Insertion of Phenylethyne-thiolate or -selenolate into Metal–Carbene Bonds: Synthons for Co-ordinated Thioacyl or Selenoacyl Anions and for Anionic Thiocarbene or Selenocarbene Complexes†

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Reaction of lithium ethynethiolate or ethyneselenolate, $LiX^1C{\equiv}CPh$ (X^1 = S or Se), with carbene complexes $[M(CO)_5\{C(OR^1)Ph\}]$ (M = Cr or W; R^1 = Me or Et) afforded, by the formation of carbon–carbon bonds, a series of adducts, $Li[M(CO)_5\{C(OR^1)PhC(Ph){=}C{=}X^1\}]$. The adducts reacted regioselectively with electrophiles: acidification with HCl gave α,β-unsaturated thio- and seleno-aldehyde complexes, $[M(CO)_5\{X^1{=}CHC(Ph){=}C(OR^1)Ph\}]$, alkylating agents $[Et_3O][BF_4]$ or MeI gave α,β-unsaturated thio-or seleno-carbene complexes, $[M(CO)_5\{C(X^1R^3)\text{-}C(Ph){=}C(OR^1)Ph]$ (X^1R^3=SEt, SMe, or SeEt), which cleanly and spontaneously converted into sulphur- or selenium-co-ordinated indene derivatives, $[M(CO)_5\{(X^1R^3)CH(C_6H_4\text{-}o)\text{-}C(OR^1){=}CPh\}]$ (X^1R^3=SEt or SeEt), and, finally, disulphides R^4SSR^4(R^4=Me, Et, or Ph) or the diselenide PhSeSePh yielded thio- or seleno-ester complexes$[M(CO)_5\{X^1{=}C(X^2R^4)C(Ph){=}C(OR^1)Ph]$ (X^2R^4=SMe, SEt, SPh, or SePh). Four *X*-ray crystal-structure determinations established the stereochemical configurations of selected members of the various classes of acyclic products. The isomeric compound to one of the thioaldehyde complexes, $[W(CO)_5\{S{=}C(Ph)CH{=}C(OEt)Ph\}]$, obtained from the adducts with X = S or Se and R^1 = Et on acidification in the presence of CS_2 or CSe_2, was also characterized structurally by single-crystal *X*-ray diffraction.

Despite considerable recent interest in Group 6 metal–carbene complexes of the Fischer type, anionic thio- and seleno-carbene compounds, $[M(CO)_5\{C(X)R\}]^-$ (M = Cr or W, X = S or Se, R = organic group), are not known. Oxygen homologues, such as $[W(CO)_5\{C(O)Ph\}]^-$, on the other hand, have been isolated and characterized as their tetrabutylammonium salts[1] and serve as precursors for neutral carbene complexes[2] and as ligands in titanium(IV) complexes.[3] Similarly, co-ordinated thio-and seleno-acyl anions, $[M(CO)_5(X{=}CR)]^-$, which are structural isomers of the anionic carbene compounds, do not exist. Seebach *et al.*[4] pioneered utilization of the comparable, but nitrogen-stabilized, free anion $S{=}CNMe_2^-$ in organic synthesis and we have used the deprotonated thiocarbamoyl complex, $[Cr(CO)_5(S{=}CNMe_2)]^-$, to prepare a trithiocarbonate complex.[5]

In this study we were concerned with the formation of anionic adducts $Li[M(CO)_5\{C(OR^1)PhC(Ph){=}C{=}X^1\}]$ (R^1 = Me or Et), from $Li[X^1C{\equiv}CPh]$ (X^1 = S or Se) and Fischer carbene complexes $[M(CO)_5\{C(OR^1)Ph\}]$ (M = Cr or W) and their subsequent conversion with various electrophiles. The objective of the investigation was three-fold: (*a*) to use the anionic adduct as a synthetic equivalent (synthon) of co-ordination complexes of two types of compounds, *viz.* thio- or seleno-acyl anions, $[M{\leftarrow}X^1{=}C(R^2)]^-$, and anionic thio- or seleno-carbenes, $[M{=}C(X^1)R^2]^-$ [R^2 = $C(Ph){=}C(OR^1)Ph$]; (*b*) to study the formal insertion of a new type of multiply bonded nucleophile, $[PhC{\equiv}CX^1]^-$, into a metal–carbene bond; (*c*) to prepare and characterize various new complexes, all containing the substituted vinyl fragment R^2.

We succeeded in preparing new classes of rare α,β-unsaturated thio- and seleno-aldehyde, unstable thio- and seleno-carbene, and thio- and seleno-ester (S or Se donor atom) complexes of chromium or tungsten pentacarbonyl. The thio- and seleno-carbene complexes convert spontaneously and quantitatively into sulphur- or selenium- co-ordinated indene derivatives. In all preparations the reaction of the chosen electrophile with the adduct is stereo- and regio-selective.

Free thioaldehydes are usually thermally unstable and have a tendency to polymerize; they are normally generated *in situ* for use in Diels–Alder-type reactions.[6] They can be stabilized by co-ordination to metals, and several complexes with π-bonded thioaldehydes have been prepared,[7] but only a few in which the thioaldehyde is σ bonded have been reported.[8] Selenoaldehyde complexes were prepared for the first time fairly recently.[9]

Thio- and seleno-carbene complexes are known,[10] but none that undergoes the rearrangement reaction shown by the new complexes $[M(CO)_5\{C(X^1Et)C(Ph){=}C(OR^1)Ph\}]$ (M = Cr, X^1 = S, R^1 = Me; M = W, X^1 = S or Se, R^1 = Et), to form mono-co-ordinated indene-derivative complexes of chromium and tungsten. We are now also able to correct a previous misinterpretation of n.m.r. data regarding the stereochemistry of the precursor thio- and seleno-carbene complexes.[11]

Although thio- and seleno-esters of the types RC(S)SR, RC(S)OR, and RC(Se)OR are known,[12] only a few complexes containing them as ligands have been reported;[13] the only ones in which the metal is in the zero oxidation state were prepared in our laboratory.[14] Nine new complexes with α,β-unsaturated thio- or seleno-ester ligands, $[M(CO)_5\{X^1{=}C(X^2R^4)R^2\}]$ (X^2R^4 = SMe, SEt, SPh, or SePh), were prepared in this study.

The stereoselective insertion reactions of nucleophilic multiple bond systems into metal–carbene bonds is well documented,[15] but none in which the heteroatom of the unsaturated system is one of the chalcogens has been noted.

We have already reported some of the synthetic uses of the new synthons.[16]

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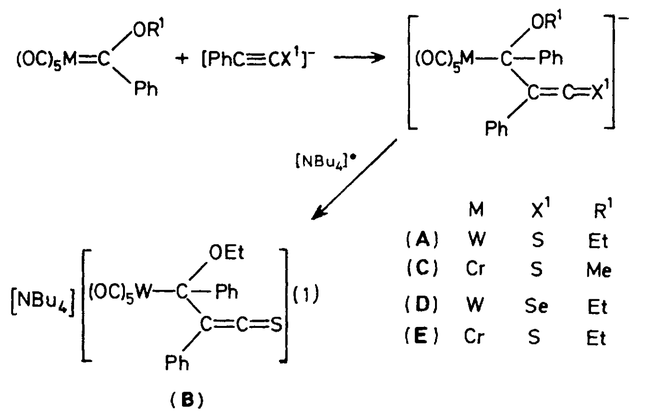
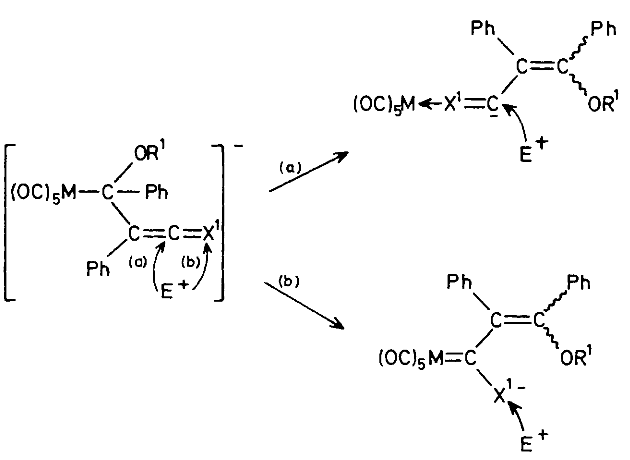
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.



	M	X^1	R^1
(A)	W	S	Et
(C)	Cr	S	Me
(D)	W	Se	Et
(E)	Cr	S	Et



Scheme 1.

Results and Discussion

Preparation and Structural Characterization of the Adducts.—Reaction of the carbene complex $[W(CO)_5\{C(OR^1)Ph\}]$ with $Li[SC{\equiv}CPh]$ in thf (tetrahydrofuran) at −30 °C gave an ionic adduct, (**A**) [equation (1)], which functioned as a synthon in further reactions. The tetrabutylammonium salt, (**B**), was isolated and characterized. It has a sharp melting point and analyzed correctly as a 1:1 adduct, but the crystals were not suitable for an *X*-ray study.

The spectroscopic data are in accordance with the structure proposed for the co-ordination complex depicted in (**A**) and (**B**). The i.r. spectrum of (**B**) (in CH_2Cl_2) shows a sharp band at 2 049 cm^{-1} and a broad band around 1 895 cm^{-1}, with shoulders at 1 945 and 1 855 cm^{-1}, a pattern consistent with an anionic $M(CO)_5L$ complex.[17] The ^{13}C n.m.r. spectrum (in $CDCl_3$) shows only two signals assignable to the (*cis* and *trans*) carbonyl carbon atoms, which confirms that the co-ordination number of the tungsten atom is six; the other signals are also consistent with the arrangement shown in (**B**): δ 176.3 (C=S), 146.8 (*C*=C=S), 144.5 and 138.5 (Ph C^1), 123.0—127.8 (Ph), and 99.5 p.p.m. (W—C). The chemical shift of 99.5 p.p.m. for W—*C*(sp^3) is close to the values reported by Fischer *et al.*[18] for adducts between carbene complexes and anionic carbon nucleophiles. The phenylalkyne-thiolate or -selenolate has two potentially nucleophilic centres which are accentuated by two resonance structures (see below). However, from the products isolated in further reactions, there was no evidence to suggest that the initial reaction with the carbene complex ever occurred through the heteroatom.

$$Ph{-}C{\equiv}C{-}X^- \longleftrightarrow Ph{-}\bar{C}{=}C{=}X$$

An alternative structure for the adduct complex, namely $[W(CO)_5\{S{=}CC(Ph){=}C(OEt)Ph\}]^-$, in which a rearrangement, entailing formal insertion of the acetylenic unit, had already taken place, was discarded on the strength of the ^{13}C n.m.r. data and the inherent instability of this type of carbanion.

The chromium-containing adducts, (**C**) and (**E**), were prepared under the same reaction conditions as (**A**) from the chromium–carbene complexes, $[Cr(CO)_5\{C(OR^1)Ph\}]$ (R^1 = Me or Et), but were not characterized. An adduct, (**D**), similar to (**A**), was assumed to form when the tungsten carbene complex was treated, at room temperature, with the alkyneselenolate $Li[SeC{\equiv}CPh]$.

Lower electrophilic reactivity of the carbene carbon in thiocarbene complexes, compared with alkoxycarbene complexes, is regarded as the reason that no adducts formed between $Li[SC{\equiv}CPh]$ and $[W(CO)_5\{C(SPh)Ph\}]$ or $[Cr(CO)_5\{C(SMe)Ph\}]$. The alkoxycarbene complex $[Cr(CO)_5\{C(OMe)Me\}]$, with an alkyl rather than a phenyl organic group, was also unreactive. The fact that $Li[SeC{\equiv}CPh]$ did not react with $[Cr(CO)_5\{C(OMe)Ph\}]$ may be ascribed to the lower nucleophilicity of the selenium-containing anion compared with phenylethynethiolate.

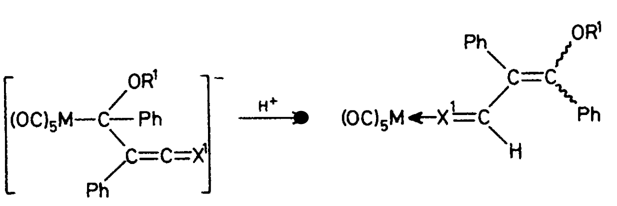
Although it was possible to store (**B**) and use it for further reactions, the anionic adducts were normally not isolated, but prepared *in situ* in thf and used immediately.

The Adducts as Synthons.—The synthetic versatility and usefulness of the adducts results from their ability to offer either the heteroatom, X^1, or the carbon atom, α to X^1, as a nucleophilic centre (Scheme 1). The locality of this effective anionic centre could be manipulated by changing the nature of the electrophile.

When the alkylating agents $[Et_3O][BF_4]$ and MeI were added to the adduct, electrophilic attack occurred at the heteroatom [Scheme 1, route (b)] and the adjacent carbon atom acquired enough carbenoid character to be trapped by the metal carbonyl unit. Other 'softer' electrophiles, like elemental sulphur and selenium and disulphides or diselenides ($R^4X^2X^2R^4$), reacted at the carbanionic centre α to the heteroatom in the anionic adducts [Scheme 1, route (a)], and an effective 'umpolung' of the normal reactivity of the original $[PhC{\equiv}CX^1]^-$ reagent was exhibited. Various thio- and selenoester complexes resulted, and although H^+ is not normally regarded as a 'soft' electrophile, protonation also provided a simple way of preparing co-ordinated thio- and seleno-aldehydes. An alternative argument that we have put forward to explain the latter type of reaction [16c] is that, initially, the H^+ ion attaches to the heteroatom and a mercaptocarbene complex forms, which, presumably due to the instability of this unknown type of complex, rearranges to form a co-ordinated thioaldehyde complex.

We briefly mention here that $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^+$ reacted similarly to Et^+ or Me^+, whereas $[Au(PPh_3)]^+$ afforded a tungsten thione complex with (**A**) by bonding to the available carbon atom. These results have been published elsewhere.[16c]

Reactions with Various Electrophiles.—Preparation of thio- and seleno-aldehyde complexes. To obtain the purple thioaldehyde complex, (**1a**) [equation (2)], adduct (**A**) was acidified with $HCl\text{–}Et_2O$. The *X*-ray crystal structure of this compound was determined and shows the stereoselective formation of an *E* isomer (the two phenyl groups are situated *trans* to each other, see Figure 1). Attempts to replace the hydrogen atom of the thioaldehyde ligand with $SiMe_3$ failed. Although we were very careful to remove any traces of H^+ from the $SiMe_3Cl$ before the reaction, an exchange occurred on the SiO_2 used for chromatography, and the thioaldehyde complex was the only product.



(2)

	M	X^1	R^1
E-(**1a**)	W	S	Et
(**1b**)	Cr	S	Et
(**1c**)	W	Se	Et

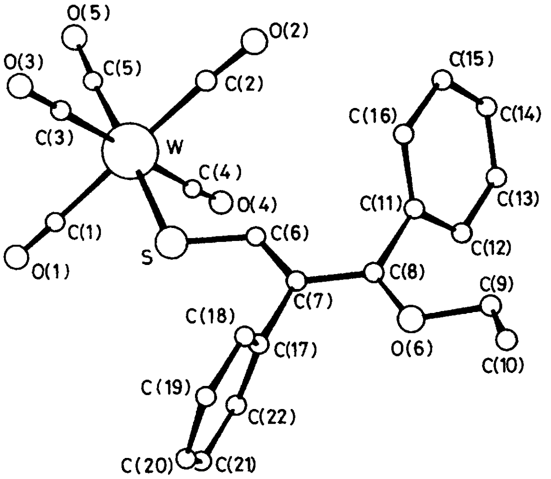


Figure 1. Crystal structure of *E*-[W(CO)$_5${S=CHC(Ph)=C(OEt)Ph}], (**1a**). Bond lengths (Å): W–S 2.508(5), S–C(6) 1.63(2), C(6)–C(7) 1.40(2), C(7)–C(8) 1.42(3), W–C(av.) 2.04(6), and C=O(av.) 1.14(3). Bond angles (°): W–S–C(6) 112(1), S–C(6)–C(7) 124(2), C(6)–C(7)–C(8) 122(2), C(6)–C(7)–C(17) 121(2), C(7)–C(8)–C(11) 120(2), C(7)–C(8)–O(6) 119(2), W–C–O(av.) 176(3), and S–C(6)–C(7)–C(8) 117(3)

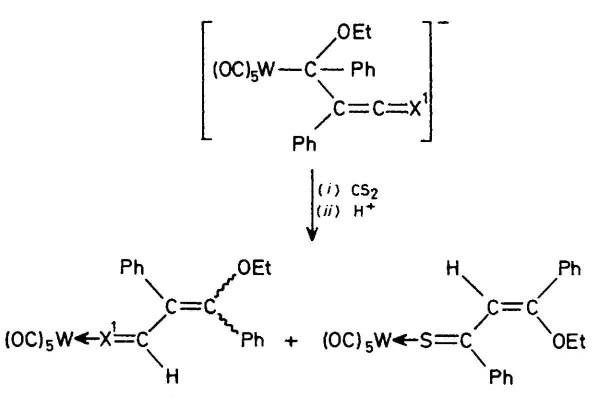
When a diethyl ether solution containing adduct (**A**) was treated with an excess of CS_2 at -30 °C, and the mixture acidified with HCl–Et_2O, the same thioaldehyde complex was obtained in a much higher yield (48%), along with an unexpected thione complex, (**2**) [equation (3)], the structure of which was resolved by *X*-ray crystallography (Figure 2). Only one geometric isomer of (**2**), the *Z*-conformer, formed (yield 23%).

The purple chromium–thioaldehyde complex, (**1b**), was prepared by acidifying the carbene–alkynethiolate adduct, (**E**), with HCl–Et_2O [equation (2)]. This complex also formed when a solution of the tungsten adduct (**A**) was added to a solution of [Cr(CO)$_5$(thf)] and the mixture chromatographed. Acidification occurred on the silica gel [equation (4)].

By treating the tungsten carbene–alkyneselenolate adduct, (**D**), with HCl in Et_2O at room temperature, the purple selenoaldehyde complex, (**1c**), was prepared [equation (2)]. It decomposed on silica gel therefore Fluorosil was used for chromatography.

When the reaction with CS_2 and HCl [equation (3)] was attempted with the seleno-adduct, (**D**), no selenone analogue of (**2**) formed, but a mixture of the selenoaldehyde complex, (**1c**), and the thione complex, (**2**), was obtained [equation (3)]. This implies that the thioketone sulphur atom of (**2**), originated from CS_2. By repeating the reaction at -30 °C (acidification at -78 °C) the selenoaldehyde complex could be obtained as the only product.

All the compounds are very soluble in polar organic solvents, like diethyl ether and dichloromethane, and less soluble in aliphatic hydrocarbons. The thioaldehyde complexes are air stable in the solid state, and stable in deoxygenated solutions. The selenoaldehyde complex is much more air sensitive, both in the solid state and in solution.



(3)

E-(**1a**)
(**1c**)

(**2**)

Evidence that the thio- and seleno-aldehyde complexes, (**1a**) and (**1c**), are Diels–Alder dienophiles was found in their reaction with cyclopentadiene. Both reactions showed the quantitative formation of a yellow product, which could be purified by column chromatography, but which decomposed in the absence of an excess of cyclopentadiene. The mass spectra of the yellow product mixtures showed molecular ions corresponding to 1:1 adducts, but it is not known whether the reaction site was the X^1=C or C=C double bond.

Preparation of thio- and seleno-carbene complexes and co-ordinated indene derivatives. When adduct (**A**) was treated with 1 equivalent of Meerwein's reagent, [Et_3O][BF_4], at -30 °C and the reaction mixture allowed to warm to room temperature, the brown thiocarbene, (**3a**) [equation (5)] could be separated from the more polar, orange dithioester complex [(**5b**), see below] (which was always a by-product of the reaction) by column chromatography. The reddish brown chromium thiocarbene complex, (**3b**), was obtained as the only product in a similar procedure using adduct (**C**). By treating adduct (**A**) at room temperature with a large excess of MeI, the brown methylthiocarbene complex (**3c**) [equation (5)] was obtained. To prepare the ethylselenocarbene complex (**3d**) [equation (5)], 1.1 mol equivalents of [Et_3O][BF_4] were added to adduct (**D**) at -30 °C. The product was chromatographed on Fluorosil and all further manipulations performed at low temperature to prevent conversion into the indene complex. A reddish brown solid was isolated, but due to its rapid conversion in solution only the i.r. spectrum of the selenocarbene complex could be obtained.

A crystal structure determination of (**3a**) showed it to have the *Z* configuration (Figure 3), but the stereochemistry of (**3b**), (**3c**), and (**3d**) is not known.

The rearrangement reaction of (**3a**), (**3b**), and (**3d**), to form S- or Se- co-ordinated indene derivatives [(**4a**)—(**4c**), equation (6)], has not been noted for thio- and seleno-carbene complexes before. It is reminiscent of the conversion of aminocarbene complexes into η^6-co-ordinated indenes in chromium tricarbonyl complexes,[19] but there are essential differences, some of which were mentioned in our preliminary report.[11] (*i*) Tungsten aminocarbene complexes did not rearrange and the chromium carbene complexes had to be heated to 120 °C for the reaction to take place. (*ii*) In the thiocarbene complex (**3a**) the phenyl group, which is eventually attached to the carbene carbon atom, is oriented *trans* with respect to the carbene. To enable the new bond to form, the energy barrier to rotation at

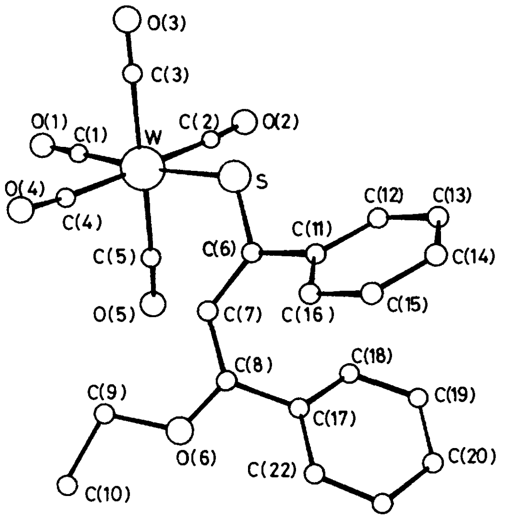
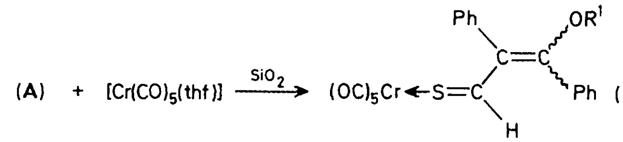
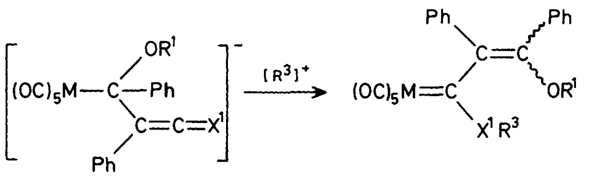


Figure 2. Crystal structure of E-[W(CO)$_5${S=C(Ph)CH=C(OEt)Ph}], (**2**). Bond lengths (Å): W–S 2.508(2), S–C(6) 1.667(6), C(6)–C(7) 1.431(9), C(7)–C(8), 1.370(9), W–C(av.) 2.022(28), and C=O(av.) 1.135(15). Bond angles (°): W–S–C(6) 119.5(2), S–C(6)–C(7) 121.9(5), S–C(6)–C(11) 114.9(4), C(6)–C(7)–C(8) 127.3(6), C(7)–C(8)–C(17) 126.2(6), C(7)–C(8)–O(6) 122.5(6), W–C–O(av.) 177.4(17), and S–C(6)–C(7)–C(8) 154(1)



(4)

(**1b**)



(5)

	M	X^1	R^1	R^3
Z-(**3a**)	W	S	Et	Et
(**3b**)	Cr	S	Me	Et
(**3c**)	W	S	Et	Me
(**3d**)	W	Se	Et	Et

the double bond has to decrease significantly. Our suggested mechanism (Scheme 2) requires substitution of the carbene carbon by a neighbouring X^1Et group[20] followed by the insertion of a free carbene into a C–H bond of the phenyl group. To form indene derivatives from aminocarbene complexes, the *cis* orientation of the phenyl group and carbene carbon atom is a prerequisite.[19]

The carbene compounds are soluble in most organic solvents, but convert into co-ordinated indene derivatives [(**4a**)—(**4c**)] on standing [equation (6)]. The relative rates of conversion for the complexes [M(CO)$_5${C(X^{1}R^3)C(Ph)=C(OR^1)Ph}] are (**3d**) $\gg$ (**3b**) > (**3a**).

Preparation of thio- and seleno-ester complexes. The orange dithioester complexes [(**5a**)—(**5c**), equation (7)] were prepared by adding R^4SSR^4 (R^4 = Me, Et, or Ph respectively) to adduct (**A**) at −30 °C and heating the mixture for 10 min at *ca.* 50 °C.

The ethylthio analogue, (**5b**), was first obtained in somewhat lower yield from the procedure used in preparing the carbene complex (**3a**). As shown by X-ray crystallography (Figure 4) (**5b**) has the E configuration (the two phenyl groups *trans* to each other). The red-brown phenylselenothio(*Se*) ester complex, (**5d**), formed on addition of PhSeSePh to the adduct. When adduct (**C**) was treated with EtSSEt [equation (7)] the red dithioester complex (**5e**) resulted.

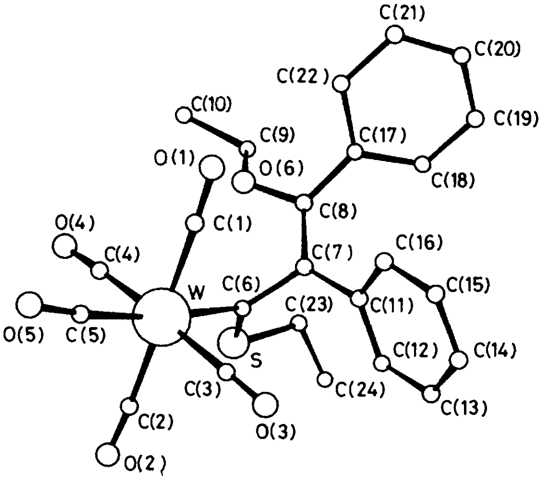
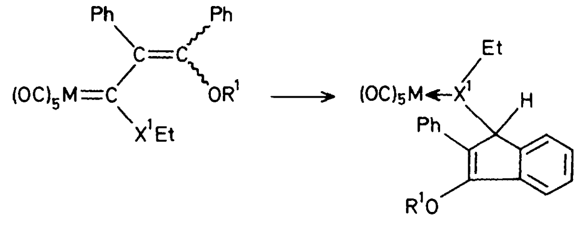


Figure 3. Crystal structure of Z-[W(CO)$_5${C(SEt)C(Ph)=C(OEt)Ph}], (**3a**). Bond lengths (Å): W–C(6) 2.159(10), C(6)–S 1.679(10), C(6)–C(7) 1.486(14), C(7)–C(8) 1.347(14), W–CO(av.) 2.016(22), and C=O(av.) 1.150(8). Bond angles (°): W–C(6)–S 120.3(5), W–C(6)–C(7) 121.1(7), C(6)–S–C(23) 112.0(6), C(6)–C(7)–C(8) 118.3(11), C(6)–C(7)–C(11) 115.0(7), C(7)–C(8)–O(6) 116.3(10), C(7)–C(8)–C(17) 127.8(11), W–C–O(av.) 176.9(18), and W–C(6)–C(7)–C(8) 94(2)



(6)

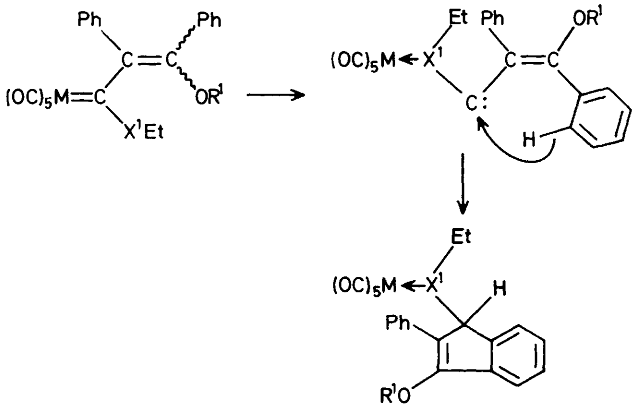
	M	X^1	R^1
(**4a**)	W	S	Et
(**4b**)	Cr	S	Me
(**4c**)	W	Se	Et

By starting from adduct (**D**) and adding 1 mol equivalent of Se and an excess of MeI the purple diselenoester complex [(**5f**), equation (8)] was prepared.

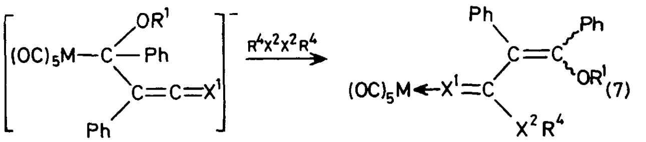
Compound (**5g**), a reddish purple diselenoester complex, was obtained under more drastic conditions (1 h, 65 °C) from adduct (**D**) and PhSeSePh [equation (7)]. The selenoaldehyde complex, (**1d**), appeared as a by-product in this reaction and the two products were separated by column chromatography on Fluorosil.

Two selenothio(*S*) ester complexes were also prepared [equation (7)]. From the reaction of adduct (**D**) with excess of R^4SSR^4 at room temperature the purple complex (**5h**) (R^4 = Me) and the reddish purple compound (**5i**) (R^4 = Ph) resulted. The X-ray crystal structure of (**5i**) was determined (Figure 5) which, surprisingly, revealed a *cis* orientation of the two phenyl groups, compared with a *trans* configuration in (**5a**). These results indicate that a delicate energy balance is responsible for the selective formation of any specific geometrical isomer of type (**5**) complexes.

The ester complexes are more soluble in polar than in non-



Scheme 2.



(7)

	M	X^1	R^1	X^2R^4
(5a)	W	S	Et	SMe
E-(5b)	W	S	Et	SEt
(5c)	W	S	Et	SPh
(5d)	W	S	Et	SePh
(5e)	Cr	S	Me	SEt
(5g)	W	Se	Et	SePh
(5h)	W	Se	Et	SMe
Z-(5i)	W	Se	Et	SPh

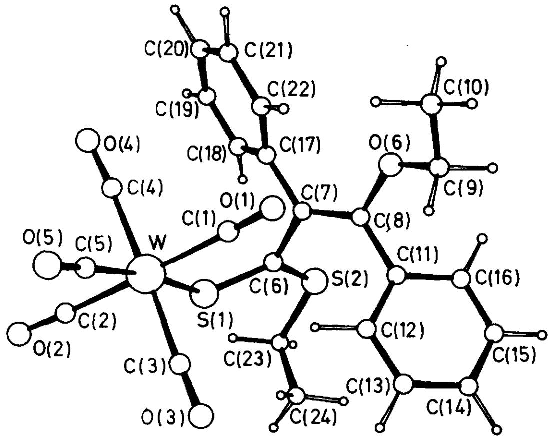
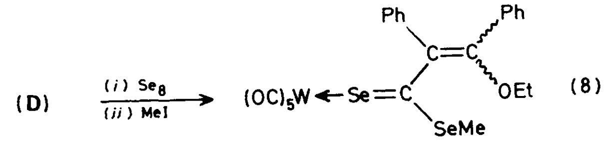


Figure 4. Crystal structure of E-[W(CO)$_5${S=C(SEt)C(Ph)=C(OEt)Ph}], (**5b**). Bond lengths (Å): W–S(1) 2.531(2), S(1)–C(6) 1.657(8), C(6)–S(2) 1.698(8), C(6)–C(7) 1.493(10), C(7)–C(8) 1.62(10), W–C(av.) 2.017(30), and C=O(av.) 1.135(11). Bond angles (°): W–S(1)–C(6) 115(2), S(1)–C(6)–S(2) 118.5(3), S(1)–C(6)–C(7) 123.1(5), C(6)–C(7)–C(8) 119.1(7), C(7)–C(8)–O(6) 117.2(8), C(7)–C(8)–C(11) 124.7(8), and W–C–O(av.) 175.9(21)

polar solvents, they are stable in solution under an inert atmosphere, and air stable in the solid state. Most of the compounds were obtained in yields of between 10 and 25%, except (**5c**), (**5h**), and (**5i**), with yields of *ca.* 40%.

Insertion of PhC_2 *or* PhC_2S *into the* M–C *Bond.*—The rearrangement initiated by the addition of an electrophile to the adduct involves a redistribution of the electrons, in which the original metal–carbene bond is broken and the vacant co-ordination site is taken up by, either the heteroatom [Scheme 1, route (a)] or the newly created carbenoid centre [route (b)]. This step finally effects the formal insertion of the acetylenic unit into the original metal–carbene bond. Therefore, unlike the insertion reactions of alkynamines, which take place in a single step, the present conversion of a carbene complex into complexes (**1**), (**2**), (**3**), and (**5**) occurs in two definable steps: first the formation of the adduct (Scheme 1) and then a rearrangement upon reaction with an electrophile.



(8)

(**5f**)

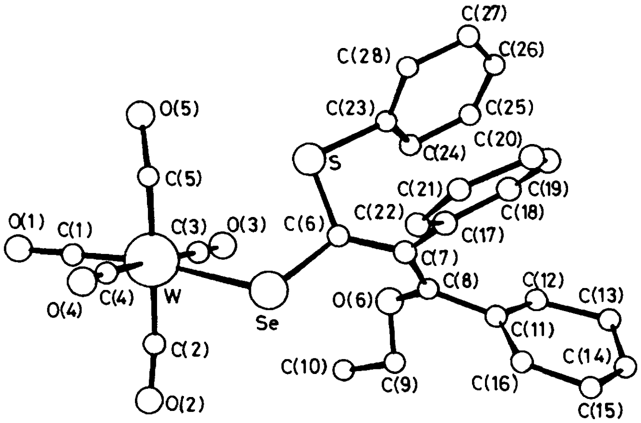
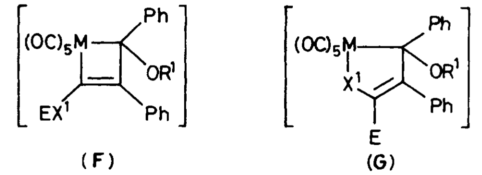


Figure 5. Crystal structure of Z-[W(CO)$_5${Se=C(SPh)C(Ph)=C(OEt)Ph}], (**5i**). Bond lengths (Å): W–Se 2.619(3), Se–C(6) 1.83(3), C(6)–S, 1.79(3), C(6)–C(7) 1.39(3), C(7)–C(8) 1.29(3), W–C(av.) 1.98(13), and C=O(av.) 1.18(12). Bond angles (°): W–Se–C(6) 117.6(11), Se–C(6)–S 113(2), C(6)–S–C(23) 103(2), Se–C(6)–C(7) 123(3), C(6)–C(7)–C(17) 119(3), C(7)–C(8)–C(11) 125(3), C(7)–C(8)–O(6) 117(3), W–C–O(av.) 168(16), and Se–C(6)–C(7)–C(8) 81(4)



(F) (G)

Scheme 3.

Insertion reactions of alkynamines and dimethylcyanamide are strictly stereoselective and several postulates regarding their mechanism have been put forward.[21] Similar arguments may apply to the stereoselective formation of our neutral compounds, but there are some important differences: (*i*) Whereas Fischer and Dötz[21] used kinetic data to postulate the first step of the insertion of an alkynamine into a metal–carbene bond, *viz.* the attack of the alkynamine at the carbene carbon, we were able to isolate the adduct which forms and thus know that it is only when the electrophile is added that the original M–C bond breaks and a new bond forms between the metal and either a heteroatom or the carbon atom α to it. (*ii*) The previously proposed seven-co-ordinate intermediate or activated complex containing a four-membered ring[21,22] may reasonably be adapted for the mechanism of reactions leading to thio- and

Table 1. Infrared data *

	$A_1^{(1)}$	B_1	E	$A_1^{(2)}$
(*a*) Thio- and seleno-aldehyde complexes				
(**1a**)	2 060w	1 974vw	1 933s 1 943s (sh)	1 922s
(**1b**)	2 055w	1 978w	1 940s	1 928s
(**1c**)	2 060w		1 930s 1 940s (sh)	1 920s
(*b*) Thio- and seleno-carbene complexes				
(**3a**)	2 065w	1 982vw	1 932s 1 940s (sh)	1 960s
(**3b**)	2 060w	1 982vw	1 945s	1 967s
(**3c**)	2 060w	1 982vw	1 933s 1 942s (sh)	1 960s
(**3d**)	2 065w		1 932s	1 965s
(*c*) Co-ordinated indene derivatives				
(**4a**)	2 078w	1 978vw	1 937s	1 922s (sh)
(**4b**)	2 070w	1 978vw	1 928s	1 922s
(*d*) Thione, thio-, and seleno-ester complexes				
(**2**)	2 060w	1 977vw	1 938s	1 922s
(**5a**)	2 075w	1 985vw	1 945s	1 930s
(**5b**)	2 066w	1 982vw	1 943s	1 926s
(**5c**)	2 070w	1 975vw	1 945s	1 929s
(**5d**)	2 070w		1 945s	1 931s
(**5e**)	2 062w	1 980vw	1 950s	1 940s
(**5f**)	2 060w	1 978vw	1 940s	1 924s
(**5g**)	2 068w		1 943s	1 929s
(**5h**)	2 065w	1 979vw	1 940s	1 923s
(**5i**)	2 068w		1 942s	1 928s

* Measured in hexane, ν(CO) in cm^{-1}.

seleno-carbene complexes [(**F**), Scheme 3], but in the other type of reaction, in which the electrophile attaches to the carbon atom [Scheme 1, route (a)] and the heteroatom to the metal (to form thione and selenone complexes), the intermediate, or activated complex, would have to contain a five-membered chelate [(**G**), Scheme 3]). We found that CO pressure made no difference to the yields of compounds, which means that no substitution of a carbonyl ligand takes place and this lends support to the proposal of a seven co-ordinate intermediate or transition state. We do not have an explanation for the fact that the addition of CS_2 to the reaction mixture for the preparation of (**1a**) [equation (3)] more than doubles the yield of the thioaldehyde complex. (*iii*) The stereoselectivity of the reactions is presumably induced during the ring opening of the intermediate, but it is difficult to rationalize the factors affecting the preference for a particular isomer in any reaction. The alkynamines yield *E* vinylic carbenes, whereas our ethylthiocarbene complex has a *Z* configuration. It is interesting[16c] that the two phenyl groups are oriented *cis* in the products obtained from the electrophiles Et^+ and $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^+$, and *trans* in the thioaldehyde complex (**1a**) and the dimetallic compound $[W(CO)_5\{S{=}C(AuPPh_3)C(Ph){=}C(OEt)Ph\}]$ mentioned above.

Spectroscopic Investigations.—Infrared data for the new compounds are summarized in Table 1. All spectra reflected the typical, slightly distorted C_{4v} local symmetry of Group 6 pentacarbonyl complexes.[23] For the thio- and seleno-aldehyde compounds, no bands indicating η^2 isomers[9c] were observed.

The $A_1^{(2)}$ bands of the carbene complexes [corresponding mainly to the *trans* ν(CO) vibration] are at significantly higher wavenumbers than those of the complexes with S-donor ligands, and are further distinctive in that they appear at higher wavenumbers than the *E* bands. Although there is very little difference between the positions of the $A_1^{(2)}$ bands of the thio- and seleno-carbene complexes, the selenocarbene ligands seem to be somewhat better π acceptors, a fact which does not correspond to the tendency found in other Fischer-type carbene complexes.[24] We do not, however, have more substantial evidence for this conclusion.

The ν(CO) frequencies for the thio- and seleno-ester complexes are generally equal to or higher than those for the thio-and seleno-aldehyde compounds. As is usual for other S-donor ligands,[25] the $A_1^{(2)}$ band appears at the low-wavenumber side of the *E* band.

Proton and ^{13}C n.m.r. data are given in the Experimental section and Table 2 respectively. The ^1H n.m.r. spectra of the dithioester complexes (**5a**), (**5b**), and (**5e**) showed broadened and unresolved resonances at room temperature and the ^{13}C n.m.r. spectra consisted of two sets of resonances. The spectra of the thiocarbene complexes (**3a**) and (**3b**) exhibited the same tendency at −14 °C. In an earlier report on the conversion of thio- and seleno-carbene complexes into co-ordinated indene compounds[11] we erroneously interpreted the two sets of signals as an indication of the presence of *E* and *Z* isomers. A variable-temperature n.m.r. study now shows that restricted rotation, rather than *E* and *Z* isomers, caused the broadening and appearance of two sets of resonances. The energy barrier for rotation of a C=C bond is in the region of 260 kJ mol^{-1},[26] whereas the approximate coalescence temperatures for our thiocarbene and dithioester complexes at 5 and 35 °C respectively correspond to much lower rotation barriers. An accurate calculation of the free energy of activation for the dynamic processes operative in these compounds is not possible from our spectra, but we have estimated values of < 1 and *ca.* 66 kJ mol^{-1} from the spectra of (**3a**) and (**5b**) respectively for the energy barriers in the two types of compounds. These values suggested restricted rotation around single bonds and we ascribe the presence of two sets of signals to restricted rotation about the $C(SR^3)$–C(Ph) or $C(SR^4)$–C(Ph) bonds. We do not know what the conformations of the rotamers in solution are, but by analogy with the α,β-unsaturated carbonyl compounds studied by Marr and Stothers[27] we suggest structures in which the unsaturated bonds, S=C or M=C and C=C, can be either coplanar (fully conjugated) or twisted (non-conjugated). Examples of both conformations were encountered in the solid-state structures of compounds in this study (compare Figures 1—5).

Some characteristic ^{13}C n.m.r. shifts shown by the new compounds are: δ *ca.* 329 (and 319) p.p.m. for W=C and 325 p.p.m. for Cr=C; δ *ca.* 231—233 and 276 p.p.m. for W–S=C and Cr–S=C respectively in thioester complexes and 216 (and 213) and 242 p.p.m. in thioaldehyde complexes; δ *ca.* 238—242 p.p.m. for W–Se=C in selenoester complexes and 221 p.p.m. in selenoaldehyde compounds.

The ^1H n.m.r. chemical shifts for the aldehydic proton in the thio- and seleno-aldehyde complexes (**1a**), (**1b**), and (**1c**) are: δ 11.70 and 10.52 p.p.m. for W–S=CH, 11.33 and 10.13 p.p.m. for Cr–S=CH, and 12.56 p.p.m. for W–S=CH. Once again, no form of isomerism is apparent in the Se containing compound.

X-*Ray Crystallography.*—*X*-Ray crystal-structure determinations of (**1a**), (**2**), (**3a**), (**5b**), and (**5i**) served mainly to confirm structures and establish the configuration of the compounds at the C=C double bond. Some structural data are given in the captions to Figures 1—5. The W–S bond lengths in (**1a**) and (**2**) are the same [2.508(5) Å], but are shorter than the 2.536(3) Å distance in a thioaldehyde complex,[8c] the 2.531(2) Å distance in the dithioester complex (**5b**), or the bond lengths of known tungsten thione compounds [2.560(6)[28] and 2.56(3) Å[29]]. The C=S bond lengths of 1.63(2) in (**1**), 1.667(6) in (**2**), and

Table 2. ^{13}C N.m.r. data[a]

(*a*) Thio- and seleno-aldehyde complexes

	Temp. (°C)	X^1=C	CO *trans*	CO *cis*	C=*C*=O	*C*=C–O	Ph	OCH_2	OCH_2CH_3
(1a)	−16	216.5	202.3	197.2	174.4	137.3	128—134	69.3	15.2
		213.7							
(1b)	−40	241.8	223.7	216.6	173.1	136.6	127—132	9.0	15.2
(1c)	30	220.8	202.1	198.1	191.1	143.1	127—235	69.2	15.0

(*b*) Thiocarbene complexes

		M=C	CO *trans*	CO *cis*	Ph and C=C	OCH_2 or OCH_3	SCH_2 or SCH_3	OCH_2CH_3	SCH_2CH_3
(3a)	−14	328.9	209.2	197.7	127—142	68.1	41.1	15.7	11.9
		319.4							
(3b)	25	325.0	225.3	220.3	150.0	57.1	39.4		14.9
					138.0				
					128—129				
(3c)	−15	329.1	208.8	197.2	126—141	67.7	30.9	15.2	
		319.6				64.9	28.2	14.8	

(*c*) Thione, thio-, and seleno-ester complexes

		X^1=C[b]	CO *trans*	CO *cis*	C=*C*–*O*	*C*=C–O and Ph	OCH_2 or OCH_3	SCH_2 or SCH_3	OCH_2CH_3	SCH_2CH_3
(2)[c]	30	222.2	202.3	197.4	171.8	126—134	67.0		14.6	
(5a)	30	234.3	202.4	196.8	156.8	127—134	67.0	22.5	15.0	
		232.5			154.4			21.8	14.8	
(5b)	30	233.4	202.4	196.9	156.9	127—135	67.1	33.2	15.1	12.7
		231.5			154.6		67.0	33.0	14.8	12.0
(5c)	−20	231.4	201.9	196.8	173.0	156.0,	67.1		15.0	
						127—135				
(5d)	24		202.4	196.8	154.0	145.2,	67.2		14.7	
						125—134				
(5e)	20	276.2	218.2	213.8	132.7	126—130	58.1	31.8		11.8
(5f)	24	239.2	202.2	197.5	151.4	125—140	67.5	18.0	14.9	
(5g)	24	242br	202.1	197.5	151.9	125—140	67.6		14.7	
(5h)[d]	−50	238.8	202.7	197.4	154.4	127—134	67.7	15.3	15.0	
		236.1			152.6		66.1	14.6	14.4	
(5i)	24	238.0	202.5	197.6	154.6	125—148	67.8		14.6	

[a] Measured in $CDCl_3$; δ in p.p.m., relative to internal $SiMe_4$. [b] X^1 = S or Se. [c] S=C*C*H: δ 119.8 p.p.m. [d] Assignments tentative, decomposes during recording.

1.657(8) Å in **(5b)** are longer than a typical C=S double bond (*e.g. ca.* 1.55 Å in CS_2[30]), but are indistinguishable from the 1.642(4) Å separation in the chromium–thioaldehyde complex $[Cr(CO)_5\{S{=}CHCH{=}C(SEt)_2\}]$.[8a] In **(1a)**, in which the S=C and C=C bonds are in the same plane, the C(6)–C(7) and C(7)–C(8) bonds are conjugated and of about the same length, but in **(2)** and **(3a)**, where the torsional angles, S–C(6)–C(7)–C(8) and W–C(6)–C(7)–C(8) are 154(1) and 94(2)° respectively, conjugation is not possible and one is able to distinguish between single and double C–C bonds. The W=C bond length of 2.159(10) Å in **(3a)** is not unusual,[31] and the C(6)–S bond [1.679(10) Å] has much the same length as in the thiophenyl carbene complex of chromium [1.690(3) Å] reported by Hoare and Mills.[32] The quality of the data for **(5i)** is too low to warrant discussion about the bond lengths and the structure determination served only to establish the geometrical configuration about the C=C bond.

Experimental

All reactions were performed under N_2 using Schlenk techniques. Solvents were dried and distilled under N_2 before use. Starting materials were either prepared according to standard methods or purchased and used without further purification. Column chromatography was performed under N_2 at −10 °C and, unless otherwise stated, Merck silica gel (0.063–0.200 mm) was used as the stationary phase. Yields were calculated on the limiting reagent and refer to the isolated mass of the pure compound after chromatography, and are not optimized. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. Elemental analyses were carried out by Pascher, Bonn, and at the Council for Scientific and Industrial Research, Pretoria. Infrared spectra were obtained on a Perkin-Elmer 297 spectrophotometer, ^{1}H n.mr. spectra on a Varian VXR 200, and ^{13}C n.mr. on a Bruker 500 MHz or Varian VXR 200 spectrometer. Mass spectra were collected on a Finnigan Matt 8200 apparatus. N.m.r. chemical shifts are given in p.p.m. relative to internal $SiMe_4$.

Crystallizations were accomplished by dissolving the product substances in a minimum amount of the more polar of the two given solvents at room temperature and adding approximately the same volume of the less polar solvent before cooling to −25 °C.

The *X*-ray crystal-structure determinations were performed using standard procedures and experimental details are given in Table 3. Atomic co-ordinates are reported in Table 4.

Additional material available from the Cambridge Crystallo-

Table 3. Crystallographic and crystal-structure determination data *

Compound	**(1a)**	**(2)**	**(3a)**	**(5b)**	**(5i)**
Crystal data					
Formula	$C_{22}H_{16}O_6SW$	$C_{22}H_{16}O_6SW$	$C_{24}H_{20}O_6SW$	$C_{24}H_{20}O_6S_2W$	$C_{28}H_{20}O_6SSeW$
Crystal habit	Red-brown plates	Red-brown prisms	Red-brown prisms	Red prisms	Brown plates
Crystal size (mm)	0.25 × 0.15 × 0.08	0.25 × 0.13 × 0.10	0.20 × 0.12 × 0.10	0.25 × 0.13 × 0.10	0.22 × 0.15 × 0.10
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2/c$	$P2_1/c$
Unit cell determination:	25 reflections, θ(Mo) < 10°	25 reflections, θ(Mo) < 8°	25 reflections, θ(Mo) < 17°	25 reflections, θ(Mo) < 15°	25 reflections, θ(Mo) < 10°
Unit cell dimensions:					
a/Å	12.288(3)	8.736 4(17)	9.975 8(10)	12.745 7(11)	10.184(3)
b/Å	12.837(3)	10.874 3(25)	10.628 7(11)	10.081 9(12)	19.073(7)
c/Å	14.524(5)	12.039 8(12)	13.037 5(28)	19.805 2(52)	15.233(2)
α/°	89.29(2)	89.000(12)	90.714(10)	90	90
β/°	84.76(2)	85.571(11)	110.068(10)	98.940(14)	105.14(2)
γ/°	78.62(2)	77.916(18)	106.712(9)	90	90
Packing:					
U/Å^3	2 236	1 115	1 234	2 514	2 856
Z	4	2	2	4	4
D_c/g cm^{-3}	1.76	1.76	1.67	1.64	1.74
M	592.3	592.3	652.5	652.5	747.4
F(000)	1 144	572	604	1 272	1 440
Experimental data					
Collection mode:	ω—2θ, θ range: 3—27°	ω—2θ, θ range: 3—25°	ω—2θ, θ range: 3—23°	ω—2θ, θ range: 3—27°	ω—2θ, θ range: 3—23°
scan width	(0.72 + 0.34 tan θ)°	(0.59 + 0.34 tan θ)°	(0.63 + 0.34 tan θ)°	(0.62 + 0.34 tan θ)°	1.4°
scan speed	variable, 2.06° min^{-1} maximum	variable, 2.35° min^{-1} maximum	variable, 3.3° min^{-1} maximum	variable, 5.5° min^{-1} maximum	variable, 3.3° min^{-1} maximum
Reflections measured	7 776	3 904	3 410	5 775	4 368
Observable reflections	5 025 with $F > 1\sigma$	2 997 with $F > 1\sigma$	2 503 with $F > 3\sigma$	3 358 with $F > 3\sigma$	1 839 with $F > 4\sigma$
Stability	3 reflections every 120 min, no variation	3 reflections every 120 min, no variation	3 reflections every 83 min, no variation	3 reflections every 60 min, no variation	3 reflections every 60 min, no variation
μ/cm^{-1}	50.5	50.7	45.8	45.8	52.1
Solution and refinement					
Hydrogen atoms	Calculated positions, 'riding' on C	Calculated positions, 'riding' on C	Calculated positions	Calculated positions	Calculated positions, 'riding' on C
Refinement	Least-squares, blocked matrix, 1 molecule per block	Least-squares, full matrix	Least-squares, full matrix	Least-squares, full matrix	Least-squares, full matrix, W, Se, S anisotropic C, O isotropic
Number of variables	2 × 277	277	288	299	170
Reflections used	4 595 with $F > 2\sigma$	3 511 with $F > 0$	2 954 with $F > 1\sigma$	3 767 with $F > 2\sigma$	1 839 with $F > 4\sigma$
Final Δ peaks	1.8 e Å^{-3} near the W atom	0.9 e Å^{-3} near the W atom	0.6 e Å^{-3} near the methylene	0.9 e Å^{-3} near the W atom	2.0 e Å^{-3} near the W atom
Final R, R'	0.0762, 0.0504	0.0585, 0.0311	0.0532, 0.0360	0.0452, 0.0317	0.0814, 0.0566

* Data collected on an Enraf-Nonius CAD4 diffractometer using graphite monochromated (Mo-K_α) radiation (λ = 0.710 73 Å). Data corrected for Lorentz polarization and absorption. Absorption corrections empirical (A. C. T. North, D. C. Phillips, and F. S. Matthews, *Acta Crystallogr., Sect. A*, 1968, **24**, 357) for **(1a)**, **(2)**, **(3a)**, and **(5b)**, and numerical (P. Coppens, *Acta Crystallogr.*, 1965, **18**, 1025) for **(5i)**. Solution using SHELX 76 (G. M. Sheldrick, SHELX 76, Program for crystal structure determination and refinement, University of Cambridge, 1976) and scattering factors were taken from International Tables ('International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4) (Present distributor D. Reidel, Dordrecht). Weighting scheme: $\sigma(F)^{-2}$.

graphic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Preparation of Lithium Phenylethynethiolate, Li[SC≡CPh], *and Lithium Phenylethyneselenolate*, Li[SeC≡CPh].—A thf solution (20 cm^3) of PhCCH (1.1 cm^3, 10 mmol) was cooled to −30 °C and 1 equivalent of LiBu was added, after which the mixture was stirred for 30 min. To the yellow solution S_8 (0.32 g, 10 mmol S) was added and the resulting red solution was warmed slowly to room temperature. When all the S_8 had dissolved, the solution was stored at −20 °C.

To prepare the selenium analogue, Se_8 was used instead of sulphur. This reaction is much slower and stirring was continued overnight between −30 and 0 °C.

Preparation of the Adducts, Li[M(CO)$_5${C(OR^1)PhC(Ph)=C=X^1}], (**A**), (**C**), (**D**), *and* (**E**).—(**A**: M = W, R^1 = Et, X^1 = S). A solution of [W(CO)$_5${C(OEt)Ph}] (*e.g.* 0.92 g, 2.0 mmol) in thf (20 cm^3) was treated with 1 mol equivalent of Li[SC≡CPh] and stirred for 30 min at −30 °C.

(**C**: M = Cr, R^1 = Me, X^1 = S). As for (**A**), starting from [Cr(CO)$_5${C(OMe)Ph}].

(**D**: M = W, R^1 = Et, X^1 = Se). As for (**A**), by substituting the thiolate with the selenate, Li[SeC≡CPh]. The reaction was carried out at room temperature.

(**E**: M = Cr, R^1 = Et, X^1 = S). As for (**A**), starting from $[Cr(CO)_5\{C(OEt)Ph\}]$.

Isolation of $[NBu_4][W(CO)_5\{C(OEt)PhC(Ph)=C=S\}]$, (**B**).—Adduct (**A**) (10 mmol) was prepared and stirred for 30 min at room temperature. The solvent was removed under reduced pressure, the residue washed repeatedly with hexane (3 × 30 cm^3) and redissolved in CH_2Cl_2 (15 cm^3). A solution of 2 equivalents of $[NBu_4]Br$ in thf–CH_2Cl_2 (1:10) (20 cm^3) was added and the mixture covered with a layer of hexane. After 24 h at −40 °C, the precipitate (2.5 g, 30.0% yield) was washed with cold (−78 °C) diethyl ether and recrystallized from CH_2Cl_2–diethyl ether to give pale yellow needles, melting point 98—100 °C (darkens at *ca.* 70 °C).

Preparations of $[W(CO)_5\{S=CHC(Ph)=C(OEt)Ph\}]$, (**1a**), $[W(CO)_5\{S=C(Ph)CH=C(OEt)Ph\}]$, (**2**), *and* $[Cr(CO)_5\{S=CHC(Ph)=C(OEt)Ph\}]$, (**1b**).—Adduct (**A**) (2 mmol) was prepared and an excess (20 mmol) of CS_2 added. The mixture was allowed to warm to room temperature and stirred for a further 30 min. The solution was cooled to −78 °C and acidified with HCl in diethyl ether. After filtration through SiO_2, column chromatography (hexane–CH_2Cl_2, 4:1) yielded the thione complex (**2**) (yield 0.27 g, 22.8%) and the thioaldehyde complex (**1a**) (yield 0.56 g, 47.3%). Both products were further purified by crystallization from diethyl ether–pentane at −30 °C.

The thioaldehyde complex (**1a**), was obtained as the only product by omitting CS_2, but the yield was lower (20.2%).

The chromium thioaldehyde complex, (**1b**), was prepared similarly (without CS_2), starting from the chromium carbene complex $[Cr(CO)_5\{C(OEt)Ph\}]$ (2 mmol) (yield 0.13 g, 14.1%).

(**1a**). Purple crystals, m.p. 95—96 °C, *m/z* 592 (M^+) (Found: C, 44.4; H, 2.75; S, 5.40. Calc. for $C_{22}H_{16}O_6SW$: C, 44.6; H, 2.75;

Table 4. Fractional co-ordinates (× 10^4, 10^5 for W) for non-hydrogen atoms of the complexes

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
(*a*) Compound (**1a**)							
W(1)	19 846(7)	28 020(6)	2 561(6)	W(2)	73 249(6)	47 471(6)	30 060(6)
S(1)	2 952(4)	1 997(4)	8 763(3)	S(2)	1 758(4)	3 651(3)	6 941(3)
O(11)	12(11)	4 092(10)	9 160(9)	O(21)	4 162(11)	4 370(12)	5 209(10)
O(12)	3 961(11)	1 566(11)	11 319(9)	O(22)	4 692(11)	4 078(11)	8 107(10)
O(13)	631(14)	914(12)	10 499(13)	O(23)	3 860(13)	7 207(12)	6 974(12)
O(14)	3 218(17)	4 783(13)	10 152(14)	O(24)	1 387(13)	6 003(13)	8 868(12)
O(15)	731(11)	3 648(11)	12 149(9)	O(25)	768(13)	6 667(12)	5 885(12)
O(16)	6 862(9)	541(10)	7 397(8)	O(26)	−2 000(9)	2 817(9)	6 571(9)
C(11)	724(15)	3 628(12)	9 531(11)	C(21)	3 560(17)	4 762(19)	5 900(16)
C(12)	3 218(15)	2 010(13)	10 942(13)	C(22)	3 951(15)	4 441(13)	7 745(13)
C(13)	1 109(17)	1 554(15)	10 406(14)	C(23)	3 408(16)	6 488(20)	6 953(14)
C(14)	2 810(20)	4 052(22)	10 130(17)	C(24)	1 875(19)	5 693(21)	8 112(19)
C(15)	1 178(13)	3 326(13)	11 422(13)	C(25)	1 416(18)	6 171(17)	6 279(15)
C(16)	4 307(13)	1 743(12)	8 777(11)	C(26)	390(13)	3 979(13)	6 862(12)
C(17)	5 038(15)	1 218(12)	8 065(12)	C(27)	−295(13)	3 226(13)	6 750(11)
C(18)	6 208(15)	975(12)	8 123(12)	C(28)	−1 386(14)	3 575(14)	6 608(12)
C(19)	8 028(13)	95(14)	7 437(14)	C(29)	−3 043(15)	3 029(15)	6 120(14)
C(110)	8 326(16)	−838(15)	6 816(15)	C(210)	−2 998(19)	2 190(17)	5 417(15)
C(111)	6 701(13)	1 231(13)	9 004(12)	C(211)	−1 945(13)	4 723(13)	6 555(13)
C(112)	6 452(14)	783(14)	9 845(13)	C(212)	−1 636(15)	5 407(16)	5 915(13)
C(113)	6 935(17)	993(16)	10 626(12)	C(213)	−2 154(17)	6 467(15)	5 909(14)
C(114)	7 605(19)	1 737(18)	10 534(15)	C(214)	−3 055(17)	6 754(16)	6 528(17)
C(115)	7 851(19)	2 165(17)	9 735(17)	C(215)	−3 388(16)	6 107(18)	7 186(16)
C(116)	7 418(16)	1 973(15)	8 918(14)	C(216)	−2 857(15)	5 073(15)	7 223(14)
C(117)	4 610(13)	933(14)	7 172(11)	C(217)	192(12)	2 044(13)	6 786(13)
C(118)	4 274(16)	1 704(15)	6 546(13)	C(218)	408(13)	1 450(16)	5 961(14)
C(119)	3 848(16)	1 449(16)	5 750(13)	C(219)	869(17)	384(15)	6 038(18)
C(120)	3 790(16)	417(17)	5 603(14)	C(220)	1 100(17)	−74(16)	6 883(22)
C(121)	4 102(17)	−369(16)	6 223(13)	C(221)	886(18)	511(18)	7 646(17)
C(122)	4 527(15)	−120(14)	7 009(12)	C(222)	415(14)	1 588(15)	7 618(13)
(*b*) Compound (**2**)							
W	21 477(4)	17 468(4)	11 649(3)	C(8)	−2 946(8)	3 471(6)	3 310(5)
S	1 631(2)	2 004(2)	3 235(2)	C(9)	−3 418(9)	4 957(7)	1 813(6)
O(1)	3 130(8)	1 259(7)	−1 367(5)	C(10)	−4 854(9)	5 850(8)	1 425(7)
O(2)	5 659(7)	1 859(7)	1 543(6)	C(11)	−332(7)	2 777(7)	5 004(5)
O(3)	3 102(9)	−1 220(6)	1 523(7)	C(12)	296(8)	1 759(7)	5 672(6)
O(4)	−1 194(8)	1 451(9)	577(7)	C(13)	167(10)	1 867(9)	6 811(7)
O(5)	1 401(8)	4 670(6)	668(5)	C(14)	−587(10)	3 002(10)	7 300(7)
O(6)	−3 967(5)	4 214(4)	2 695(4)	C(15)	−1 180(9)	3 981(8)	6 639(7)
C(1)	2 785(10)	1 437(9)	−444(7)	C(16)	−1 102(8)	3 895(7)	5 510(6)
C(2)	4 400(10)	1 830(8)	1 416(7)	C(17)	−3 759(7)	2 853(7)	4 206(5)
C(3)	2 742(10)	−164(10)	1 430(7)	C(18)	−3 176(8)	1 660(7)	4 547(6)
C(4)	−31(11)	1 585(10)	829(8)	C(19)	−3 938(10)	1 105(8)	5 399(7)
C(5)	1 635(10)	3 610(10)	872(7)	C(20)	−5 342(10)	1 758(8)	5 892(6)
C(6)	−157(7)	2 689(6)	3 766(5)	C(21)	−5 993(9)	2 940(8)	5 521(6)
C(7)	−1 356(8)	3 293(6)	3 077(5)	C(22)	−5 214(8)	3 494(7)	4 694(5)

Table 4 (*continued*)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
(*c*) Compound (**3a**)							
W	−22 524(6)	70 319(6)	67 828(4)	C(9)	2 850(15)	10 055(11)	9 576(12)
S	806(4)	8 729(3)	6 301(3)	C(10)	2 244(17)	10 981(13)	9 956(13)
O(1)	−1 366(11)	6 334(9)	9 246(7)	C(11)	1 020(12)	5 636(11)	7 561(9)
O(2)	−3 317(13)	7 719(11)	4 335(8)	C(12)	735(12)	4 678(10)	8 245(9)
O(3)	−1 703(14)	10 046(10)	7 511(9)	C(13)	564(13)	3 396(11)	7 929(10)
O(4)	−2 825(12)	4 057(9)	5 862(8)	C(14)	689(14)	3 060(11)	6 971(11)
O(5)	−5 508(12)	6 326(13)	6 831(10)	C(15)	968(13)	3 996(13)	6 283(10)
O(6)	1 604(9)	8 893(8)	9 039(6)	C(16)	1 113(12)	5 283(12)	6 566(10)
C(1)	−1 664(14)	6 583(12)	8 357(11)	C(17)	2 865(15)	7 364(13)	9 856(11)
C(2)	−2 890(16)	7 475(14)	5 211(11)	C(18)	2 815(16)	7 488(12)	10 877(11)
C(3)	−1 895(16)	8 948(14)	7 271(11)	C(19)	3 801(21)	7 131(17)	11 770(13)
C(4)	−2 621(16)	5 128(13)	6 214(11)	C(20)	4 900(23)	6 609(18)	11 721(14)
C(5)	−4 344(17)	6 574(16)	6 750(12)	C(21)	4 998(18)	6 440(15)	10 791(15)
C(6)	102(12)	7 596(10)	7 020(8)	C(22)	4 002(13)	6 834(10)	10 006(9)
C(7)	1 146(12)	7 042(11)	7 860(9)	C(23)	2 838(14)	9 132(13)	6 724(11)
C(8)	1 912(13)	7 750(12)	8 852(10)	C(24)	3 284(19)	9 036(14)	5 766(13)
(*d*) Compound (**5b**)							
W	12 391(3)	17 427(4)	13 467(2)	C(9)	5 697(7)	2 815(9)	848(5)
S(1)	959(2)	3 192(3)	290(1)	C(10)	6 252(7)	2 898(10)	1 557(5)
S(2)	1 971(2)	4 689(3)	−715(1)	C(11)	3 936(6)	2 597(9)	−215(5)
O(1)	3 748(5)	1 390(9)	11 640(4)	C(12)	3 289(7)	1 488(9)	−300(5)
O(2)	−1 277(5)	1 814(9)	1 214(4)	C(13)	3 334(8)	607(9)	−839(5)
O(3)	1 098(6)	−673(8)	318(4)	C(14)	4 024(9)	844(11)	−1 307(6)
O(4)	1 324(6)	4 112(8)	2 410(4)	C(15)	4 655(8)	1 952(12)	−1 218(5)
O(5)	1 307(7)	−252(8)	2 553(4)	C(16)	4 630(7)	2 855(9)	−685(5)
O(6)	4 867(4)	3 803(6)	769(3)	C(17)	3 001(7)	5 048(9)	1 096(5)
C(1)	2 861(8)	1 589(10)	1 505(5)	C(18)	2 333(7)	6 161(9)	1 002(5)
C(2)	−374(7)	1 811(13)	1 244(4)	C(19)	2 298(7)	7 063(11)	1 526(5)
C(3)	1 151(8)	172(12)	699(5)	C(20)	2 902(7)	6 895(13)	2 155(5)
C(4)	1 320(7)	3 284(13)	2 005(5)	C(21)	3 575(7)	5 806(10)	2 244(5)
C(5)	1 268(8)	509(11)	2 113(5)	C(22)	3 623(7)	4 883(9)	1 734(5)
C(6)	2 003(6)	3 936(8)	55(4)	C(23)	726(7)	4 194(11)	−1 218(5)
C(7)	3 035(6)	4 132(8)	516(4)	C(24)	727(8)	2 849(11)	−1 517(5)
C(8)	3 919(7)	3 506(9)	368(5)				
(*e*) Compound (**5i**)							
W	25 234(17)	10 501(7)	10 604(10)	C(11)	187(4)	−237(2)	261(2)
Se	1 291(4)	−99(2)	1 348(2)	C(12)	72(3)	−271(2)	211(2)
S	2 702(11)	131(4)	3 328(6)	C(13)	44(4)	−343(2)	220(2)
O(1)	380(2)	234(1)	40(1)	C(14)	133(4)	−379(2)	280(2)
O(2)	−39(3)	168(1)	10(2)	C(15)	250(4)	−353(2)	340(2)
O(3)	270(2)	196(1)	273(2)	C(16)	273(4)	−280(2)	319(2)
O(4)	295(2)	26(1)	−63(2)	C(17)	30(3)	−123(1)	310(2)
O(5)	529(3)	32(1)	205(2)	C(18)	−92(3)	−88(1)	275(2)
O(6)	327(2)	−148(1)	229(1)	C(19)	−199(4)	−93(2)	315(2)
C(1)	327(3)	182(2)	67(2)	C(20)	−205(4)	−135(2)	388(3)
C(2)	56(4)	149(2)	44(3)	C(21)	−78(4)	−165(2)	423(2)
C(3)	208(5)	159(2)	199(3)	C(22)	32(3)	−161(1)	388(2)
C(4)	291(4)	55(2)	7(2)	C(23)	315(3)	−40(1)	436(2)
C(5)	438(4)	56(2)	166(3)	C(24)	246(4)	−27(2)	501(2)
C(6)	178(4)	−47(2)	249(2)	C(25)	272(4)	−67(1)	580(2)
C(7)	141(2)	−115(1)	269(2)	C(26)	377(3)	−115(2)	588(2)
C(8)	214(3)	−165(1)	251(2)	C(27)	447(3)	−127(2)	528(2)
C(9)	365(4)	−192(2)	163(2)	C(28)	424(3)	−86(1)	448(2)
C(10)	446(4)	−163(2)	123(3)				

S, 5.40%). ^{1}H N.m.r.: δ($CDCl_3$) 11.70 and 10.52 (1 H, 2 br s, S=CH), 6.8—7.7 (10 H, m, 2 Ph), 3.86 (2 H, q, OCH_2), and 1.15 (3 H, br t, OCH_2CH_3).

(**1b**). Purple crystals, m.p. 79—81 °C, *m*/*z* 460 (M^+) (Found: C, 57.2; H, 3.45; O, 20.9; S, 6.95. Calc. for $C_{22}H_{16}CrO_6S$: C, 57.4; H, 3.50; O, 20.8; S, 6.95%). ^{1}H N.m.r.: δ($CDCl_3$) 10.13 and 11.33 (1 H, 2 s, S=CH), 7.0—7.6 (10 H, m, 2 Ph), 3.83 (2 H, q, OCH_2), and 1.08 (3 H, t, OCH_2CH_3).

(**2**). Purple, m.p. 104—105 °C, *m*/*z* 592 (M^+) (Found: C, 44.8; H, 2.85; O, 16.7; S, 5.40. Calc. for $C_{22}H_{16}O_6SW$: C, 44.6; H, 2.75; O, 16.2; S, 5.40%). ^{1}H N.m.r.: δ($CDCl_3$) 6.82 (1 H, s, CH), 6.8—7.6 (10 H, m, 2 Ph), 4.45 (2 H, q, OCH_2), and 1.61 (3 H, t, OCH_2CH_3).

Preparation of $[W(CO)_5\{Se{=}CHC(Ph){=}C(OEt)Ph\}]$, (**1c**).—A solution of adduct (**D**) (5 mmol) was prepared, acidified with HCl (2 mol dm^{-3} in diethyl ether, 5 mmol), and filtered through SiO_2. Chromatography on Fluorosil (CH_2Cl_2–hexane, 1:4) yielded an unidentified green product (0.15 g) and the selenoaldehyde complex, (**1c**) (yield 0.75 g, 23.5%): purple crystals, m.p. 86—87 °C, *m/z* 556 ($M - 3CO$)$^+$ (Found: C, 40.9; H, 2.50; Se, 12.0. Calc. for $C_{22}H_{16}O_6SeW$: C, 41.35; H, 2.50; Se, 12.2%). ^1H N.m.r.: $\delta(CDCl_3)$ 12.56 (1 H, br s, Se=CH), 7.1—7.8 (10 H, m, 2 Ph), 3.77 (2 H, q, OCH_2), and 1.21 (3 H, t, OCH_2CH_3).

Preparation of $[W(CO)_5\{C(SEt)C(Ph)=C(OEt)Ph\}]$, (**3a**).—Adduct (**A**) (2.5 mmol) was prepared in thf (10 cm^3) and $[Et_3O][BF_4]$(0.48 g, 2.5 mmol) was added. The mixture was warmed to room temperature and stirred for a further 30 min before being filtered through SiO_2. The solvent was removed and the residue chromatographed (hexane–CH_2Cl_2, 6:1) to produce, first, the thiocarbene complex (**3a**) (yield 0.59 g, 38.1%) and then the thioester complex (**5b**) (yield 0.22 g, 13.5%).

(**3a**). Brown crystals, m.p. 84—86 °C, *m/z* 620 (M^+) (Found: C, 46.3; H, 3.25; O, 15.8; S, 5.05. Calc. for $C_{24}H_{20}O_6SW$: C, 46.5; H, 3.25; O, 15.5; S, 5.15%). ^1H N.m.r.: $\delta(CDCl_3)$ 7.0—7.7 m (10 H, m, 2 Ph), 3.75 (2 H, q, OCH_2), 3.13 (2 H, q, SCH_2), 1.45 (3 H, t, OCH_2CH_3), and 1.25 (3 H, t, SCH_2CH_3).

Preparation of $[Cr(CO)_5\{C(SEt)C(Ph)=C(OMe)Ph\}]$, (**3b**).— Prepared similarly to (**3a**) starting from adduct (**C**) (1.9 mmol) (yield 0.18 g, 20.0%): reddish brown crystals, m.p. 120 °C (decomp.), *m/z* 474 (M^+) (Found: C, 58.0; H, 3.80. Calc. for $C_{23}H_{18}CrO_6S$: C, 58.2; H, 3.80%). ^1H N.m.r.: $\delta(CDCl_3)$ 6.8—7.5 (10 H, m, 2 Ph), 3.42 (3 H, s, OCH_3), 3.39 (2 H, q, SCH_2), and 1.72 (3 H, t, SCH_2CH_3).

Preparation of $[W(CO)_5\{C(SMe)C(Ph)=C(OEt)Ph\}]$, (**3c**).—A thf (15 cm^3) solution of adduct (**A**) (3.8 mmol) was prepared. The solution was warmed to room temperature and an excess of MeI (2.0 cm^3) added. After 4 h the mixture was filtered through SiO_2, the solvent removed, and the residue chromatographed (hexane–CH_2Cl_2, 2:1). The pure thiocarbene complex (**3c**) was obtained (yield 0.7 g, 30.2%) and was recrystallized from diethyl ether–hexane: brown crystals, m.p. 94—96 °C, *m/z* 606 (M^+) (Found: C, 45.5; H, 2.95; O, 16.3; S, 5.30. Calc. for $C_{23}H_{18}O_6SW$: C, 45.5; H, 3.00; O, 15.8; S, 5.30). ^1H N.m.r.: δ(60 MHz, $CDCl_3$) 6.6—7.4 (10 H, m, 2 Ph), 3.58 (2 H, q, OCH_2), 2.68 (3 H, s, SCH_3), and 1.21 (3 H, t, OCH_2CH_3).

Preparation of $[W(CO)_5\{C(SeEt)C(Ph)=C(OEt)Ph\}]$, (**3d**).—A solution of adduct (**D**) (4.7 mmol) was prepared, cooled to −30 °C, and stirred for 90 min, before $[Et_3O][BF_4]$ (0.98 g, 1.1 mol equivalents) was added. After 1 h the solvent was removed and the residue chromatographed on Fluorosil (hexane–CH_2Cl_2, 3:1). The reddish brown band was collected at −60 °C and all further manipulations were carried out at this temperature. The selenocarbene complex (**3d**) (yield 0.58 g, 18.4%) was recrystallized from diethyl ether–hexane: reddish brown crystals, m.p. 85—87 °C, *m/z* 668 (M^+) (Found: C, 43.1; H, 3.05; O, 15.0; Se, 11.7. Calc. for $C_{24}H_{20}O_6SeW$: C, 43.2; H, 3.00; O, 14.4; Se, 11.8%).

Formation of Co-ordinated Indene Derivatives, $[M(CO)_5\{X^1(Et)CH(C_6H_4\text{-}o)C(OR^1)=CPh\}]$, (**4a**), (**4b**), *and* (**4c**).—(**4a**: M = W, X^1 = S, R^1 = Et). A solution of complex (**3a**) (0.32 g) in CH_2Cl_2 (15 cm^3) was stirred at room temperature and the conversion into (**4a**) monitored by thin-layer chromatography (t.l.c.) and ^1H n.m.r. spectroscopy. After 1 month the mixture was stripped of solvent, hexane was added, and the solution left at −40 °C to crystallize (yield 0.29 g, 90%).

(**4b**: M = Cr, X^1 = S, R^1 = Me). Prepared similarly to (**4a**), starting from (**3b**). Total conversion in 5 d.

(**4c**: M = W, X^1 = Se, R^1 = Et). Prepared similarly to (**4a**), starting from (**3d**). Total conversion in 3 h.

(**4a**). Yellow crystals, m.p. 114—115 °C, *m/z* 620 (M^+). ^1H N.m.r.: $\delta(CDCl_3)$ *ca.* 7.4 (9 H, m, aromatic), 5.08 (1 H, s, CH), 4.2—4.10 and 4.1—3.9 (2 H, 2 m, OCH_2), 2.75 (2 H, q, SCH_2), and 1.30 (6 H, m, OCH_2CH_3 and SCH_2CH_3).

(**4b**). Yellow crystals, m.p. 90 °C (decomp.), *m/z* 474 (M^+) (Found: C, 58.0; H, 3.80. Calc. for $C_{23}H_{18}CrO_6S$: C, 58.2; H, 3.80%). ^1H N.m.r.: $\delta(CDCl_3)$ 7.6—7.8 (5 H, m, Ph), 7.2—7.5 (4 H, m, C_6H_4), 4.71 (1 H, s, CH), 3.86 (3 H, s, OCH_3), 3.47 (2 H, q, SCH_2), and 1.20 (3 H, t, SCH_2CH_3).

(**4c**). Yellow crystals. ^1H N.m.r.: $\delta(CDCl_3)$ 7.2—7.4 (9 H, m, aromatic), 5.27 (1 H, s, CH), 4.03 and 4.10 (2 H, 2q, OCH_2), 2.73 (2 H, q, $SeCH_2$), and 1.37 (6 H, t, $SeCH_2CH_3$ and OCH_2CH_3).

Preparation of $[W(CO)_5\{S=C(SMe)C(Ph)=C(OEt)Ph\}]$, (**5a**).—Adduct (**A**) (1.2 mmol) was prepared in thf and stirred for 40 min, before MeSSMe (3.0 cm^3, 3.6 mmol) was added. The mixture was heated at 50 °C for 10 min, the solvent removed, and the residue chromatographed (hexane–CH_2Cl_2, 3:1) to yield the pure dithioester compound (**5a**) (yield 0.15 g, 19.5%). The complex was recrystallized from diethyl ether–pentane: orange crystals, m.p. 91—93 °C, *m/z* 638 (M^+) (Found: C, 43.6; H, 3.00; S, 10.0. Calc. for $C_{23}H_{18}O_6S_2W$: C, 43.3; H, 2.85; S, 10.0%). ^1H N.m.r.: $\delta(CDCl_3$, −20 °C) 6.9—7.5 (10 H, m, 2 Ph), 3.62 and 3.82 (2 H, 2q, OCH_2), 2.50 and 2.59 (3 H, 2 s, SCH_3), 1.20 and 1.30 (3 H, 2t, OCH_2CH_3).

Preparation of $[W(CO)_5\{S=C(SEt)C(Ph)=C(OEt)Ph\}]$, (**5b**).—To a thf solution of adduct (**A**) (1.6 mmol), an excess of EtSSEt (4.8 cm^3, 15.7 mmol) was added. The mixture was heated and stirred at 30 °C for 20 min. The solvent was removed and the residue chromatographed to separate the thioester complex from a purple by-product, (yield 0.2 g, 20%): orange crystals, m.p. 103—105 °C, *m/z* 652 (M^+) (Found: C, 44.6; H, 3.25; O, 14.3; S, 9.50. Calc. for $C_{24}H_{20}O_6S_2W$: C, 44.2; H, 3.10; O, 14.7; S, 9.85%). ^1H N.m.r.: $\delta(CDCl_3$, 40 °C) 7.2—7.6 (10 H, m, 2 Ph), 3.61 (2 H, q, OCH_2), 3.27 (2 H, q, SCH_2), 1.42 (3 H, br t, OCH_2CH_3), and 1.21 (3 H, t, SCH_2CH_3).

Preparation of $[W(CO)_5\{S=C(SPh)C(Ph)=C(OEt)Ph\}]$, (**5c**).—Prepared similarly to (**5a**) from adduct (**A**) (2.2 mmol) and using PhSSPh (0.53 g, 1.1 mol equivalents) instead of MeSSMe, yield 0.74 g (48.1%): purple crystals, m.p. 125—127 °C, *m/z* 700 (M^+) (Found: C, 48.5; H, 3.05; S, 9.05. Calc. for $C_{28}H_{20}O_6S_2W$: C, 48.0; H, 2.90; S, 9.15%). ^1H N.m.r.: $\delta(CDCl_3)$ 6.7—7.7 (15 H, m, 3 Ph), 3.68 (2 H, q, OCH_2), and 1.28 (3 H, t, OCH_2CH_3).

Preparation of $[W(CO)_5\{S=C(SePh)C(Ph)=C(OEt)Ph\}]$, (**5d**).—Prepared similarly to (**5a**) from adduct (**A**) (2.6 mmol) using PhSeSePh (0.97 g, 1.2 mol equivalents) instead of MeSSMe and stirring for 30 min at room temperature and 30 min at 60 °C (yield 0.2 g, 10.3%): red-brown oil, *m/z* 692 ($M - 2CO$)$^+$ (Found: C, 45.4; H, 3.00; S, 4.45; Se, 10.2. Calc. for $C_{28}H_{20}O_6SSeW$: C, 45.0; H, 2.70; S, 4.30; Se, 10.6%). ^1H N.m.r.: δ(60 MHz, $CDCl_3$) 6.6—7.4 (15 H, m, 3 Ph), 3.52 (2 H, q, OCH_2), and 1.20 (3 H, t, OCH_2CH_3).

Preparation of $[Cr(CO)_5\{S=C(SEt)C(Ph)=C(OMe)Ph\}]$, (**5e**).—Prepared similarly to (**5b**) from adduct (**C**) (1.57 mmol (yield 0.10 g, 7.0%): red crystals, m.p. 112—115 °C, *m/z* 506 (M^+) (Found: C, 54.6; H, 3.70. Calc. for $C_{23}H_{18}CrO_6S_2$: C, 54.5; H, 3.60%). ^1H N.m.r.: $\delta(CDCl_3$, −20 °C) 7.0—7.5 (10 H, m, 2 Ph), 3.61 and 3.43 (3 H, br s, OCH_3), 3.12 and 3.24 (2 H, 2q, SCH_2), 1.34 and 1.10 (3 H, 2t, SCH_2CH_3).

Preparation of $[W(CO)_5\{Se=C(SeMe)C(Ph)=C(OEt)Ph\}]$, (**5f**).—Adduct (**D**) (4.0 mmol) was prepared and elemental Se (0.32 g, 4.1 mmol) added. After 24 h an excess of MeI (2 cm^3) was added. Thin-layer chromatography indicated the presence of two purple products. After 1 h very little of the less polar product remained and the mixture was filtered through SiO_2. The solvent was removed and the residue chromatographed (hexane–CH_2Cl_2, 3:1- to isolate the more polar, purple compound (**5f**- (yield 0.51 g, 17.4%-. The diselenoester complex was recrystallized from diethyl ether–pentane: purple crystals, m.p. 88—90 °C, *m/z* 594 (*M* – 5CO-$^+$ (Found: C, 37.6; H, 2.15; Se, 21.9. Calc. for $C_{23}H_{18}O_6Se_2W$: C, 37.7; H, 2.50; Se, 21.6%-. ^{1}H N.m.r.: δ($CDCl_3$- 7.0—7.6 (10 H, m, 2 Ph-, 3.71 (2 H, q, OCH_2-, 2.40 (3 H, s, $SeCH_3$-, and 1.26 (3 H, t, OCH_2CH_3-.

Preparation of [W(CO-$_5${Se=C(SePh-C(Ph-=C(OEt-Ph}], (**5g**-.—Adduct (**D**- (3.9 mmol- was prepared. After 10 min PhSeSePh (1.3 g, 4.1 mmol- was added and t.l.c. indicated the presence of the selenoaldehyde complex (**4**- as a major by-product. A further 0.27 g (0.86 mmol- PhSeSePh was added, the reaction mixture was stirred at 65 °C for 1 h, and then overnight at room temperature. Addition of a further 0.32 g (1 mmol- of PhSeSePh failed to increase the yield of (**5g**- significantly. The mixture was filtered through SiO_2, chromatographed on SiO_2 (hexane–CH_2Cl_2, 6:1-, and the reddish purple fraction collected at –60 °C. From this the pure diselenoester complex (**5g**- was obtained (yield 0.65 g, 21.0%-. The compound was recrystallized from diethyl ether–hexane: reddish purple crystals, m.p. 114—118 °C, *m/z* 794 (M^+- (Found: C, 42.5; H, 2.60; O, 12.2; Se, 20.1. Calc. for $C_{28}H_{20}O_6Se_2W$: C, 42.3; H, 2.55; O, 12.1; Se, 19.9%-. ^{1}H N.m.r.: δ(60 MHz, $CDCl_3$- 6.3—7.4 (15 H, m, 3 Ph-, 3.57 (2 H, q, OCH_2-, and 1.19 (3 H, t, OCH_2CH_3-.

Preparation of [W(CO-$_5${Se=C(SMe-C(Ph-=C(OEt-Ph}], (**5h**-.—Adduct (**D**- (4.2 mmol- was prepared and after 30 min an excess of MeSSMe (5.0 cm^3- was added. After 45 min the mixture was filtered through SiO_2, the solvent removed, and the residue chromatographed (hexane–CH_2Cl_2, 4:1-. The pure selenothio(*S*- ester complex (**5h**- was obtained (yield 0.91 g, 31.6%- and recrystallized from diethyl ether–hexane: purple crystals, m.p. 90—93 °C, *m/z* 630 (*M* – 2CO-$^+$ (Found: C, 41.0; H, 2.80; O, 14.3; S, 4.90; Se, 11.7. Calc. for $C_{23}H_{18}O_6SSeW$: C, 40.3; H, 2.65; O, 14.0; S, 4.70; Se, 11.5%-. ^{1}H N.m.r.: δ(60 MHz, $CDCl_3$- 7.2—7.7 (10 H, m, 2 Ph-, 3.72 (2 H, q, OCH_2-, 2.43 (3 H, s, SCH_3-, and 1.29 (3 H, t, OCH_2CH_3-.

Preparation of [W(CO-$_5${Se=C(SPh-C(Ph-=C(OEt-Ph}], (**5i**-.—Adduct (**D**- (5.1 mmol- was prepared and PhSSPh (1.1 g, 5.1 mmol-, dissolved in thf (1 cm^3-, added after 15 min. After a further 15 min the mixture was filtered through Fluorosil and chromatographed on SiO_2 (hexane–CH_2Cl_2, 3:1- to yield the pure selenothio(*S*- ester complex, (**5i**- (yield 1.6 g, 43.0%-. The compound was recrystallized from diethyl ether–hexane: reddish purple crystals, m.p. 96—98 °C, *m/z* 747 (M^+- (Found: C, 45.1; H, 2.75; S, 4.40; Se, 10.8. Calc. for $C_{28}H_{20}O_6SSeW$: C, 45.0; H, 2.70; S, 4.30; Se, 10.6%-. ^{1}H N.m.r.: δ(60 MHz, $CDCl_3$- 6.3—7.4 (15 H, m, 3 Ph-, 3.55 (2 H, q, OCH_2-, and 1.22 (3 H, t, OCH_2CH_3-.

Reaction of Adduct (**A**- *with* $SiMe_3Cl$.—A solution of $SiMe_3Cl$ (5 cm^3- in diethyl ether (10 cm^3- was filtered through a short column of basic alumina and then stirred over K_2CO_3 for 3 h to remove any traces of acid. Adduct (**A**- (3.1 mmol- was prepared, the solvent removed, and the residue redissolved in dry acetone (10 cm^3-. The solution was cooled to –110 °C, and the $SiMe_3Cl$ solution added, whereupon the reaction mixture immediately turned dark blue. The pure thioaldehyde complex (**1a**-, the only product, was purified by chromatography and a yield of 0.37 g (20.0%- was obtained.

Diels–Alder Reaction of the Thio- and Seleno-aldehyde Complexes, (**1a**- *and* (**1c**-, *with Cyclopentadiene.*—Both reactions were carried out in the same way and in a typical experiment complex (**1a**- (0.09 g, 0.15 mmol- was dissolved in freshly distilled cyclopentadiene and the mixture warmed to room temperature. The dark blue colour of the aldehyde complex started to disappear almost immediately and had completely disappeared after 10 min. Thin-layer chromatography at this stage showed the presence of a pale yellow (main- product which could be purified by column chromatography (hexane–CH_2Cl_2, 2:1-.

In both experiments a yellow oil was obtained of which a mass spectrum was recorded. The yield from the thioaldehyde complex was *ca.* 45% and from the selenoaldehyde complex *ca.* 80%. At room temperature both products decomposed rapidly to their respective starting materials.

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