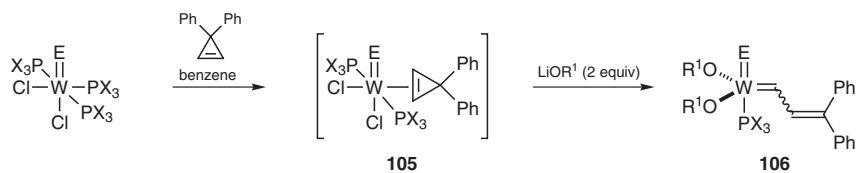
A soln of $[\text{W}(\text{Cp}^*)_2(=\text{O})]$ (120 mg, 0.26 mmol) in Et_2O (10 mL) was treated with $\text{HBF}_4 \cdot \text{OEt}_2$ (excess) at -78°C . The mixture was warmed to rt and the product was deposited as a white solid which was isolated by filtration; yield: 75 mg (50%); IR (Nujol) $\tilde{\nu}_{\text{max}}$: (WO–H) 3340 (s, br) cm^{-1} ; ^1H NMR (benzene- d_6 , δ): 1.88 (s, C_5Me_5).

**2.6.9 Product Subclass 9:
Miscellaneous Complexes**

Synthesis of Product Subclass 9

**2.6.9.1 Method 1:
Allylidene Complexes from Cyclopropenes**

Ring-opening reactions of 3,3-disubstituted cyclopropenes yield allylidene complexes, a synthetic route of particular utility for the generation of ruthenium-based alkene metathesis catalysts.^[47] This methodology has been extended to tungsten allylidene compounds using tungsten(IV) oxo^[177] or imido^[178] precursors (Scheme 48). These reactions proceed via initial formation of the η^2 -cyclopropene adduct **105**, followed by ring opening. Metathesis of the chloride ligands with electron-withdrawing alkoxide groups furnishes alkene metathesis catalysts **106** (see Section 2.6.1.5).

Scheme 48 Allylidene Complexes from Cyclopropenes^[177,178]E = O, NC₆H₃-2,6-iPr₂PX₃ = PMePh₂, PEt₂Ph, P(OMe)₃OR¹ = OMe(CF₃)₂

Dichloro(2,6-diisopropylphenylimido)(3,3-diphenylallylidene)bis(trimethyl phosphite) tungsten (105, E = NC₆H₃-2,6-iPr₂; X = OMe); Typical Procedure:^[178]

A soln of 3,3-diphenylcyclopropene (1.84 g, 9.55 mmol) in benzene (30 mL) was added via cannula to a soln of [WCl₂(=NC₆H₃-2,6-iPr₂){P(OMe)₃}₃] (7.12 g, 8.88 mmol) in benzene (60 mL), and the mixture was then stirred for 2 h at 80 °C. The solvent was removed in vacuo, and the resulting orange oil was left under dynamic vacuum for an additional 12 h. The product was then dissolved in THF (95 mL), and the resulting orange soln was filtered. After all but THF (10 mL) had been removed in vacuo, addition of pentane (150 mL) yielded an orange powder; yield: 5.50 g (72%); ¹H NMR (90 MHz, toluene-*d*₈, δ): 12.85 (dt, 1H, *J*_{HH} = 12.75, *J*_{HP} = 6.37, *H*_ω), 10.23 (dt, 1H, *J*_{HH} = 12.75, *J*_{HP} = 2.45, *H*_β), 3.65 [t, 18H, P(OMe)₃].

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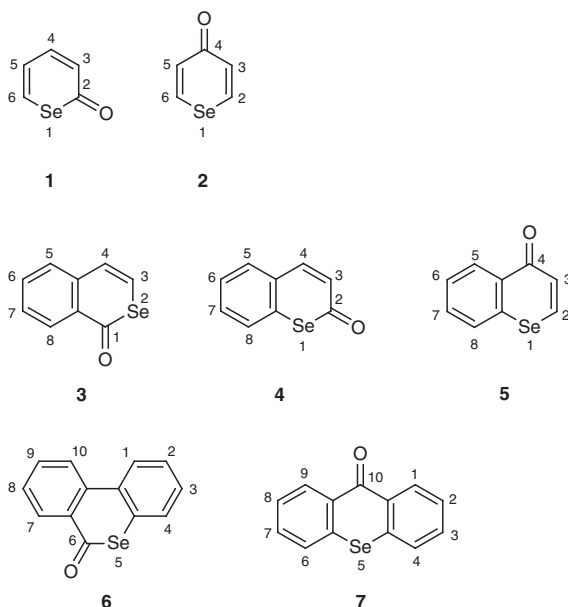
Product Class 11: Selenopyranones and Benzoselenopyranones

P. J. Murphy

General Introduction

The synthesis and chemistry of 2*H*-selenopyran-2-one (**1**; CAS name 2*H*-selenin-2-one), 4*H*-selenopyran-4-one (**2**; CAS name 4*H*-selenin-4-one), 1*H*-2-benzoselenopyran-1-one (**3**; CAS name 1*H*-2-benzoselenin-1-one), 2*H*-1-benzoselenopyran-2-one (**4**; CAS name 2*H*-1-benzoselenin-2-one), 4*H*-1-benzoselenopyran-4-one (**5**; CAS name 4*H*-1-benzoselenin-4-one), 10*H*-dibenzo[*b,e*]selenopyran-10-one, 6*H*-dibenzo[*b,d*]selenopyran-6-one (**6**; CAS name 6*H*-dibenzo[*b,d*]selenin-6-one), and (**7**; CAS name 9*H*-selenoxanthen-9-one; Scheme 1), have not been reviewed as a specific topic in an exhaustive manner, and there is no previous specific entry in the *Houben–Weyl* series. A monograph on general organic selenium chemistry is, however, worthy of note as it provides some coverage of the area.^[1]

Scheme 1 Selenopyranones and Benzoselenopyranones



Many methods exist for the formation of selenopyranones and benzoselenopyranones, but by far the most useful are those which involve the formation of one or two Se–C bonds in a heterocyclization process.

SAFETY: The vast majority of organoselenium compounds should be handled using the standard precautions generally taken with other potentially hazardous substances found in a modern chemical laboratory. Inorganic selenium compounds, however, do present special hazards, as they are highly toxic, and exposure routes such as inhalation, ingestion, and skin or eye contact should be avoided. Common symptoms include drowsiness, headaches, nausea, abdominal pains, and a garlic odor of the breath, and these sub-

stances may have effects on the central nervous system. Long-term exposure has indicated that selenium and related compounds could cause malformations in human babies, and pregnant women should, therefore, avoid exposure to these substances. It is recommended that organoselenium compounds should be treated with similar care.

Some of the preparations included in this section use perchloric acid or inorganic perchlorate salts. Finely divided mixtures of perchlorates and organic matter frequently react explosively. Organic perchlorate salts are all potentially self-contained explosives, and should thus be handled with extreme care.

**14.11.1 Product Subclass 1:
2H-Selenopyran-2-ones and 4H-Selenopyran-4-ones**

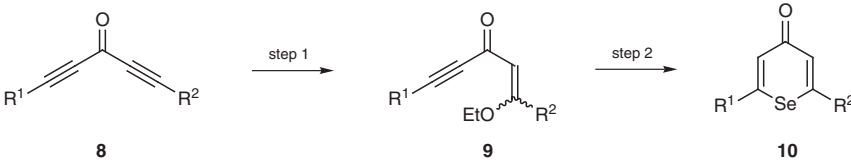
14.11.1.1 Synthesis by Ring-Closure Reactions

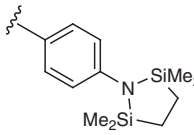
14.11.1.1.1 By Formation of Two Se—C Bonds

**14.11.1.1.1.1 Method 1:
4H-Selenopyran-4-ones by Addition of Dibasic Selenide to
Diethynyl Ketones**

The most widely reported synthesis of 4H-selenopyran-4-ones involves the addition of sodium selenide to diynones **8**, leading to the 4H-selenopyran-4-ones **10** (Table 1).^[2–10] Sodium selenide is generated in situ by treatment of elemental selenium with sodium borohydride. This is then added to a sodium ethoxide solution, which is in turn added to the substrate **8**, generally in ethanolic solution containing sodium ethoxide.

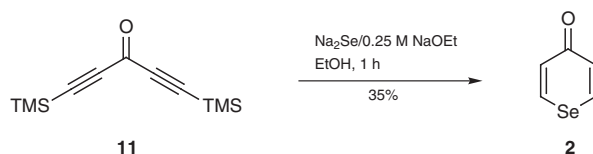
An extensive study of this reaction^[2] has found that the best method for the synthesis of the 4H-selenopyran-4-ones **10** is to allow **8** to react with the sodium ethoxide first, to give the intermediate enol ethers **9**, which are then added to a solution of sodium selenide salt in ethanolic sodium ethoxide to give **10**. The results of this study are shown in Table 1, together with several other preparations of symmetrical and unsymmetrical 4H-selenopyran-4-ones using a similar method.^[6,7] Two early examples^[8] of this reaction used a combination of hydrogen selenide and triethylamine; however, the yields are inferior to the newer method.

Table 1 Synthesis of 4*H*-Selenopyran-4-ones by the Addition of Dibasic Selenide to Diethynyl Ketones^[2–10]


R ¹	R ²	Conditions	Yield (%)	mp (°C)	Ref
<i>t</i> -Bu	<i>t</i> -Bu	1. 0.07 M NaOEt/EtOH, 25 °C, 3 h; 2. Na ₂ Se, 0.1 M NaOEt/EtOH, 15 min	89	98–102	[2]
Ph	Ph	1. 0.07 M NaOEt/EtOH, 25 °C, 450 s; 2. Na ₂ Se, 0.1 M NaOEt/EtOH, 15 min	89	147–148	[2,3]
4-Me ₂ NC ₆ H ₄	4-Me ₂ NC ₆ H ₄	1. 0.25 M NaOEt/EtOH/THF, 50 °C, 30 min; 2. Na ₂ Se, 0.1 M NaOEt/EtOH, 15 min	89	215 (dec)	[2,4]
2-thienyl	2-thienyl	1. 0.25 M NaOEt/EtOH, 25 °C, 30 min; 2. Na ₂ Se, 0.1 M NaOEt/EtOH, 15 min	87	153–154	[2]
Ph	4-Me ₂ NC ₆ H ₄	1. 0.25 M NaOEt/EtOH/THF, 50 °C, 30 min; 2. Na ₂ Se, 0.1 M NaOEt/EtOH, 15 min	68	155–156	[2,5]
Me	Me	1. 0.05 M NaOEt/EtOH; 2. Na ₂ Se, 0.5 M NaOEt/EtOH, 1 h	56	84–87	[6]
<i>t</i> -Bu	<i>t</i> -Bu	1. 0.05 M NaOEt/EtOH; 2. Na ₂ Se, 0.5 M NaOEt/EtOH, 1 h	70	98–102	[6]
Ph	Ph	1. 0.05 M NaOEt/EtOH; 2. Na ₂ Se, 0.5 M NaOEt/EtOH, 1 h	70	147–148	[6]
Ph		1. 0.25 M NaOEt/EtOH/THF, 25 °C, 2 h; 2. Na ₂ Se, 0.25 M NaOEt, 2 h	63 ^a	181–183	[7]
Me	Me	H ₂ Se, Et ₃ N, MeOH, 20 min	57	88–89	[8,9]
Ph	Ph	H ₂ Se, Et ₃ N, MeOH, 20 min	17	145–146	[8,9]

^a Isolated as the amine, R² = 4-H₂NC₆H₄.

If the trimethylsilylated diyne **11** is used in this reaction, the final product obtained is the parent 4*H*-selenopyran-4-one (**2**) in 35% overall yield, the silyl groups being hydrolyzed during workup (Scheme 2).^[10]

Scheme 2 Preparation of 4*H*-Selenopyran-4-one^[10]

2,6-Di-2-thienyl-4*H*-selenopyran-4-one (**10**, R¹ = R² = 2-Thienyl); Typical Procedure:^[2]

A soln of Na₂Se was prepared from the action of NaBH₄ (0.08 g, 2.2 mmol) on powdered Se (0.174 g, 2.2 mmol) was suspended in 0.25 M NaOEt in EtOH (20 mL), which was stirred until a clear soln was obtained. Diynone **8** (R¹ = R² = 2-thienyl; 0.48 g, 2.0 mmol) was dissolved

for references see p 142

in 0.25 M NaOEt in EtOH (20 mL) and after 30 min was added to the Na₂Se soln. After 15 min, the mixture was added to H₂O (200 mL), extracted with CH₂Cl₂ (3 × 30 mL), and the combined organic extracts were washed with brine, dried (MgSO₄), and then concentrated; yield: 0.562 g (87%); mp 153–154 °C (EtOH).

4*H*-Selenopyran-4-one (**2**):^[10]

NaBH₄ (0.52 g, 15 mmol) and Se shot (0.79 g, 10 mmol) were added to 0.25 M NaOEt in EtOH (10 mL), which was refluxed for 1.5 h (until a clear soln was obtained), then cooled to rt. The diyone **11** (1.11 g, 5 mmol) was dissolved in EtOH (10 mL) and added to this soln. The resulting mixture was stirred for 1 h, then diluted with H₂O (100 mL) and extracted with CH₂Cl₂ (3 × 50 mL), and the combined organic extracts were washed with brine, dried (Na₂SO₄), and concentrated. Recrystallization (toluene) gave **2** as a yellow crystalline solid; yield: 0.279 g (35%); mp 114–115.5 °C.

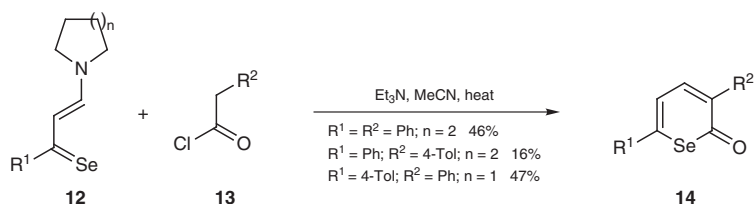
14.11.1.1.2 By Formation of One Se–C and One C–C Bond

14.11.1.1.2.1 Method 1:

2*H*-Selenopyran-2-ones from 2-Aminovinyl Selenoketones

The only known synthesis of non-benzoannulated 2*H*-selenopyran-2-ones **14** occurs on treatment of 2-aminovinyl selenoketones **12** with the acid chlorides **13** and triethylamine in acetonitrile; the yields for this process are generally poor and only three examples have been reported (Scheme 3).^[11]

Scheme 3 Preparation of 2*H*-Selenopyran-2-ones from 2-Aminovinyl Selenoketones^[11]



14.11.1.2 Synthesis by Substituent Modification

There are very few reports relating to the modification of preformed selenopyranones and no addition reactions have been described. The only known reactions are limited to one report of substitution via a metalation sequence.^[12]

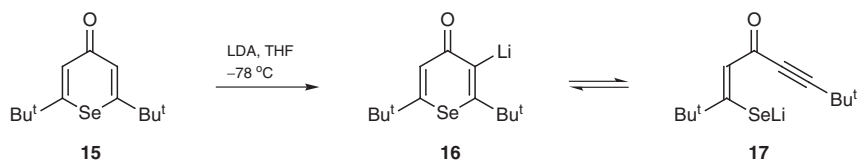
14.11.1.2.1 Substitution of Existing Substituents

14.11.1.2.1.1 Of Hydrogen

14.11.1.2.1.1 Method 1:

Lithiation of 4*H*-Selenopyran-4-ones

2,6-Di-*tert*-butyl-4*H*-selenopyran-4-one (**15**) can be metalated at the 3-position by treatment with lithium diisopropylamide at –78 °C to give (2,6-di-*tert*-butyl-4-oxo-4*H*-selenopyran-3-yl)lithium (**16**), which is in equilibrium with the ring-opened form **17** (Scheme 4).^[12]

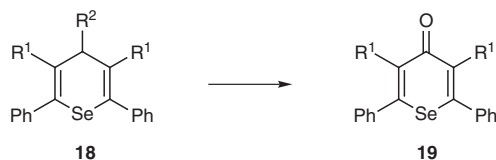
Scheme 4 Lithiation of a 4*H*-Selenopyran-4-one^[12]**(2,6-Di-*tert*-butyl-4-oxo-4*H*-selenopyran-3-yl)lithium (16):**^[12]

BuLi (1 equiv) was added dropwise to a stirred and cooled ($-78\text{ }^{\circ}\text{C}$) soln of $i\text{Pr}_2\text{NH}$ (1 equiv) in THF ($5\text{ mL}\cdot\text{mmol}^{-1}$), and the mixture was warmed to $0\text{ }^{\circ}\text{C}$ for 30 min, then cooled again to $-78\text{ }^{\circ}\text{C}$. 2,6-Di-*tert*-butyl-4*H*-selenopyran-4-one (**15**; 1 equiv) dissolved in THF ($5\text{ mL}\cdot\text{mmol}^{-1}$) was then added dropwise, and the resulting soln was stirred for 1 h to generate (2,6-di-*tert*-butyl-4-oxo-4*H*-selenopyran-3-yl)lithium (**16**), which was used immediately (see Section 14.11.1.2.1.1.1).

14.11.1.2.1.1.2

Method 2:**4*H*-Selenopyran-4-ones by Oxidation of 4*H*-Selenopyrans**

4*H*-Selenopyrans **18** are reported to be oxidized to the corresponding 4*H*-selenopyran-4-ones **19** in fair yields by either potassium permanganate^[13] or hydrogen peroxide;^[14] however, very limited experimental details are given (Scheme 5).

Scheme 5 Preparation of 4*H*-Selenopyran-4-ones by Oxidation of 4*H*-Selenopyrans^[13,14]

R ¹	R ²	Conditions	Yield (%)	mp ^a (°C)	Ref
H	H	KMnO ₄ , MeCN, heat	45	145–147	[13]
H	H	H ₂ O ₂ , benzene, 24 h	40	n.r.	[14]
H	H	H ₂ O ₂ , acetone, 24 h	48	n.r.	[14]
Me	H	KMnO ₄ , acetone, heat	62	141–143	[13]
H	OMe	H ₂ O ₂ , benzene, 24 h	38	n.r.	[14]

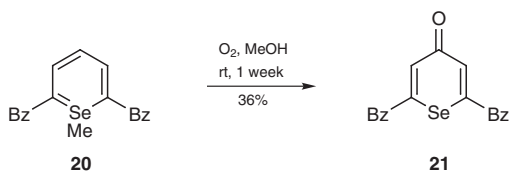
^a n.r. = not reported.

14.11.1.2.1.1.3

Method 3:**4*H*-Selenopyran-4-ones by Oxidation of 1-Methyl-1λ⁴-selenopyrans**

The 1-methyl-1λ⁴-selenopyran **20** undergoes hydrolysis and oxidation on exposure to oxygen for one week to give 2,6-dibenzoyl-4*H*-selenopyran-4-one (**21**) in 36% yield (Scheme 6).^[15]

Scheme 6 Preparation of a 4*H*-Selenopyran-4-one by Oxidation of a 1-Methyl-1 λ^4 -selenopyran^[15]



14.11.1.2.1.2 Of Metals

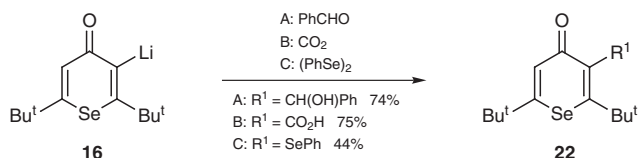
14.11.1.2.1.2.1 Of Lithium

14.11.1.2.1.2.1.1 Method 1:

Reaction of (2,6-Di-*tert*-butyl-4-oxo-4*H*-selenopyran-3-yl)lithium with Electrophiles

(2,6-Di-*tert*-butyl-4-oxo-4*H*-selenopyran-3-yl)lithium (**16**, see Section 14.11.1.2.1.1.1) reacts with either benzaldehyde, carbon dioxide, or diphenyl diselenide to give the substituted 4*H*-selenopyran-4-ones **22** in good to excellent yields (Scheme 7).^[12] Attempted reaction with methyl trifluoromethanesulfonate gave a methylated ring-opened product.

Scheme 7 Reaction of (2,6-Di-*tert*-butyl-4-oxo-4*H*-selenopyran-3-yl)lithium with Electrophiles^[12]



2,6-Di-*tert*-butyl-4-oxo-4*H*-selenopyran-3-carboxylic Acid (22, R¹ = CO₂H):^[12]

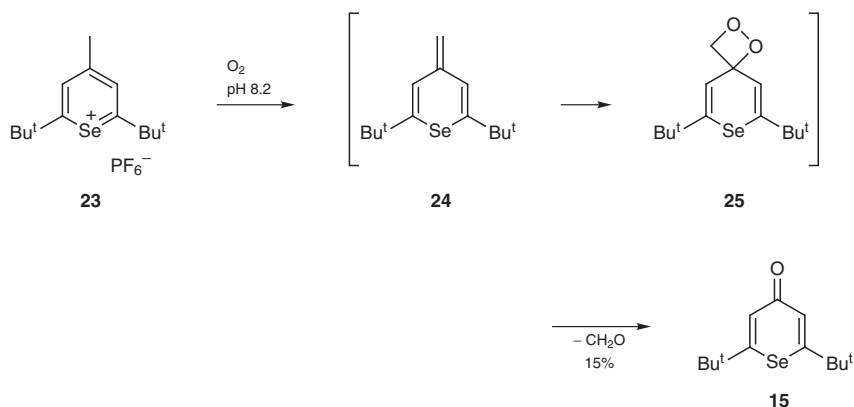
CO₂ gas was bubbled into a stirred, cooled (−78 °C) soln of (2,6-di-*tert*-butyl-4-oxo-4*H*-selenopyran-3-yl)lithium (**16**; 5 mmol, see Section 14.11.1.2.1.1.1) in THF until the color of the mixture faded. The mixture was poured into 0.1 M NaOH (100 mL) and the aqueous layer was extracted with CH₂Cl₂ (3 × 25 mL). The aqueous layer was acidified with cold 10% aq HCl and extracted with CH₂Cl₂ (3 × 50 mL). The combined organic extracts of the acid layer were washed with brine, dried (Na₂SO₄), and concentrated. Purification by recrystallization (MeCN) gave **22** (R¹ = CO₂H); yield: 1.18 g (75%); mp 165 °C (dec).

14.11.1.2.1.3 Of Carbon Functionalities

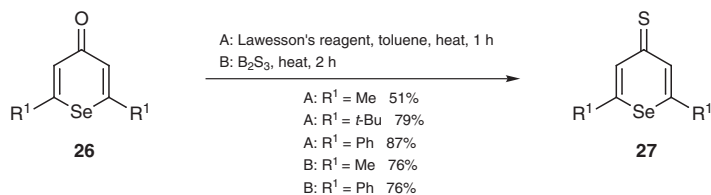
14.11.1.2.1.3.1 Method 1:

4*H*-Selenopyran-4-ones by Oxidation of 4-Methylene-4*H*-selenopyrans

The selenopyrylium salt **23** is deprotonated in basic buffer to give the 4-methylene-4*H*-selenopyran **24**. This undergoes air oxidation to give the dioxetane intermediate **25**, which in turn is thought to eliminate formaldehyde to give the 4*H*-selenopyran-4-one **15** in 15% yield (Scheme 8).^[16]

Scheme 8 Preparation of a 4*H*-Selenopyran-4-one by Oxidation of a 4-Methylene-4*H*-selenopyran^[16]**14.11.1.2.2 Modification of Substituents****14.11.1.2.2.1 Method 1:****4*H*-Selenopyran-4-thiones from 4*H*-Selenopyran-4-ones**

4*H*-Selenopyran-4-ones **26** can be converted into the corresponding 4*H*-selenopyran-4-thiones **27** (Scheme 9) by treatment with Lawesson's reagent [2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane 2,4-disulfide]^[6] or diboron trisulfide.^[9,17]

Scheme 9 Preparation of 4*H*-Selenopyran-4-thiones from 4*H*-Selenopyran-4-ones^[6,9,17]**2,6-Dimethyl-4*H*-selenopyran-4-thione (27, R¹ = Me):^[17]**

2,6-Dimethyl-4*H*-selenopyran-4-one (**26**, R¹ = Me; 0.505 g, 2.7 mmol) was dissolved in CHCl₃ (50 mL) and B₂S₃ (1.0 g, 8.5 mmol) was added. The mixture was then refluxed under argon for 2 h in the absence of light. The mixture was then cooled to rt, filtered, and concentrated to dryness. The residue obtained was then extracted by trituration with hot CHCl₃, and the extracts were concentrated and purified by column chromatography (silica gel, petroleum ether then benzene). The fractions containing the product were concentrated, and the product **27** (R¹ = Me) was purified by recrystallization (petroleum ether/EtOH 1:1) to give violet crystals; yield: 0.417 g (76%); mp 115 °C.

**14.11.2 Product Subclass 2:
Benzo- and Dibenzoselenopyranones**

14.11.2.1 Synthesis by Ring-Closure Reactions

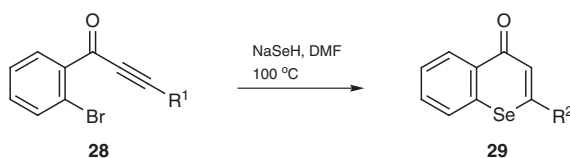
14.11.2.1.1 By Annulation to an Arene

14.11.2.1.1.1 By Formation of Two Se—C Bonds

**14.11.2.1.1.1 Method 1:
By Reaction of 2-Bromophenyl Ethynyl Ketones with
Sodium Hydrogen Selenide**

A very convenient synthesis of 2-substituted 4*H*-1-benzoselenopyran-4-ones **29** is found in the reaction of 2-bromophenyl ethynyl ketones **28** with sodium hydrogen selenide in dimethylformamide at 100 °C. The reaction is general for alkyl and aryl substituents (Scheme 10) and reaction of the trimethylsilylated ketone **28** ($R^1 = \text{TMS}$) leads to the parent compound **29** ($R^2 = \text{H}$) in excellent yield.^[18]

Scheme 10 Preparation of 4*H*-1-Benzoselenopyran-4-ones by the Reaction of 2-Bromophenyl Ethynyl Ketones with Sodium Hydrogen Selenide^[18]



R^1	R^2	Yield (%)	mp (°C)	Ref
Me	Me	48	97–98	[18]
Bu	Bu	90	oil	[18]
<i>t</i> -Bu	<i>t</i> -Bu	93	89–91	[18]
(CH ₂) ₅ Me	(CH ₂) ₅ Me	79	oil	[18]
(CH ₂) ₇ Me	(CH ₂) ₇ Me	86	oil	[18]
Ph	Ph	84	133–134	[18]
TMS	H	59	92–93	[18]

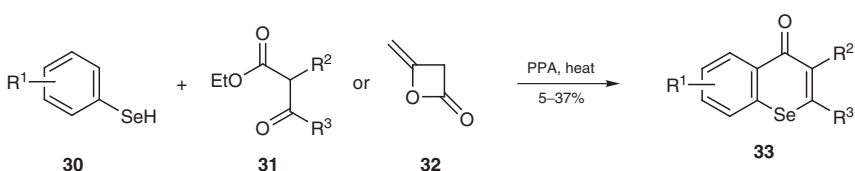
4*H*-1-Benzoselenopyran-4-ones 29; General Procedure:^[18]

A soln of a 2-bromophenyl ethynyl ketone **28** (10 mmol) in DMF (20 mL) was slowly added over 1 h at 100 °C to a stirred soln of NaSeH [12 mmol; prepared from Se powder (0.95 g) and NaBH₄ (0.54 g)] in DMF (40 mL). After 2–5 h, the mixture was cooled, diluted with H₂O (100 mL), filtered, and extracted with benzene (3 × 100 mL). The combined organic extracts were washed with H₂O (3 × 200 mL) and brine (2 × 200 mL), then dried (MgSO₄), concentrated, and purified by column chromatography (silica gel, hexane/acetone 50:1); yield: 48–93%.

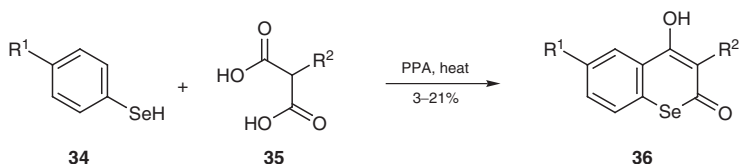
14.11.2.1.1.2 **By Formation of One Se—C and One C—C Bond**14.11.2.1.1.2.1 **Method 1:
By the Simonis Reaction**

It has been reported^[19–22] that reaction of benzeneselenenols with either β -oxo esters or malonic acid derivatives in the presence of a strong acid (a Simonis-type reaction) leads to 1-benzoselenopyran-4-ones and/or 1-benzoselenopyran-2-ones. For example, reaction of the substituted benzeneselenenols **30** with β -oxo esters **31** or diketene **32** leads to the 4*H*-1-benzoselenopyran-4-ones **33**; however, the yields are always low (Scheme 11).^[19,20] Similarly, reaction of the benzeneselenenols **34** with malonic acids **35** leads to the 4-hydroxy-2*H*-1-benzoselenopyran-2-ones **36**; again, the yields for this process are poor.^[21] A slightly different reaction occurs when the malonic esters **37** are utilized in this reaction, in that the 2-(phenylselenanyl)-4*H*-1-benzoselenopyran-4-ones **38** are obtained in 20–30% yield (Scheme 11).^[22]

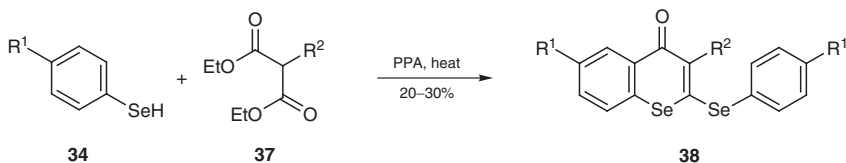
Scheme 11 Preparation of Benzoselenopyranones by the Simonis Reaction^[19–22]



$\text{R}^1 = \text{H, Me, (CH=CH)}_2$; $\text{R}^2 = \text{H, Me, Et, Ph}$; $\text{R}^3 = \text{H, Me, Ph}$



$\text{R}^1 = \text{H, Me}$; $\text{R}^2 = \text{H, Me, Et, Bu, Pr, Ph}$



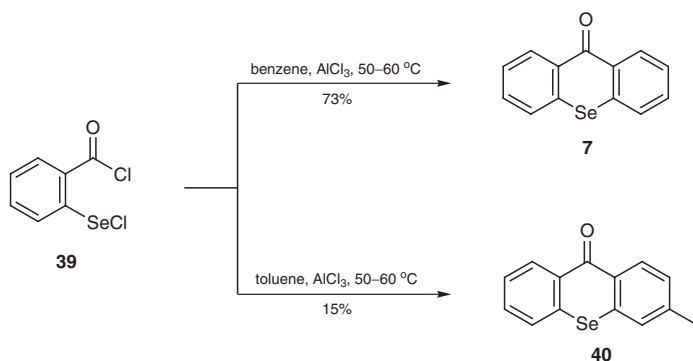
$\text{R}^1 = \text{H, Me}$; $\text{R}^2 = \text{H, Me, Et}$

14.11.2.1.1.2.2 **Method 2:
From 2-(Chloroselanyl)benzoyl Chloride via
Electrophilic Aromatic Substitution**

In one of the earliest reported preparations of 10*H*-dibenzoselenopyran-10-ones, 2-(chloroselanyl)benzoyl chloride (**39**) was reacted with benzene to give the parent 10*H*-dibenzo[*b,e*]selenopyran-10-one (**7**) in 73% yield (Scheme 12).^[23] Also reported was the reaction of the benzoyl chloride **39** with toluene to give a substituted product in an unreported yield, a reaction which was later repeated,^[24] in which the structure was shown to be 3-

methyl-10*H*-dibenzo[*b,e*]selenopyran-10-one (**40**). The yields for this reaction were generally found to be very poor, which limit its usefulness.

Scheme 12 Preparation of 10*H*-Dibenzoselenopyran-10-ones from 2-(Chloroselenyl)benzoyl Chloride via Electrophilic Aromatic Substitution^[23,24]



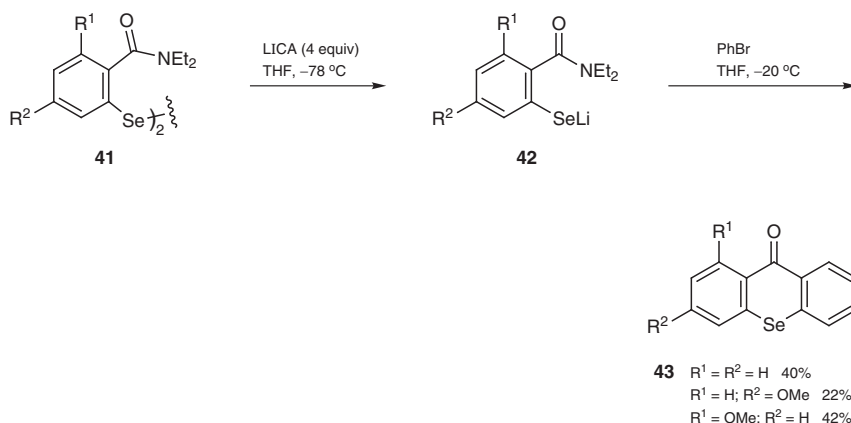
14.11.2.1.1.2.3

Method 3:

By Reaction of Se-Lithiated Selenosalicylamide Derivatives with Benzynes

Treatment of the dimeric selenosalicylamide derivatives **41** with a fourfold excess of lithium isopropylcyclohexylamide generates the corresponding Se-lithiated selenosalicylamides **42** (Scheme 13), which on reaction with benzyne, generated in situ from bromobenzene, leads to 10*H*-dibenzoselenopyran-10-ones **43**.^[25]

Scheme 13 Preparation of 10*H*-Dibenzoselenopyran-10-ones by the Reaction of Se-Lithiated Selenosalicylamide Derivatives with Benzynes^[25]



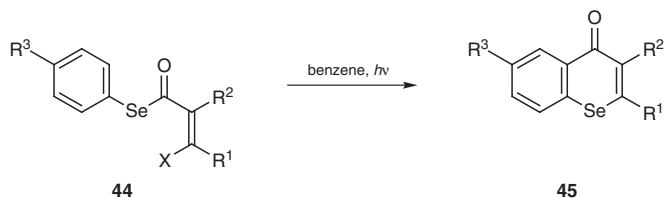
10*H*-Dibenzo[*b,e*]selenopyran-10-one (**43**, $\text{R}^1 = \text{R}^2 = \text{H}$):^[25]

A soln of diselenide **41** ($\text{R}^1 = \text{R}^2 = \text{H}$; 1.18 g, 4.61 mmol) in THF (30 mL) was added to a soln of LICA (16.59 mmol) in THF (50 mL) at -78 °C. After 1 h at this temperature, the cooling bath was removed and the mixture was warmed to -20 °C over 10 min, at which point a soln of PhBr (1.45 g, 9.22 mmol) in THF (20 mL) was added. The mixture was stirred overnight at rt, quenched with sat. NH_4Cl soln, concentrated, and the residue was extracted with CHCl_3 . After drying (Na_2SO_4) and concentration, the product **7** was isolated by chromatography (benzene), followed by recrystallization (EtOH/hexane); yield: 0.48 g (40%); mp 182–185 °C.

14.11.2.1.1.2.4 Method 4: By Photochemical Rearrangement of Aryl Selenoesters

Photolysis of the aryl selenoesters **44** in benzene leads to the formation of the 10*H*-dibenzo[*b,e*]selenopyran-10-ones **45** [$R^1, R^2 = (CH=CH)_2$] or the annulated 4*H*-1-benzoselenopyran-4-ones **45** [$R^1, R^2 = (CH_2)_3$, $N=CH-CH=CH$, $CH=CH-Se$, $Se-CH=CH$] in poor yields (Scheme 14).^[26–30] A number of byproducts are formed in these reactions, with the most prevalent being diaryl diselenides.

Scheme 14 Preparation of Annulated 4*H*-Benzoselenopyran-4-ones by Photochemical Rearrangement of Aryl Selenoesters^[26–30]



R^1, R^2	R^3	X	Yield (%)	mp (°C)	Ref
$(CH=CH)_2$	H	Cl	19	– ^a	[26]
$(CH=CH)_2$	Me	SOMe	3	108–110	[27]
$(CH_2)_3$	Me	S-4-Tol	14	120–125	[28]
$N=CH-CH=CH$	Me	Cl	25	128–130	[29]
$CH=CH-Se$	Me	Br	4	126–127	[30]
$Se-CH=CH$	Me	H	16	149–150	[30]

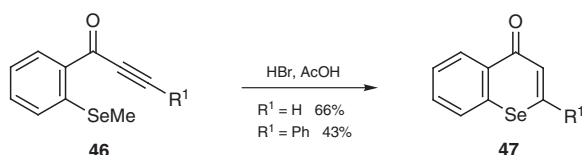
^a mp not reported.

14.11.2.1.1.3 By Formation of One Se–C Bond

14.11.2.1.1.3.1 Method 1: By Cyclization of Ethynyl 2-(Methylselenanyl)phenyl Ketones

Reaction of the ethynyl 2-(methylselenanyl)phenyl ketones **46** with concentrated hydrobromic acid effects cyclization to the 4*H*-1-benzoselenopyran-4-ones **47** in good yields (Scheme 15).^[31]

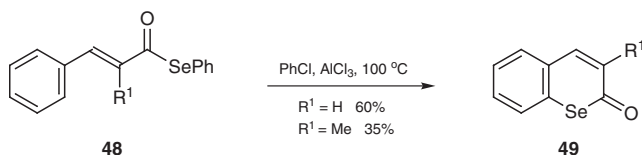
Scheme 15 Formation of 4*H*-1-Benzoselenopyran-4-ones by Cyclization of Ethynyl 2-(Methylselenanyl)phenyl Ketones^[31]



14.11.2.1.1.3.2 **Method 2:**
By Cyclization of Phenyl Selenocinnamates

The phenyl selenocinnamates **48** undergo cyclization on treatment with aluminum trichloride to give the parent 2*H*-1-benzoselenopyran-2-one (**49**, R¹ = H) in 60% yield or 3-methyl-2*H*-1-benzoselenopyran-2-one (**49**, R¹ = Me) in 35% yield (Scheme 16).^[32]

Scheme 16 Formation of 2*H*-1-Benzoselenopyran-2-ones by Cyclization of Phenyl Selenocinnamates^[32]



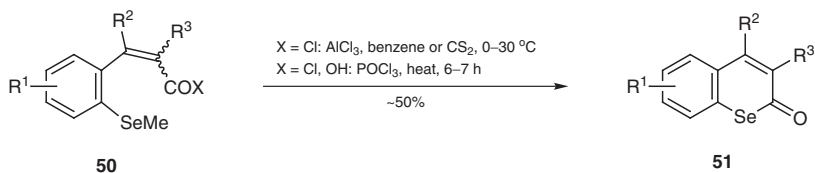
2*H*-1-Benzoselenopyran-2-one (49, R¹ = Me):^[32]

The phenyl selenocinnamate **48** (R¹ = H; 1.0 g, 3.5 mmol) was added to AlCl₃ (3 g, 22.5 mmol) in PhCl (25 mL) and heated on a steam bath for 30 min. When the color of the mixture changed from yellow to red, and TLC indicated the consumption of **48** (R¹ = H), the mixture was diluted with ice-cold dil HCl and extracted with CHCl₃. The extracts were washed with H₂O, dried, and concentrated. Column chromatography, eluting first with hexane to remove diphenyl diselenide (0.09 g) and then with benzene/hexane (1:1), gave the product; yield: 0.42 g (60%); mp 69–71 °C.

14.11.2.1.1.3.3 **Method 3:**
By Electrophilic Cyclization of Methyl Selenides

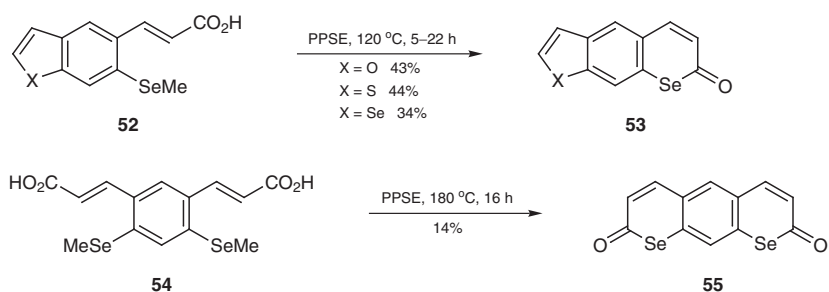
One of the most convenient methods for the formation 2*H*-1-benzoselenopyran-2-ones **51** is from the aluminum trichloride or phosphoryl chloride catalyzed electrophilic cyclization of aryl methyl selenides **50**.^[33] This reaction, first reported in the late 1960s,^[33,34] appears to be a fairly general method for the preparation of alkyl-, aryl-, and cyano-substituted 2*H*-1-benzoselenopyran-2-ones (Scheme 17).

Scheme 17 Preparation of 2*H*-1-Benzoselenopyran-2-ones by Electrophilic Cyclization of Aryl Methyl Selenides^[33,34]

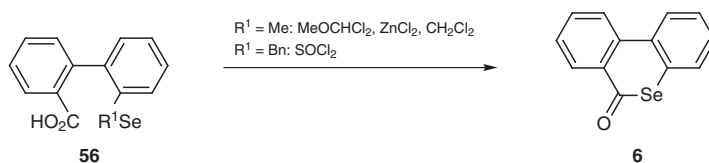


R¹ = H, 6-Me, 7-Me, 8-Me; R² = H, Me, Ph; R³ = H, Me, Ph, CN

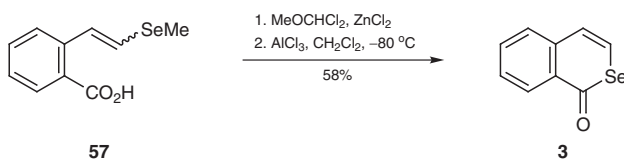
A similar cyclization of the substrates **52** using trimethylsilyl polyphosphate (PPSE) gave, in reasonable yield, the annulated 2*H*-1-benzoselenopyran-2-ones **53**, which are selenium analogues of the psoralen class of compounds used in photochemotherapy.^[35,36] The bis(2*H*-selenopyran-2-one) derivative **55** has also been prepared, from **54**, using this methodology, however the yield was very poor (Scheme 18).^[37]

Scheme 18 Preparation of Psoralen Analogues by Electrophilic Cyclization of Aryl Methyl Selenides^[35–37]

It has been reported that 6*H*-dibenzo[*b,d*]selenopyran-6-one (**6**) can be prepared by the zinc chloride mediated cyclization of the acid chloride derived from carboxylic acid **56** ($R^1 = \text{Me}$), and that the carboxylic acid **56** ($R^1 = \text{Bn}$) is converted into **6** on treatment with thionyl chloride;^[38] however, no details or yields were given for these processes (Scheme 19).

Scheme 19 Preparation of 6*H*-Dibenzo[*b,d*]selenopyran-6-one^[38]

The parent heterocyclic system 1*H*-2-benzoselenopyran-1-one (**3**) has been prepared in 58% yield using a related process whereby the methyl vinyl selenide **57** was treated sequentially with anhydrous zinc chloride and dichloromethyl methyl ether, followed by aluminum trichloride (Scheme 20).^[39]

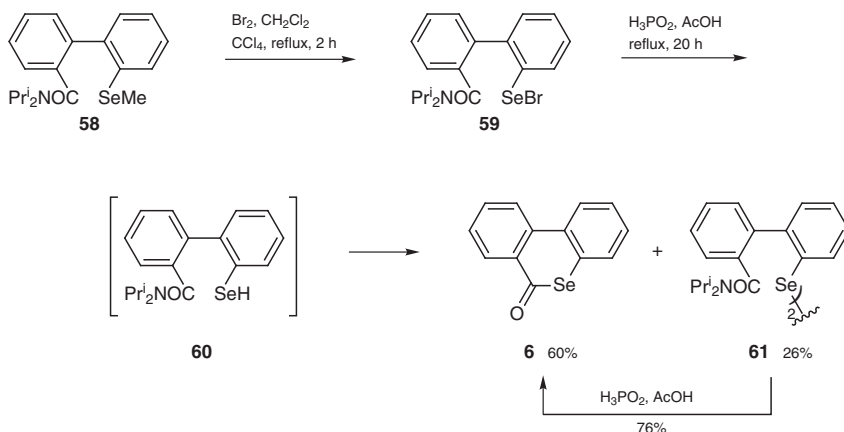
Scheme 20 Preparation of 1*H*-2-Benzoselenopyran-1-one^[39]**1*H*-2-Benzoselenopyran-1-one (3):**^[39]

2-[2-(Methylselanyl)vinyl]benzoic acid (**57**; 2.4 g, 10 mmol) and anhyd ZnCl_2 (100 mg) were dissolved in MeOCHCl_2 (10 mL) and the mixture was stirred overnight at rt. The excess MeOCHCl_2 was removed by evaporation, and dry CH_2Cl_2 (50 mL) was added to the residue. This soln was cooled to $-80\text{ }^\circ\text{C}$, and AlCl_3 (1.33 g, 10 mmol) was added with efficient stirring. After the mixture had warmed slowly to rt, it was poured into ice H_2O (100 mL) and extracted with CHCl_3 . The extracts were dried and concentrated; yield: 1.21 g (58%); mp $79\text{--}80\text{ }^\circ\text{C}$ (hexane).

14.11.2.1.1.3.4 **Method 4:**
By Selenolactonization

6*H*-Dibenzo[*b,d*]selenopyran-6-one (**6**) is conveniently prepared from the aryl methyl selenide **58** via a two-stage process to give initially the selenyl bromide **59**, which on subsequent reduction with hypophosphorous acid yields the selenol **60** (Scheme 21). This is not isolated, but undergoes cyclization to give **6** in 60% yield, together with the diselenide **61** in 26% yield, which can also be converted into **6** in 76% yield by treatment with hypophosphorous acid in acetic acid.^[38]

Scheme 21 Preparation of 6*H*-Dibenzo[*b,d*]selenopyran-6-one by Selenolactonization^[38]



6*H*-Dibenzo[*b,d*]selenopyran-6-one (6**):**^[38]

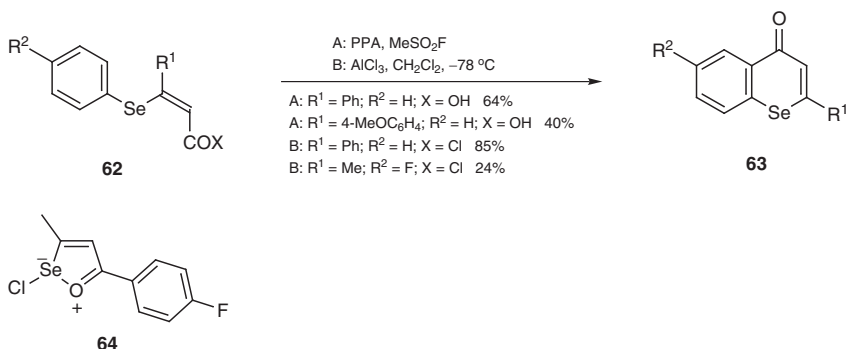
The aryl methyl selenide **58** (8.0 g, 21 mmol) was dissolved in $\text{CH}_2\text{Cl}_2/\text{CCl}_4$ (1:1, 60 mL), following which Br_2 (1.2 mL, 24 mmol) was added. This mixture was refluxed for 2 h, then evaporated to dryness and redissolved in AcOH (30 mL), to which was added H_3PO_2 (15 mL), and the resulting mixture was refluxed for 20 h. The mixture was then poured into ice H_2O (150 mL), extracted with CH_2Cl_2 , and the extract was washed with 8.4% aq NaHCO_3 , dried (MgSO_4), filtered, and concentrated. The residue was purified by column chromatography (toluene) to give **6**; yield: 3.4 g (60%); mp 113–115 °C and the diselenide **61**; yield: 2 g (26%); mp 210 °C.

14.11.2.1.1.4 **By Formation of One C–C Bond**

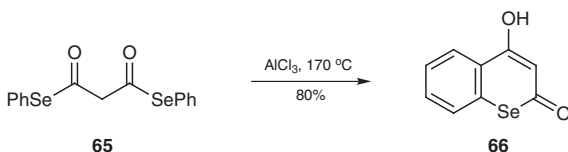
14.11.2.1.1.4.1 **Method 1:**
By Aromatic Electrophilic Substitution

Many examples of the synthesis of benzoselenopyranones and dibenzoselenopyranones by electrocyclization onto an aromatic ring have been reported.

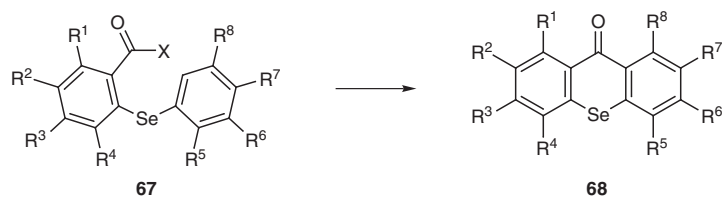
4*H*-1-Benzoselenopyran-4-ones **63** are formed from the electrocyclization of the acid derivatives **62** ($\text{X}=\text{OH}$) on treatment with polyphosphoric acid,^[40] or from the acid chlorides **62** ($\text{X}=\text{Cl}$) with aluminum trichloride,^[41] together with the *ipso*-substitution products in some cases (e.g., compound **64** in 36% yield where $\text{R}^1=\text{Me}$ and $\text{R}^2=\text{F}$) (Scheme 22). This reaction is, however, very limited as most other examples have led to the formation of the *ipso*-substitution products exclusively.^[40,41]

Scheme 22 Preparation of 4*H*-1-Benzoselenopyran-4-ones by Aromatic Electrophilic Substitution^[40,41]

An excellent method for the preparation of 4-hydroxy-2*H*-1-benzoselenopyran-2-one (**66**) is the aluminum trichloride mediated cyclization of the diphenyl propanediselenoate **65**, which proceeds in 80% yield (Scheme 23).^[42] Attempts to extend the scope of this reaction to substituted diphenyl propanediselenoates were largely unsuccessful with yields of 0–5% being reported.^[21]

Scheme 23 Preparation of 4-Hydroxy-2*H*-1-benzoselenopyran-2-one^[42]

The first reported synthesis of 10*H*-dibenzo[*b,e*]selenopyran-10-ones **68** was from the electrocyclization of 2-(phenylselenanyl)benzoic acids **67** (X = OH) using strong acids (Table 2).^[23,24,43–47] In the case of reactions involving unsubstituted precursors, or those containing electron-donating substituents (Table 2, entries 1–10), cyclization can be effected using a range of conditions including polyphosphoric acid, sulfuric acid, or a mixture of trifluoroacetic anhydride and trifluoroacetic acid. The presence of electron-withdrawing groups on selenide **67** (Table 2, entries 11–22) has a detrimental effect on the yield of the product **68** under the standard acidic conditions [PPA, polyphosphate ester (PPE), P₂O₅/MsOH, or TFA/TFAA]; however, it was found that trimethylsilyl polyphosphate (PPSE) was by far the most superior reagent for effecting this cyclization (Table 2, entries 19–22).^[47] One example of a Friedel–Crafts reaction has been reported (Table 2, entry 23);^[24] however, the authors of this paper suggest the methodology and yields are inferior to the acid-catalyzed processes.

Table 2 Preparation of 10*H*-Dibenzo[*b,e*]selenopyran-10-ones by Electrocyclization^[23,24,43–47]

Entry	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶	R ⁷	R ⁸	X	Conditions ^a	Yield ^b (%)	mp ^b (°C)	Ref
1	H	H	H	H	H	H	H	H	OH	PPA, heat	82	191–192	[24]
2	H	H	H	H	H	H	H	H	OH	PPA, 100 °C, 3 h	97	190	[44]
3	H	H	H	H	H	H	Me	H	OH	PPA, heat	53	111	[24]
4	H	H	Me	H	H	H	H	H	OH	PPA, heat	65	110–111	[24]
5	H	H	H	H	H	H	H	H	OH	H ₂ SO ₄	n.r.	n.r.	[23,43]
6	H	H	H	H	CO ₂ H	H	H	H	OH	H ₂ SO ₄	n.r.	n.r.	[23,43]
7	H	H	H	H	H	H	H	H	OH	H ₂ SO ₄ , 95 °C	88	190–191	[45]
8	H	H	H	H	H	H	Cl	H	OH	H ₂ SO ₄ , 95 °C, 90 min	88	156	[45]
9	H	H	H	H	OMe	(CH=CH) ₂	OMe	OH	TFAA, TFA	88	139–141	[46]	
10	H	H	H	H	OMe	Me	Me	OMe	OH	TFAA, TFA	83	101–102	[46]
11	H	H	OMe	H	NO ₂	H	H	Cl	OH	PPA	18	229–232	[47]
12	H	OMe	H	H	NO ₂	H	H	Cl	OH	PPE	12	222–224	[47]
13	H	H	H	H	NO ₂	H	H	Cl	OH	PPA	43	196–197	[47]
14	H	H	H	H	NO ₂	H	H	Cl	OH	PPE	44	196–197	[47]
15	H	H	H	H	NO ₂	H	H	Cl	OH	P ₂ O ₅ , MsOH	40	196–197	[47]
16	H	H	H	H	NO ₂	H	H	Cl	OH	TFA, TFAA	55	196–197	[47]
17	Cl	H	H	NO ₂	H	H	H	H	OH	TFA, TFAA	70	196–197	[47]
18	H	H	OCH ₂ O	H	NO ₂	H	H	Cl	OH	TFA, TFAA, H ₃ PO ₄	55	241–243	[47]
19	H	H	H	H	NO ₂	H	H	Cl	OH	PPSE, P ₂ O ₅ , 210 °C	99	196–197	[47]
20	Cl	H	H	NO ₂	H	H	H	H	OH	PPSE, P ₂ O ₅ , 210 °C	87	196–197	[47]
21	H	H	OMe	H	NO ₂	H	H	Cl	OH	PPSE, P ₂ O ₅ , 210 °C	94	229–232	[47]
22	H	OMe	H	H	NO ₂	H	H	Cl	OH	PPSE, P ₂ O ₅ , 210 °C	63	222–224	[47]
23	H	H	H	H	H	H	H	H	Cl	ZnCl ₂	38	191–192	[24]

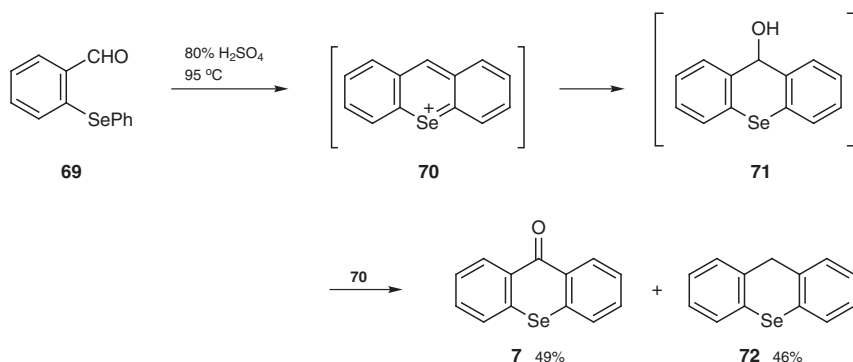
^a PPSE = trimethylsilyl polyphosphate.

^b n.r. = not reported.

The sulfuric acid mediated electrocyclization of 2-(phenylselanyl)benzaldehyde (**69**) leads to a mixture of 10*H*-dibenzo[*b,e*]selenopyran-10-one (**7**) in 49% yield and 10*H*-dibenzo[*b,e*]selenopyran (9*H*-selenoxanthene, **72**) in 46% yield.^[48] The reaction is thought to proceed via the corresponding dibenzoselenopyrylium intermediate **70**; this is hydrolyzed to 10*H*-dibenzo[*b,e*]selenopyran-10-ol (9*H*-selenoxanthene-9-ol, **71**), which acts as a hydride-

transfer reagent reducing a further molecule of **70** to the dibenzoselenopyran **72** and yielding **7** (Scheme 24).

Scheme 24 Preparation of 10*H*-Dibenzo[*b,e*]selenopyran-10-one and 10*H*-dibenzo[*b,e*]selenopyran^[48]



When a similar cyclization of the selenoacetoacetate ester **73** was attempted using polyphosphoric acid,^[20] the reaction took a different course and instead of the expected benzoselenopyran-2-one product, the rearranged 2-methyl-4*H*-1-benzoselenopyran-4-one (**74**) was obtained in 40% yield (Scheme 25).

Scheme 25 Preparation of 2-Methyl-4*H*-1-benzoselenopyran-4-one^[20]



1-Chloro-8-methoxy-4-nitro-10*H*-dibenzo[*b,e*]selenopyran-10-one (68, R¹ = R³ = R⁴ = R⁶ = R⁷ = H; R² = OMe; R⁵ = NO₂; R⁸ = Cl; Table 2, Entry 22):^[47]

Carboxylic acid **67** (R¹ = R³ = R⁴ = R⁶ = R⁷ = H; R² = OMe; R⁵ = NO₂; R⁸ = Cl; X = OH; 6.0 g, 15.5 mmol) was added to a heated (210 °C), mechanically stirred mixture of PPSE syrup (200 g) and P₂O₅ (24 g) and stirred for 20 min. The mixture was then poured onto an ice-cold soln of HCl and stirred for a further 3 h. The resulting orange precipitate was collected by filtration and recrystallized (MeCN); yield: 3.58 g (63%); mp 222–224 °C.

10*H*-Dibenzo[*b,e*]selenopyran-10-one (7) and 10*H*-Dibenzo[*b,e*]selenopyran (72):^[48]

2-(Phenylselanyl)benzaldehyde (**69**; 10.0 g, 38.3 mmol) was added to 80% H₂SO₄ (100 mL) and heated to 95 °C for 30 min. The mixture was then poured onto crushed ice and extracted with CH₂Cl₂, following which the extracts were washed with H₂O, dried (MgSO₄), and concentrated to dryness. Column chromatography of the residue (benzene/hexane 1:5) gave **72**; yield: 4.3 g (46%). Further elution with neat benzene gave 10*H*-dibenzo[*b,e*]selenopyran-10-one (**7**); yield: 4.9 g (49%), which was recrystallized (EtOH) to give pale yellow needles; mp 192–193 °C.

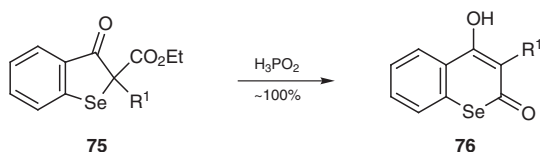
14.11.2.2 Synthesis by Ring Transformation

14.11.2.2.1 Method 1:

By Rearrangement of Substituted Benzo[*b*]selenophen-3(2*H*)-ones

The substituted benzo[*b*]selenophen-3(2*H*)-ones **75** undergo rearrangement to the corresponding 4-hydroxy-2*H*-1-benzoselenopyran-2-ones **76** in quantitative yield on treatment with hypophosphorous acid (Scheme 26).^[49]

Scheme 26 Preparation of 4-Hydroxy-2*H*-1-benzoselenopyran-2-ones by Rearrangement of Substituted Benzo[*b*]selenophen-3(2*H*)-ones^[49]



R¹ = H, Me, CO₂Et

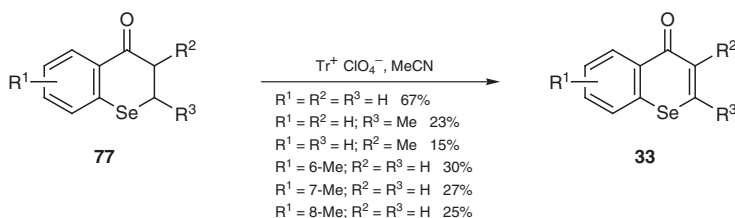
14.11.2.3 Aromatization

14.11.2.3.1 Method 1:

By Dehydrogenation of 2,3-Dihydro-4*H*-1-benzoselenopyran-4-ones

Preparation of 4*H*-1-benzoselenopyran-4-one (**33**, R¹ = R² = R³ = H) in 67% yield by the triphenylcarbenium perchlorate oxidation of 2,3-dihydro-4*H*-1-benzoselenopyran-4-one (**77**, R¹ = R² = R³ = H; Scheme 27) has been reported,^[50] a reaction which was used later^[51] to prepare a range of substituted 4*H*-1-benzoselenopyran-4-ones **33** in somewhat lower yields (15–30%).

Scheme 27 Preparation of 4*H*-1-Benzoselenopyran-4-ones by Oxidation of 2,3-Dihydro-4*H*-1-benzoselenopyran-4-ones^[50,51]



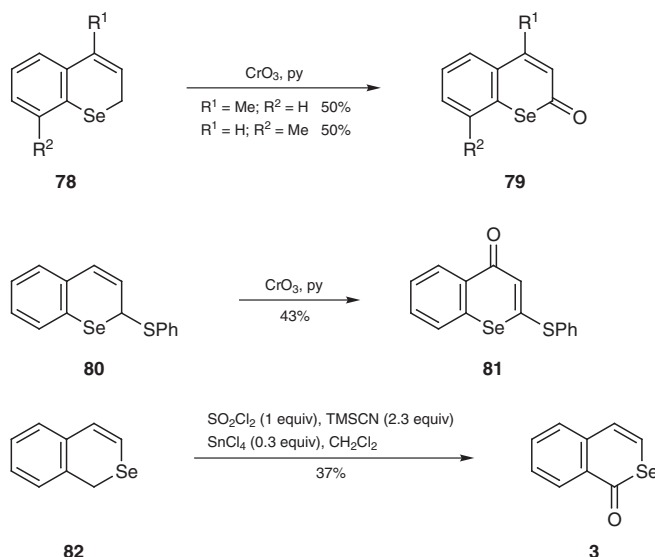
4*H*-1-Benzoselenopyran-4-one (33, R¹ = R² = R³ = H):^[50]

Triphenylcarbenium perchlorate (**CAUTION: explosive**) (3.42 g, 10 mmol) was added to a soln of 2,3-dihydro-4*H*-1-benzoselenopyran-4-one (**77**, R¹ = R² = R³ = H; 2.11 g, 10 mmol) in MeCN (15 mL), and the mixture was heated to 50 °C for 15 min. After cooling, charcoal was added and the soln was filtered. Dry Et₂O (30 mL) was added to precipitate 4-hydroxybenzoselenopyrylium chloride [mp 118 °C (dec)], which was removed by filtration. The salt was neutralized by addition to an excess of aq NaHCO₃, followed by extraction with Et₂O, drying, and concentration. Recrystallization (ligroin) gave the product; yield: 1.40 g (67%); mp 93–94 °C.

14.11.2.3.2

**Method 2:
Oxidation of Benzoselenopyrans**

Oxidation of the 2*H*-1-benzoselenopyrans **78** using chromium(VI) oxide in pyridine leads to the 2*H*-1-benzoselenopyran-2-ones **79** in 50% yield;^[52] a similar oxidation of the substrate **80** led to the 4*H*-1-benzoselenopyran-4-one **81** in 43% yield.^[53] The parent 1*H*-2-benzoselenopyran-1-one (**3**) has been prepared from 1*H*-2-benzoselenopyran (**82**) by oxidation with sulfuryl chloride (Scheme 28).^[54]

Scheme 28 Preparation of Benzoselenopyranones by Oxidation of Benzoselenopyrans^[52–54]**2-(Phenylsulfanyl)-4*H*-1-benzoselenopyran-4-one (**81**):^[53]**

CrO_3 (2 g, 20 mmol) was dissolved in pyridine (30 mL) and cooled (0 °C), whereupon 2-(phenylsulfanyl)-2*H*-1-benzoselenopyran (**80**; 1 g, 3.3 mmol) was added in small portions over 10 min with stirring. After 2 h at this temperature the reaction was warmed to rt and stirred for a further 4 h. After addition of H_2O (50 mL) and CH_2Cl_2 (50 mL), sufficient 1 M HCl was added to dissolve any precipitate and the organic layer was separated. The aqueous layer was extracted with further CH_2Cl_2 (3 \times 25 mL) and the combined extracts were washed with 1 M HCl (50 mL) and H_2O (100 mL), dried, and concentrated. Recrystallization of the residue (hexane/benzene) gave **81**; yield: 0.45 g (43%); mp 107–108 °C.

14.11.2.4 Synthesis by Substituent Modification**14.11.2.4.1 Substitution of Existing Substituents**

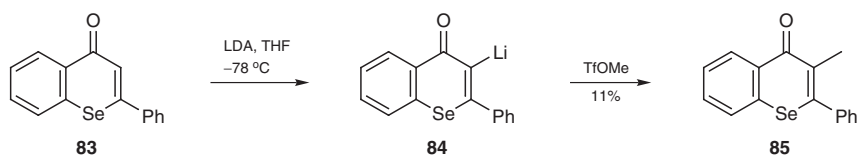
No general methods exist for the substitution of existing substituents on benzo- or dibenzoselenopyranones and only a limited number of examples of substitution reactions have been reported. Several useful oxidative preparations of benzo- and dibenzoselenopyranones are known (see Sections 14.11.2.3.2 and 14.11.2.4.1.1.3).

The hydrolysis of a dibenzoselenopyran-10-imine derivative yields 10*H*-dibenzo[*b,e*]selenopyran-10-one (**7**) in 95% yield.^[55] Similarly, the hydrolysis of a cyanohydrin derivative of a dibenzoselenopyran-10-one can be achieved using aqueous sodium hydroxide solution.^[56]

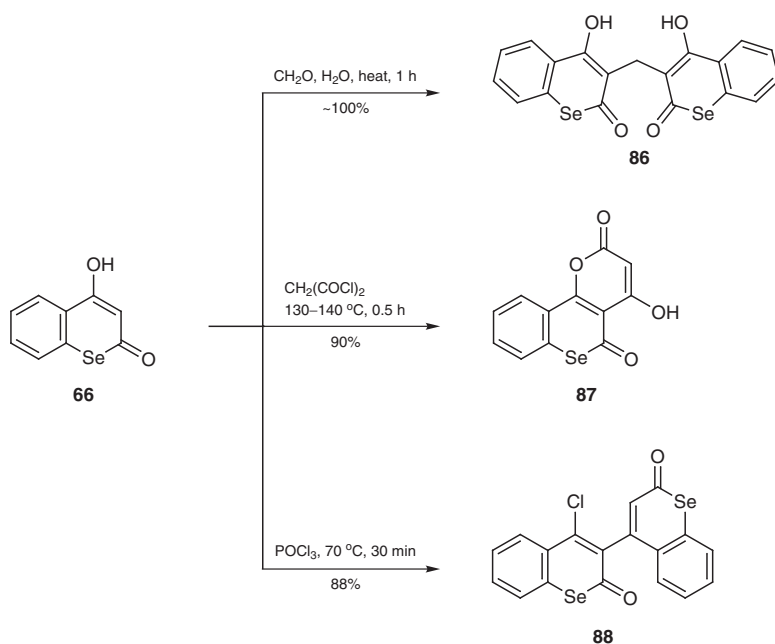
14.11.2.4.1.1 Of Hydrogen

14.11.2.4.1.1.1 Method 1:
Lithiation of 4*H*-1-Benzoselenopyran-4-ones

Metalation of 2-phenyl-4*H*-1-benzoselenopyran-4-one (**83**) using lithium diisopropylamide at $-78\text{ }^{\circ}\text{C}$ has been reported and leads to the 3-metallated product **84**. However, reactions of this intermediate are known to lead to a complex mixture of products and are generally not synthetically useful; for example, methylation using methyl trifluoromethanesulfonate led to the 3-methyl product **85** in only 11% yield (Scheme 29).^[12]

Scheme 29 Lithiation of a 4*H*-1-Benzoselenopyran-4-one^[12]14.11.2.4.1.1.2 Method 2:
Electrophilic Alkylation of 4-Hydroxy-2*H*-1-benzoselenopyran-2-one

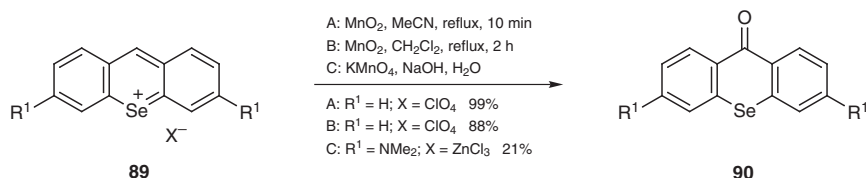
Reaction of 4-hydroxy-2*H*-1-benzoselenopyran-2-one (**66**) with aqueous formaldehyde leads to the dimeric product **86** in quantitative yield, whilst reaction with malonyl dichloride gives the lactone **87** in 90% yield. Attempted chlorination of **66** with phosphoryl chloride gives the dimerized product **88** in 88% yield (Scheme 30).^[42]

Scheme 30 Electrophilic Alkylation of 4-Hydroxy-2*H*-1-benzoselenopyran-2-one^[42]

14.11.2.4.1.1.3 **Method 3:**
Oxidation of Dibenzoselenopyrylium Salts

Oxidation of dibenzoselenopyrylium salts **89** using either manganese(IV) oxide^[57] or potassium permanganate^[58] leads to the parent 10*H*-dibenzo[*b,e*]selenopyran-10-one (**90**, R¹ = H) in excellent yield or amine **90** (R¹ = NMe₂) in poor yield (Scheme 31).

Scheme 31 Preparation of 10*H*-Dibenzo[*b,e*]selenopyran-10-ones by Oxidation of Dibenzoselenopyrylium Salts^[57,58]

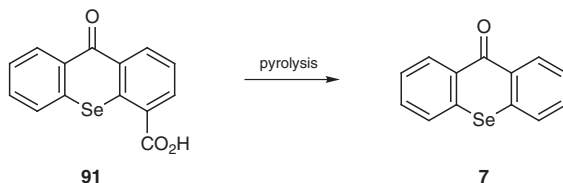


14.11.2.4.1.2 **Of Carbon Functionalities**

14.11.2.4.1.2.1 **Method 1:**
Decarboxylation

The decarboxylation of 10-oxo-10*H*-dibenzo[*b,e*]selenopyran-4-carboxylic acid (**91**) by pyrolysis in the presence of calcium hydroxide is reported to give 10*H*-dibenzo[*b,e*]selenopyran-10-one (**7**, Scheme 32), although a detailed experimental procedure was not given.^[23]

Scheme 32 Preparation of 10*H*-Dibenzo[*b,e*]selenopyran-10-one by Decarboxylation^[23]

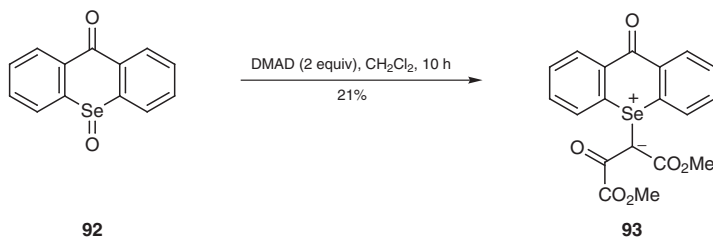


14.11.2.4.1.3 **Of Oxygen**

14.11.2.4.1.3.1 **Method 1:**
Preparation of a 10*H*-Dibenzo[*b,e*]selenopyran-10-one Ylide

Treatment of 10*H*-dibenzo[*b,e*]selenopyran-10-one 5-oxide (**92**) with 2 equivalents of dimethylacetylene dicarboxylate in refluxing dichloromethane for 10 hours generates the selenium ylide **93** in 21% yield (Scheme 33).^[59]

Scheme 33 Preparation of a 10*H*-Dibenzo[*b,e*]selenopyran-10-one Ylide^[59]



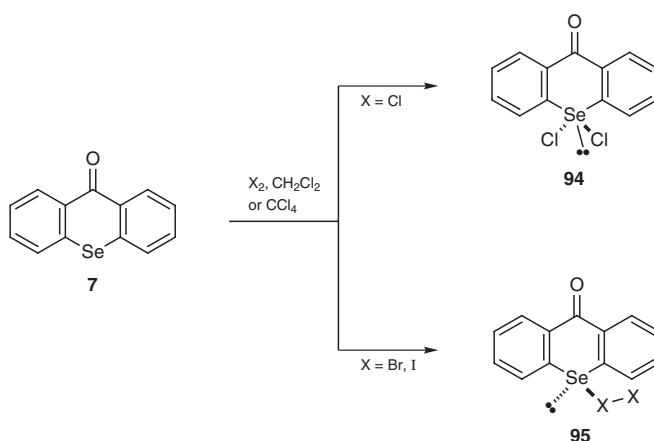
14.11.2.4.2 Addition Reactions

14.11.2.4.2.1 Method 1:
Oxidation of the Selenium Atom

10*H*-Dibenzo[*b,e*]selenopyran-10-one 5-oxide (**92**) was originally prepared by treatment of 10*H*-dibenzo[*b,e*]selenopyran-10-one (**7**) with chromium(VI) oxide.^[23,43] It is more conveniently prepared by oxidation of **7** with 3-chloroperoxybenzoic acid^[59] which is reported to give **92** in high yield, although no experimental details were given (Scheme 34).

Scheme 34 Preparation of 10*H*-Dibenzo[*b,e*]selenopyran-10-one 5-Oxide^[59]14.11.2.4.2.2 Method 2:
Addition of Dihalogen to the Selenium Atom

Chlorine, bromine, and iodine all react with 10*H*-dibenzo[*b,e*]selenopyran-10-one (**7**) to give the corresponding *Se,Se*-dihalides in excellent yield;^[60–63] however, the nature of the species formed is dictated by the halogen in question. The structure of the chlorine adduct is trigonal bipyramidal in which two *Se*–Cl bonds exist (i.e., **94**); however, iodine and bromine both form molecular complexes **95**, which are tetrahedral at selenium (Scheme 35).

Scheme 35 Halogenation of 10*H*-Dibenzo[*b,e*]selenopyran-10-one^[60–63]

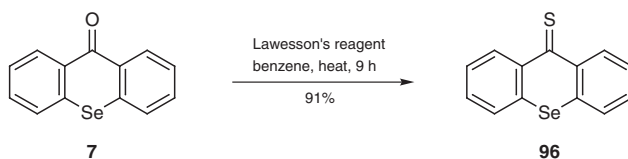
14.11.2.4.3 Modification of Substituents

Very few substituent modification reactions have been reported for benzo- or dibenzoselenopyranones, with only two of interest being discussed in detail. It has, however, been reported that a range of derivatives of 10-oxo-10*H*-dibenzo[*b,e*]selenopyran-4-carboxylic acid (**91**) including the acid chloride, esters, and amides can be prepared using standard methods.^[23,43]

14.11.2.4.3.1 Method 1: Preparation of Benzo- and Dibenzoselenopyranthiones

The preparation of 2*H*-benzoselenopyran-2-thiones by the action of phosphorus pentasulfide on the corresponding 2*H*-benzoselenopyran-2-ones has been reported,^[34] however, no preparative details and only limited analytical data were given for these reactions.^[64] It was later reported (Scheme 36)^[65] that 10*H*-dibenzo[*b,e*]selenopyran-10-one (**7**) can be converted into the corresponding dibenzoselenopyran-10-thione **96** in 91% yield by treatment with Lawesson's reagent [2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane 2,4-disulfide] under similar conditions to those used for the preparation of 4*H*-selenopyran-4-thiones (see Section 14.11.1.2.2.1).

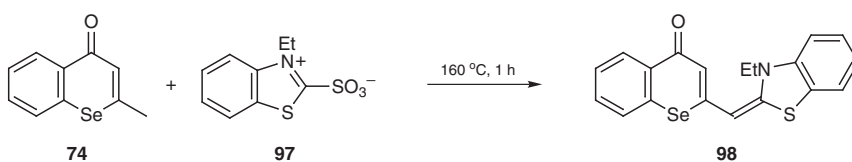
Scheme 36 Preparation of 10*H*-Dibenzo[*b,e*]selenopyran-10-thione Using Lawesson's Reagent^[65]



14.11.2.4.3.2 Method 2: By Condensation of 2-Methyl-4*H*-1-benzoselenopyran-4-one with a Thiazolium Betaine

2-Methyl-4*H*-1-benzoselenopyran-4-one (**74**) undergoes reaction with the thiazolium betaine **97** on heating to give the condensation product **98**; no yield was reported for this process (Scheme 37).^[66]

Scheme 37 Condensation of 2-Methyl-4*H*-1-benzoselenopyran-4-one with a Thiazolium Betaine^[66]



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