Synthesis and structural characterization of heterocyclic thiocarbene, selenocarbene, thione, and selone complexes of tungsten pentacarbonyl or chromium pentacarbonyl

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are consistent with the species proposed.

In the analogous "Ir$_2$(DPPM)$_2$" chemistry chloride removal from [Ir$_2$Cl$_2$(CO)$_2$(μ-alkyne)(DPPM)$_2$] and alkyne addition to [Ir$_2$(CO)$_2$(μ-Cl)(DPPM)$_2$]$^+$ resulted in different isomers, the latter of which slowly rearranged to the more stable one.[5b] In the "Rh$_2$(DMPM)$_2$" chemistry only one isomer is observed in these cationic alkyne adducts, that corresponding to the thermodynamically more stable diiridium species. While it may be that only this isomer is formed, it may also be that alkyne attack at [Rh$_2$(CO)$_2$-(μ-Cl)(DMPM)$_2$]$^+$ yields the unstable isomer, analogous to the iridium system, but that rearrangement to the more stable one is extremely facile. This presumed more rapid isomerization is consistent with the greater lability of the second-row metals over their third-row counterparts and with the smaller DMPM ligand facilitating such a process, although it must be stressed that our presumption of another isomer being involved is based solely on analogies with the Ir$_2$(DPPM)$_2$ chemistry.

Conclusions

The series of "Rh$_2$(DMPM)$_2$" complexes reported is quite analogous, although not identical, to those of rhodium and iridium containing the larger and less basic DPPM ligand. Both differences in ligand properties (bulk and basicity) are evident in the observed chemical differences for these complexes. Not surprisingly, the more basic Me$_2$PCH$_2$PMe$_2$ ligand results in better π donation to carbonyl ligands from the metals such that the chemistry of the "Rh$_2$(DMPM)$_2$" complexes more closely resemble the DPPM analogues of iridium than of rhodium. This is seen most clearly in the alkyne adducts where the dicarbonyl complexes [M$_2$Cl$_2$(CO)$_2$(μ-alkyne)(diphosphine)$_2$] and [M$_2$Cl(CO)$_2$(μ-alkyne)(diphosphine)$_2$]$^+$ (M = Rh, diphosphine = DMPM; M = Ir, diphosphine =

DPPM) are in contrast with the only observed "Rh$_2$-(DPPM)$_2$" species, [Rh$_2$Cl$_2$(μ-CO)(μ-alkyne)(DPPM)$_2$]. Similarly the tetracarbonyl species [Rh$_2$Cl(CO)$_3$(μ-CO)-(DMPM)$_2$]$^+$ and [Rh$_2$(CO)$_4$(μ-S)(DMPM)$_2$] were obtained with the DMPM group whereas with DPPM only the tricarbonyl [Rh$_2$(CO)$_2$(μ-Cl)(μ-CO)(DPPM)$_2$]$^+$ and the dicarbonyl [Rh$_2$(CO)$_2$(μ-S)(DPPM)$_2$] were obtained.

The smaller steric bulk of the DMPM group appears to allow more facile ligand rearrangements over the two metals, so the observation of only one isomer of [Rh$_2$Cl-(CO)$_2$(μ-alkyne)(DMPM)$_2$]$^+$ rather than the two observed with the "Ir$_2$(DPPM)$_2$" system[5b] may be due to facile isomerization. In addition it may be that the greater lability of [Rh$_2$(CO)$_2$(μ-Cl)(μ-CO)(DMPM)$_2$]$^+$ compared with its DPPM analogue is due to more facile rearrangement within the complex.

Synthesis and Structural Characterization of Heterocyclic Thiocarbene, Selenocarbene, Thione, and Selone Complexes of Tungsten Pentacarbonyl or Chromium Pentacarbonyl

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Various pentacarbonyl complexes of W and Cr containing heterocyclic ligands were prepared from the synthon formed by the addition of PhC≡CXLi (X = S or Se) to carbene complexes [M(CO)$_5$|C(OEt)Ph|] (M = Cr, W). The nature of the electrophile (S or Se) that was added, as well as the temperature at which the reaction was carried out, determined whether the synthon acted mainly as an anionic thio- or selenocarbene complex to give rise to carbene complexes [W(CO)$_5$L] (L = ĊC(Ph)=C(Ph)SeS̄, ĊC(Ph)-=C(Ph)SS̄e, ĊC(Ph)=C(Ph)SeS̄e) or as a thio- or selenoacyl anion to form thione or selone complexes [Cr(CO)$_5$|S=ĊC(Ph)=C(Ph)S̄S̄|] and [W(CO)$_5$L] (L = S=ĊC(Ph)=C(Ph)S̄S̄, Se=ĊC(Ph)=C(Ph)S̄S̄, Se=ĊC(Ph)=C(Ph)SeS̄e).

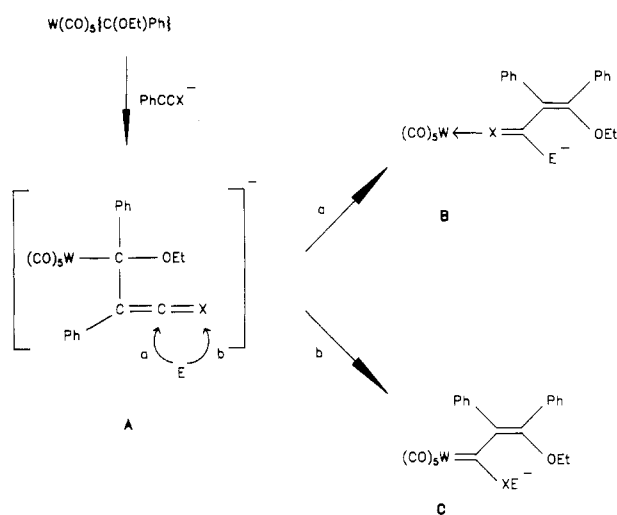## Introduction

In our study of the insertion of the anionic species PhC≡CS$^-$ and PhC≡CSe$^-$ into the carbene bond in [W-(CO)$_5$|C(OEt)Ph|],[1] we found that the anionic adduct re-

sulting from the addition of PhC≡CX$^-$ (X = S, Se) to the carbene complex could be used to prepare various novel

(1) Raubenheimer, H. G.; Kruger, G. J.; Marais, C. F. *J. Chem. Soc., Chem. Commun.* **1984**, 634.

Scheme I

W(CO)$_5$$\{$C(OEt)Ph$\}$

A

complexes containing heterocyclic ligands, some of which had not been synthesized before.[2]

From preliminary results,[1] it is known that either the heteroatom or the carbon atom α to the sulfur or selenium in the anionic adduct A (Scheme I) could act as a nucleophilic center. One therefore has a synthon for complexes of both thio- or selenoacyl anions and anionic thio- or selenocarbenes, which leads to structures like B or C after treatment of the adduct with a particular electrophile. These conversions involve breaking of the original metal–carbene bond and coordination of either a heteroatom to eventually form thione and selone complexes or a carbon atom to give rise to thio- and selenocarbene complexes.

In this report we describe tungsten and chromium complexes of various sulfur- and selenium-containing heterocyclic ligands that were prepared under very mild conditions, by selecting elemental sulfur or selenium as the electrophile and acidifying the mixture.

Although we have not isolated any of the uncoordinated heterocycles, it is of interest that synthetic methods for 3*H*-1,2-selenathiole, 3*H*-1,2-thiaselenole, and 3*H*-1,2-diselenole are known.[2] Several procedures also exist[3] for the preparation of 1,2-dithiole-3-thione, but preparations for 1,2-dithiole-3-selone and 1,2-diselenole-3-selone have not been reported yet. No tungsten or chromium complexes of any of the ligands are known.
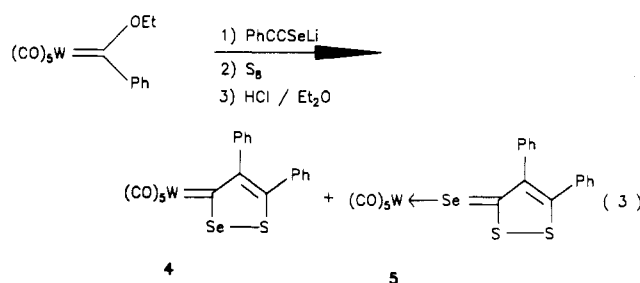
Results

When a solution of the Fischer carbene complex [M-(CO)$_5$$\{$C(OEt)Ph$\}$] (M = Cr, W) in tetrahydrofuran (THF) was treated at room temperature with an excess of PhC≡CSLi and 2 mol equiv of S (as S$_8$), then redissolved in CH$_2$Cl$_2$, and treated with [Et$_3$O][BF$_4$], the purple complexes 1 and 2 formed (eq 1). These complexes were purified by column chromatography and were obtained in yields of 86% for M = W and 4% for M = Cr.

1 : M = W

2 : M = Cr
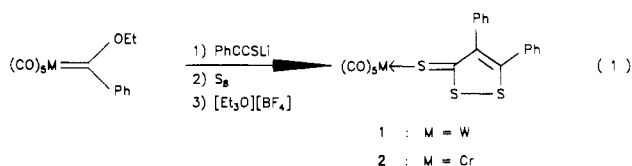
When a slight excess of PhC≡CSLi and either 1 or 2 mol equiv of Se (as Se$_8$) were added to a solution of the starting carbene complex at –30 °C and the mixture was stirred for 30 h at room temperature, the reddish complex 3 formed (eq 2). After column chromatography the yield was 8.6%.
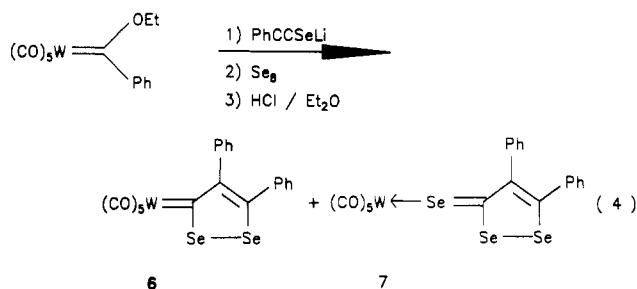
3
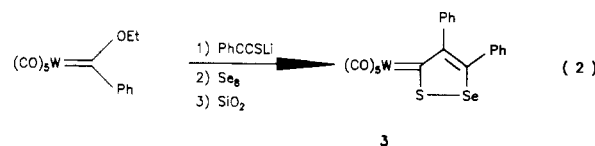
Addition of 1 mol equivalent of PhC≡CSeLi and 2 mol equiv of S (as S$_8$) to a THF solution of [W(CO)$_5$$\{$C(OEt)-Ph$\}$] at room temperature and acidification of the mixture with HCl in ether led to the formation of a purple selenocarbene complex, 4 (16.3% yield), and a light blue selone complex, 5 (5.1% yield) (eq 3), which could be separated by column chromatography.

4   5

The selone complex 5 could be obtained as the main product (10% yield) by doing the reaction at –30 °C. The reaction was repeated and the amount of sulfur added varied, but temperature seemed to be the main factor affecting the relative yields of the products.

The cyclic selenocarbene complex 6 and the selone complex 7 (eq 4) were obtained by adding a solution of

6   7

[W(CO)$_5$$\{$C(OEt)Ph$\}$] in THF to 1 mol equiv of PhC≡CSeLi at –30 °C, adding 2 mol equiv of Se (as Se$_8$) after 30 min, and acidifying the mixture at –78 °C after it had been stirred for 40 h at 0 °C. The two compounds were separated by chromatography to give a 9% yield of 6 (purple) and a 26% yield of 7 (turquoise). The thione complex 2 was the only chromium compound in the series that we were able to prepare; attempts to prepare the chromium analogues of complexes 3–7 were unsuccessful. All the compounds are soluble in polar organic solvents like CH$_2$Cl$_2$ and diethyl ether and less soluble in nonpolar solvents like hexane. Solutions of the complexes are fairly stable under nitrogen at room temperature. The X-ray crystal structures of 1[1] (Figure 1), 3, and 6 were determined. Some bond lengths and angles are given in the captions to figures, but all distances and angles are available as supplementary material.

X-ray Crystal Structure of 3. The structure of 3 is shown in Figure 2. The metal–C(carbene) bond [2.262

(2) Detty, M. R. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Eds.; Pergamon: Oxford, 1984; Vol. 6, p 947.

(3) Pedersen, C. T. *Adv. Heterocycl. Chem.* **1982**, *31*, 63.

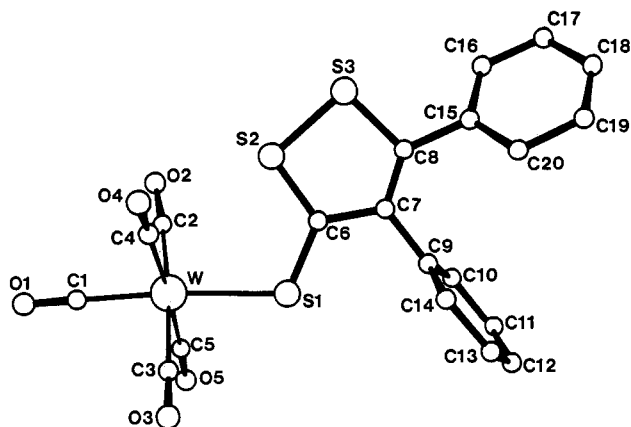(4) Wei, C. H. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1983**, *C38*, 1079.

Figure 1. X-ray crystal structure of [W(CO)₅{S=CC(Ph)=C-(Ph)SS}] (1).
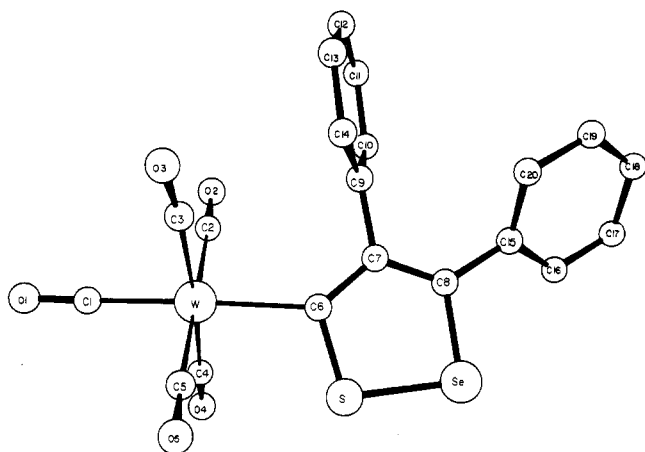
Figure 2. X-ray crystal structure of [W(CO)₅{CC(Ph)=C-(Ph)SeS}] (3). Some relevant bond lengths (Å): W–C(6), 2.262 (7); C(6)–C(7), 1.401 (9); C(6)–S, 1.694 (7); C(7)–C(8), 1.380 (9); C(8)–Se, 1.854 (6); S–Se, 2.181 (2).

(7) Å] is unusually long when compared to (alkoxyalkyl-carbene)pentacarbonyltungsten complexes, in which the length of this bond is on average about 2.15 Å. It must be added, however, that a search in the Cambridge crystallographic data base yielded the structures of only five pentacarbonyltungsten carbene complexes, and of these the W=C bond length varied between 2.086 (17) Å in [W(CO)₅{C(OMe)Cp}][5] and 2.32 (2) Å in the (ethoxy-ruthenocenylcarbene)pentacarbonyltungsten complex.[6]

Least-squares calculations showed that the five-membered ring is essentially planar and that the planes defined by C(6)–S–Se and C(1)–C(3)–C(4)–C(6) are at an angle of 48°, which means that the five-membered ring does not lie in any of the planes defined by carbonyl carbon atoms. This would imply that there is very little π-interaction and therefore not much double-bond character between the metal and carbene atoms, and this attribute is reflected in the relatively long metal–C(carbene) bond.

Because of the small differences relative to the standard deviations in the bond lengths, it is impossible to distinguish between single- and double-bond character in the C(6)–C(7) and C(7)–C(8) bonds.

Only one example of a S–Se bond in a five-membered ring, similar to that found in 3, could be traced—a naph-
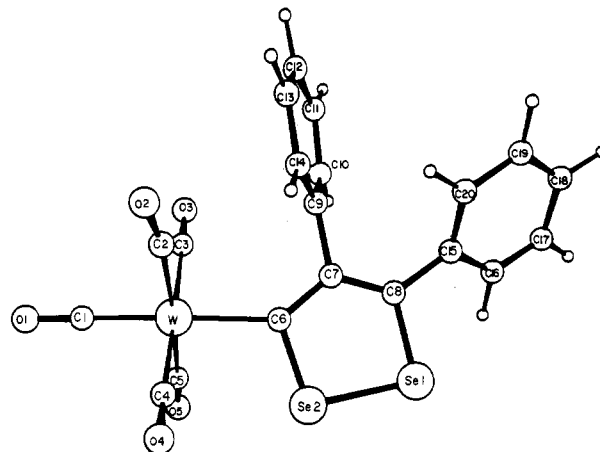

Figure 3. X-ray crystal structure of [W(CO)₅{CC(Ph)=C-(Ph)SeSe}] (6). Some relevant bond lengths (Å): W–C(6), 2.187 (12); C(6)–C(7), 1.40 (2); C(6)–Se(2), 1.858 (11); C(7)–C(8), 1.37 (2); C(8)–Se(1), 1.873 (12), Se(1)–Se(2), 2.295 (2).
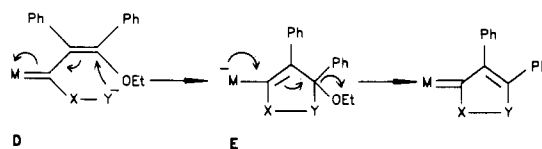
Scheme II

Table I. Infrared Data[a]

	A₁⁽¹⁾	B₁	E	A₁⁽²⁾
1	2065 (w)	1980 (vw)	1938 (st)	1925 (st)
2	2055 (w)	1978 (vw)	1945 (st)	1929 (st)
3	2065 (w)	1979 (vw)	1948 (st)	1923 (st)
4	2057 (w)		1942 (st)	1922 (st)
5	2065 (w)	1980 (vw)	1938 (st)	1925 (st)
6	2062 (w)	1980 (vw)	1942 (st)	1926 (st)
7	2065 (w)	1982 (vw)	1942 (st)	1925 (st)

[a] In cm⁻¹; hexane solutions.

thalene derivative in which the S–Se bond length is ~2.24 Å[7] (no standard deviation mentioned), which is similar to the distance of 2.181 (2) Å determined for 3.

X-ray Crystal Structure of 6. The crystal structures of compounds 3 and 6 (Figure 3) are very similar, but some significant differences are caused by substituting the sulfur atom in 3 with a selenium atom.

A marked difference lies in the W–C(6) bond length, which is much shorter in 6 [2.187 (12) Å] than in 3 [2.262 (7) Å].

A search in the Cambridge data base for similar unco-ordinated five-membered rings once again yielded only derivatives of aromatic compounds, and in these the Se–Se distance is around 2.32 Å; for 6 it is 2.295 (2) Å. The C–Se bond lengths of 1.873 (12) and 1.858 (11) Å are comparable with those of 1.913 (6) and 1.919 (6) Å in similar compounds determined by Endres and Keller.[8]

Once again the C(6)–C(7) bond length [1.40 (2) Å] cannot be distinguished from that of the formal double bond [1.37 (2) Å] between C(7) and C(8).

Discussion

The proposed mechanism for the rearrangements that occur upon addition of an electrophile to the anionic ad-

(5) Toledano, C. A.; Parlier, A.; Rudler, H.; Daran, J.-C.; Jeannin, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 576.
(6) Fischer, E. O.; Gammel, F. J.; Besenhard, J. O.; Frank, A.; Neugebauer, D. *J. Organomet. Chem.* **1980**, *191*, 261.

(7) Meinwald, J.; Duplaise, D. *J. Am. Chem. Soc.* **1977**, *99*, 7744.
(8) Endres, H.; Keller, H. J.; Queckborner, J.; Schweitzer, D.; Veigel, J. *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *B38*, 2855.

Table II. ^{13}C NMR Data[a]

	temp (°C)	W=C	C=X	CO trans	CO cis	C=C—X	C=C—X	Ph
1	-65		213.53	201.66	197.65	172.69	145.50	129–134
2	25		316.00	224.22	216.80	171.77	147.28	129–134
3	30	259.60		202.53	197.00	182.49	162.59	128–139
5	-20		209.38	201.42	197.66	169.90	148.15	128–133
6	30	270.07		203.21	196.30	185.52	166.67	128–140
7	30		216.56	200.74	197.61	173.99	152.76	126–137

[a] In ppm; internal reference TMS; CDCl$_3$ solutions.

Table III. UV/Vis Spectroscopic Data[a]

	λ_{max} (log ϵ)
1	332.0 (3.97); 531.6 (4.01)
2	358.2 (4.61); 547.6 (4.57)
3	246.8 (4.73); 351.6 (4.16); 514.0 (3.93)
4	246.8 (4.71); 351.6 (4.16); 522.4 (3.95)
5	334.8 (4.04); 576.4 (4.08)
6	247.0 (4.66); 352.0 (4.14); 540.8 (3.78)
7	239.2 (5.07); 364.8 (4.39); 605.2 (4.38)

[a] λ in nm; ϵ in 10^{-2} m^2 mol^{-1}; THF solutions.

duct, A (Scheme I), involves formal insertion of the acetylenic unit into the metal–carbene bond to give, depending on the nature of the electrophile (and in one instance upon the temperature), complexes of either type B or type C. Isolation and characterization of A will be described in a future publication.

After addition of the sulfur or selenium to A, cyclization can occur via an internal Michael-type addition. The terminal heteroatom would attach to the original carbene carbon atom (D, Scheme II), and this would be followed by β-elimination of the OEt group (E, Scheme II). In Scheme II, this speculative mechanism is presented for a carbene complex. It is difficult to explain why, in some cases, only one heteroatom added to the anionic adduct A (at the heteroatom of the adduct) to give thio- and selenocarbene complexes while, in others, two heteroatoms added to the adduct (at the carbon atom next to the heteroatom of the adduct) and thione and selone complexes were obtained. We were also unable to prepare a complex of a 1,2-dithiole analogue in which the ligand is coordinated as a thiocarbene ligand.

In eq 3, temperature was the main factor affecting the outcome of the reaction: although 2 mole equiv of sulfur were added to the reaction that was done at room temperature, only one sulfur atom added to the heteratom of the adduct and the selenocarbene complex 4 formed; at the lower temperature two sulfur atoms added to the nucleophilic carbon atom of the adduct, and the selone complex 5 was obtained. The relatively low yields of the compounds do not, however, permit too much discussion of factors affecting reaction rates.

On the infrared spectra (Table I) of the new compounds, no significant differences are discernible in the frequencies of ν(CO) vibrations of the thione, selone, and thio- and selenocarbene complexes. All the compounds seem to have

a slightly distorted C_{4v} local symmetry (B$_1$ bands are present), and in all cases the A$_1$[(2)] bands appear at lower frequencies than the E bands. (For the thio- and selenocarbene complexes prepared by the Fischer group[9] the positions of these bands are reversed.)

The ^{13}C NMR data are shown in Table II. The chemical shifts for corresponding carbon atoms in the ligands do not differ significantly, and only minor changes occur with variation of the heteroatoms. A very large downfield shift ($\sim$100 ppm) for the thione carbon is observed on moving from W (1, 213.53 ppm) to Cr (2, 316.00 ppm).

From the UV/vis spectroscopic data of the tungsten compounds (Table III) a clear distinction between thione (and selone) and carbene complexes is apparent. The high-energy transitions for carbene complexes are at $\sim$246 nm whereas those for thione and selone complexes (with the exception of 7) lie in the range 332–339 nm. The low-energy transitions for both the carbene [W-(CO)$_5$$\overline{\text{CXYC(Ph)}}$=C(Ph)] and thione/selone [W-(CO)$_5$$\overline{\text{Z}}$=$\overline{\text{CXYC(Ph)}}$=C(Ph)] complexes show a bathochromic shift as X and Y become heavier. A similar trend is shown by noncoordinated compounds of the type Z=$\overline{\text{CXC(R)}}$=C(R)Y.[2]

Experimental Section

All manipulations were done under an inert atmosphere (N$_2$). Solvents were dried and distilled under N$_2$ before use. Column chromatography was done at -10 °C, using Merck silica gel (0.063–0.200 mm) as the stationary phase. Reagents were used without further purification, and [W(CO)$_5${C(OEt)Ph}] was prepared according to the published method.[10]

Infrared spectra were obtained on a Perkin-Elmer 297 spectrophotometer, ^{13}C NMR spectra on a Bruker 500 MHz spectrometer, and mass spectra on Hitachi Perkin-Elmer RMU-6H and Finnigan Mat 8200 spectrometers. Melting points were determined on a Kofler hot stage apparatus and are uncorrected. Elemental analyses were done by Pascher and Pascher, Bonn, FRG.

Table IV contains the physical and analytical data of all the new compounds. Yields were calculated on the limiting reagent.

The crystal structures of 3 and 6 were determined by routine crystallographic procedures. The details are given in Table V. Fractional coordinates are given in Tables VI and VII.

Preparation of Lithium Ethynethiolate and Lithium Ethyneselenolate, PhC≡CSLi and PhC≡CSeLi. A THF

Table IV. Physical and Analytical Data

	mp (°C)	mol formula	m/z	elemental anal. found (calcd) C	H	S	Se
1	$\sim$182 dec	C$_{20}$H$_{10}$O$_5$S$_3$W	610 (M)	39.64 (39.35)	1.58 (1.65)	15.64 (15.75)	
2	160 dec	C$_{20}$H$_{10}$O$_5$S$_3$Cr	478 (M)	50.38 (50.20)	2.07 (2.10)	20.21 (20.10)	
3	145–148	C$_{20}$H$_{10}$O$_5$SSeW	626 (M)	38.54 (38.42)	1.63 (1.61)	5.30 (5.12)	11.8 (12.6)
4[a]	135–137	C$_{20}$H$_{10}$O$_5$SSeW	626 (M)	38.33 (38.42)	1.70 (1.62)	5.00 (5.13)	12.7 (12.6)
5	dec	C$_{20}$H$_{10}$O$_5$S$_2$SeW	574 (M – 3CO)	36.38 (36.54)	1.55 (1.53)	9.75 (9.75)	11.8 (12.0)
6[b]	132–134	C$_{20}$H$_{10}$O$_5$Se$_2$W	672 (M)	35.98 (35.74)	1.58 (1.50)		23.4 (23.5)
7		C$_{20}$H$_{10}$O$_5$Se$_3$W	611 (M – 5CO)	32.33 (31.98)	1.48 (1.34)		

[a] % O: found, 12.7; calcd, 12.8. [b] % O: found, 10.9; calcd, 10.7.

Table V. Crystallographic Data for [W(CO)₅{CC(Ph)=C(Ph)SeS}] (3) and [W(CO)₅{CC(Ph)=C(Ph)SeSe}] (6) and Structure Determination Details

	3	6
	Crystal Data	
formula	$C_{20}H_{10}O_5SSeW$	$C_{20}H_{10}O_5Se_2W$
cryst habit	cubes	square plates
cryst size (mm)	0.25 (all edges)	0.10 × 0.26 × 0.26
space group	$P2_1/c$	$P2_1/c$
unit-cell determinatn:		
least-squares fit to	25 reflections, θ(Mo) < 13°	25 reflections, θ(Mo) < 18°
unit-cell dimensns		
a, Å	10.225 (5)	10.218 (8)
b, Å	13.260 (6)	13.260 (9)
c, Å	14.654 (6)	14.675 (9)
β, deg	92.8 (1)	93.0 (1)
packing: V (Å³), Z	1984, 4	1986, 4
D_{calcd} (g cm⁻³), M, F(000)	2.09, 625.2, 1176	2.25, 672.1, 1248
	Experimental Data	
diffractometer	Philips PW1100	Philips PW1100
radiatn	Mo Kα (0.7107 Å)	Mo Kα (0.7107 Å)
monochromator	graphite	graphite
collectn mode	ω–2θ scans, θ range 3–23°	ω–2θ scans, θ range 3–23°
scan width (deg)	1.30	1.38
scan speed (deg s⁻¹)	0.052	0.057
observable reflctns	2410 with F > 1.6σ	2176 with F > 1.6σ
stability	3 reflctns every 60 min, no variatn	3 reflctns every 60 min, no variatn
correctns	Lp, absorptn	Lp, absorptn
μ (cm⁻¹)	74.8	91.6
absorptn correctns	empirical[11]	numerical[12]
	Solution and Refinement	
soln	SHELX76[12]	SHELX76[12]
refinement	least squares, full matrix	least squares, full matrix
hydrogen positns	calcd positns	calcd positns
reflctions used	2732 observed with F > 0	2578 observed with F > 0
weighting scheme	$w = (\sigma(F))^{-2}$	$w = (\sigma(F))^{-2}$
final Δ peaks	0.6 e Å⁻³ near the W atom	1.8 e Å⁻³ near the W atom
final R, R_w	0.0385, 0.0316	0.0631, 0.0339

solution (20 mL) of PhC≡CH (1.1 mL, 10.0 mmol) was cooled to –30 °C and 1 equiv of BuLi added, after which the mixture was stirred for 30 min. To this yellow solution was added S₈ (0.32 g, 10 mmol S), and the red solution was slowly warmed to room temperature. When all S₈ had dissolved, the solution was stored at –20 °C.

To prepare the selenium analogue, Se₈ instead of sulfur was used. This reaction is much slower and had to be stirred overnight between –30 °C and 0 °C.

Preparation of [M(CO)₅{S=CC(Ph)=C(Ph)SS}] (M = W, 1; M = Cr, 2). A solution of [M(CO)₅C(OEt)Ph] (4.9 mmol) in diethyl ether (10 mL) was treated at room temperature with 2 mol equiv of PhC≡CSLi (in THF) over 15 min. Elemental sulfur (0.31 g, 9.8 mmol; as S₈) was added, the solution stirred for 10 min and the solvent removed. The residue was dissolved in CH₂Cl₂ and [Et₃O][BF₄] added until thin-layer chromatography indicated a maximum yield of a single purple product. The mixture was filtered through SiO₂, the solvent removed, and the residue chromatographed (hexane/CH₂Cl₂, 1:1). The compound was

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Table VI. Fractional Coordinates (×10⁴, ×10⁵ for W) and Equivalent Isotropic Temperature Factors (Å², ×10³, ×10⁴ for W, S, Se) for [W(CO)₅{CC(Ph)=C(Ph)SeS}] (3)[a]

	x/a	y/b	z/c	U_{eq}
W	13767 (3)	−1309 (2)	29017 (2)	314 (1)
Se	2792 (1)	2028 (1)	230 (1)	484 (2)
S	1414 (2)	1347 (2)	1138 (1)	458 (5)
O(1)	−212 (5)	−1134 (5)	4450 (4)	64 (2)
O(2)	3642 (6)	412 (6)	4372 (4)	82 (2)
O(3)	2555 (6)	−2321 (4)	2615 (4)	70 (2)
O(4)	10 (8)	1941 (5)	3390 (5)	109 (2)
O(5)	−826 (6)	−765 (5)	1397 (5)	84 (2)
C(1)	369 (7)	−755 (5)	3888 (5)	39 (2)
C(2)	2844 (8)	224 (6)	3825 (5)	50 (2)
C(3)	2188 (7)	−1528 (6)	2696 (5)	42 (2)
C(4)	497 (9)	1200 (7)	3203 (5)	56 (2)
C(5)	−67 (8)	−539 (6)	1957 (6)	49 (2)
C(6)	2472 (6)	636 (5)	1790 (5)	31 (2)
C(7)	3784 (6)	722 (5)	1569 (4)	29 (2)
C(8)	4133 (6)	1371 (5)	886 (4)	29 (2)
C(9)	4814 (6)	116 (5)	2084 (4)	34 (2)
C(10)	5733 (7)	578 (6)	2686 (5)	45 (2)
C(11)	6741 (8)	−15 (8)	3097 (6)	63 (3)
C(12)	6838 (8)	−1022 (7)	2912 (6)	62 (3)
C(13)	5919 (8)	−1466 (6)	2336 (6)	53 (2)
C(14)	4915 (7)	−911 (5)	1920 (5)	41 (2)
C(15)	5448 (7)	1602 (5)	565 (4)	33 (2)
C(16)	5745 (8)	2581 (6)	273 (5)	43 (2)
C(17)	6950 (9)	2789 (6)	−52 (5)	58 (2)
C(18)	7915 (9)	2044 (7)	−112 (5)	56 (2)
C(19)	7618 (8)	1070 (6)	168 (5)	50 (2)
C(20)	6402 (7)	859 (5)	499 (5)	38 (2)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*(\mathbf{a}_i\cdot\mathbf{a}_j)$.

Table VII. Fractional Coordinates (×10⁴, ×10⁵ for W) and Equivalent Isotropic Temperature Factors (Å², ×10³, ×10⁴ for W, Se) for [W(CO)₅{CC(Ph)=C(Ph)SeSe}] (6)[a]

	x/a	y/b	z/c	U_{eq}
W	13731 (6)	−1049 (4)	29216 (4)	356 (1)
Se(1)	2793 (2)	2069 (1)	191 (1)	493 (4)
Se(2)	1260 (1)	1415 (1)	1115 (1)	498 (4)
O(1)	−171 (10)	−1087 (8)	4462 (7)	67 (3)
O(2)	3743 (11)	361 (8)	4375 (7)	91 (4)
O(3)	2517 (11)	−2301 (7)	2594 (7)	76 (3)
O(4)	24 (14)	1925 (8)	3461 (9)	114 (5)
O(5)	−873 (11)	−727 (8)	1463 (7)	88 (4)
C(1)	421 (13)	−716 (10)	3869 (10)	45 (4)
C(2)	2934 (14)	207 (10)	3859 (9)	57 (4)
C(3)	2191 (13)	−1501 (11)	2661 (10)	53 (4)
C(4)	498 (15)	1210 (14)	3257 (11)	73 (5)
C(5)	−118 (15)	−482 (10)	2001 (10)	57 (4)
C(6)	2413 (11)	642 (8)	1845 (8)	30 (3)
C(7)	3700 (12)	766 (8)	1586 (8)	30 (3)
C(8)	4085 (13)	1389 (8)	904 (8)	34 (3)
C (9)	4775 (13)	168 (9)	2106 (9)	48 (4)
C(10)	5661 (15)	629 (10)	2690 (9)	62 (4)
C(11)	6727 (13)	96 (13)	3085 (8)	59 (4)
C(12)	6794 (14)	−911 (11)	2966 (11)	70 (5)
C(13)	5883 (14)	−1408 (11)	2398 (10)	62 (5)
C(14)	4878 (14)	−856 (9)	1973 (9)	47 (4)
C(15)	5420 (13)	1589 (10)	570 (8)	37 (4)
C(16)	5763 (14)	2546 (10)	294 (8)	44 (4)
C(17)	6924 (16)	2760 (11)	−16 (9)	56 (5)
C(18)	7902 (16)	1993 (12)	−109 (9)	61 (5)
C(19)	7571 (14)	1023 (10)	156 (9)	48 (4)
C(20)	6332 (13)	847 (10)	492 (8)	38 (4)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*(\mathbf{a}_i\cdot\mathbf{a}_j)$.

recrystallized from CH₂Cl₂/hexane (yield: 1, 86% (24% after crystallization); 2, 4%).

Preparation of [W(CO)₅{CC(Ph)=C(Ph)SeS}] (3). To a solution of [W(CO)₅{C(OEt)Ph}] (1.2 g, 2.6 mmol) at –30 °C was added 1.2 mol equiv of PhC≡CSLi over 10 min. One mole equivalent of Se (as Se₈) was added and the mixture stirred for 30 h at room temperature. Thin-layer chromatography showed

that a small amount of the vinylic thioaldehyde complex[1] had also formed. The mixture was filtered through SiO_2, the solvent removed, and the residue chromatographed (hexane/CH_2Cl_2, 3:1). The reddish purple carbene complex (0.14 g) was obtained in 8.6% yield (0.14 g).

Preparation of [W(CO)₅{CC(Ph)=C(Ph)SSe}] (4) and [W-(CO)₅{Se=CC(Ph)=C(Ph)SS}] (5). A solution of [W(CO)₅{C-(Ph)OEt}] (1.8 g, 4.0 mmol) in THF was treated at room temperature with 1 equiv of PhC≡CSeLi, and 2 mol equiv of S (as S_8) were added immediately. After 1 h the mixture was acidified with HCl in diethyl ether and the solvent removed. The residue was chromatographed, and the purple carbene complex 4 was isolated as the main product in a yield of 16.3% (0.41 g). The more polar light blue selone complex 5 appeared as a side product but was obtained as the main product in a yield of 10% by doing the reaction at −30 °C.

Preparation of [W(CO)₅{CC(Ph)=C(Ph)SeSe}] (6) and [W(CO)₅{Se=CC(Ph)=C(Ph)SeSe}] (7). A solution of [W-(CO)₅{C(OEt)Ph}] (1.2 g, 2.6 mmol) in THF was added to 1 mol equiv of PhC≡CSeLi at −30 °C. After 30 min 2 mol equiv of Se (as Se_8) were added and the mixture was stirred at 0 °C for 40

h. The reaction mixture was cooled to −78 °C and acidified with HCl in diethyl ether. The solvent was removed and the residue chromatographed (hexane/CH_2Cl_2, 1:2) to give the purple carbene complex 6 (0.15 g, 9% yield) and the more polar turquoise selone complex 7 (0.50 g, 26% yield).

Electron-Transfer Chemistry of (Me₅C₅)₂Yb: Cleavage of Diorganoperoxide and Related Chalcogenides To Give (Me₅C₅)₂Yb(ER)(L) (E = O, S, Se, or Te; L = a Lewis Base). Crystal Structure of (Me₅C₅)₂Yb(TePh)(NH₃)

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The divalent metallocenes of ytterbium (Me₅C₅)₂Yb(OEt₂) or (Me₅C₅)₂Yb(NH₃)₂ react with molecules of the type REER to give the trivalent ytterbium complexes (Me₅C₅)₂Yb(ER)(L), where L is OEt₂ or NH₃, E is S, Se, or Te, and R is a phenyl or substituted phenyl group. The ammonia complexes are easier to characterize than the diethyl ether complexes since the latter complexes lose ether in the solid state and give unsatisfactory microanalytical data whereas the ammonia complexes give satisfactory elemental analyses. In addition, the line width of the Me₅C₅ protons in the ¹H NMR spectra of the diethyl ether complexes is ca. 500 Hz whereas the line width at half-height is ca. 50 Hz for the ammonia complexes, consistent with the notion that the barrier to chemical exchange is higher for the ammonia complexes. The peroxides ROOR, where R is Me₃C or Me₃Si, give the alkoxides (Me₅C₅)₂Yb(OR)(NH₃), and Et₂NC(S)SS(S)CNEt₂ gives the known (Me₅C₅)₂Yb(S₂CNEt₂). In contrast, dialkyl dithiophosphinates give (Me₅C₅)₂Yb(S₂PR₂) and R₂PPR₂, where R is Me or Et. The synthetic routes developed in this work are the best methods currently available for synthesis of these trivalent species. The crystal structure of (Me₅C₅)₂Yb(TePh)(NH₃) has been done. The crystals are orthorhombic, $P2_12_12_1$, with $a = 11.823$ (3) Å, $b = 25.917$ (6) Å, $c = 8.539$ (2) Å, and $V = 2616.5$ Å³. For $Z = 4$, the calculated density is 1.69 g cm⁻³. The structure was refined by full-matrix least squares to a conventional R factor of 0.046 [4991 data, $F^2 > \sigma(F^2)$]. The Yb–Te distance is 3.039 (1) Å, and the Yb–Te–C(Ph) angle is 113.0 (3)°.

The divalent ytterbium metallocene (Me₅C₅)₂Yb(OEt₂) reacts with a wide variety of transition-metal carbonyls and substituted metal carbonyls with single metal–metal bonds as shown in eq 1, where X is Co(CO)₄,[1a] Mn(CO)₅,[1b]

$$2(Me_5C_5)_2Yb(L) + XX \rightarrow 2Me_5C_5Yb(X)(L) \quad (1)$$
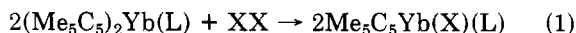
CpFe(CO)₂,[1c] and CpMo(CO)₃.[1c] The reaction in eq 1 involves the transfer of an electron from (Me₅C₅)₂Yb(OEt₂)

to the lowest unoccupied molecular orbital of the dimeric transition-metal carbonyl which is primarily metal–metal antibonding. The net reaction is formation of a (Me₅C₅)₂Yb^III fragment which is bonded to the transition metal by way of M–CO–Yb bonds. The electron-transfer process that results in oxidation of (Me₅C₅)₂Yb to (Me₅C₅)₂Yb^III is an exothermic one by ca. 1.35 V (ca. 30

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