The Reaction of Molybdenum and Tungsten Carbyne Complexes with Sulphur and Selenium; Crystal Structures of $[Mo\{\eta^2\text{-}(S_2CCH_2Bu^t)\}(CO)_2(\eta\text{-}C_5H_5)]$ and $[W\{\eta^2\text{-}(S_2CC_6H_4Me\text{-}4)\}(CO)_2(\eta\text{-}C_5H_5)]$ †

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Reaction of $[M(\equiv CR)L_2(\eta\text{-}C_5H_5)]$[M = Mo, R = CH_2Bu^t, L = $P(OMe)_3$ or CO; M = W, R = $C_6H_4Me\text{-}4$, L = CO] with sulphur affords the complexes $[M\{\eta^2\text{-}(S_2CR)\}L_2(\eta\text{-}C_5H_5)]$. Similar reactions between $[Mo(\equiv CCH_2Bu^t)(CO)_2(\eta\text{-}C_5H_5)]$ or $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ and selenium give the related complexes $[M\{\eta^2\text{-}(Se_2CR)\}(CO)_2(\eta\text{-}C_5H_5)]$ (M = Mo, R = CH_2Bu^t; M = W, R = $C_6H_4Me\text{-}4$). *X*-Ray diffraction studies on the isostructural products obtained from sulphur and the molybdenum or tungsten carbonyl carbyne complexes show that a $M(CO)_2(\eta\text{-}C_5H_5)$ (M = Mo or W) moiety is bonded to a thioacetate ligand forming a planar MS_2C ring of dimensions M–S 2.47, C–S 1.68 Å, S–M–S 68, and S–C–S 110 °. The metal atom can be regarded as seven-co-ordinate with the cyclopentadienyl group occupying three co-ordination sites. Both structures are monoclinic, space group $P2_1/c$; the molybdenum compound has been refined to *R* 0.033 for 2 165 reflections and the tungsten compound to *R* 0.042 for 2 382 reflections. The mechanism of formation of these complexes is discussed in terms of initial electrophilic attack on the carbyne carbon.

The metal to carbon triple bond which is present in carbyne or alkylidyne metal complexes is a potential site for attack by electrophilic reagents. In principle, such reactions can be either frontier orbital- or charge-controlled. Extended-Hückel molecular-orbital (m.o.) calculations on the carbyne complex $[Mo(\equiv CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ [1,2] and Fenske–Hall calculations [3] on the isoelectronic cationic carbyne $[Mn(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]^+$ (R = Me, Ph, or $SiMe_3$) suggest that the highest occupied molecular orbital (h.o.m.o.) is located on the metal with a build up of charge on the carbyne carbon. Thus protonation of the carbyne-molybdenum compound apparently occurs [2] at the carbon atom, as does protonation of the osmium compound $[Os(\equiv CPh)Cl(CO)(PPh_3)_2]$.[4] It was observed by Roper and co-workers [4] that S, Se, and Te react with the carbyne-osmium complex to give η^2-thio-, seleno-, and telluro-acyl complexes $[Os(\eta^2\text{-}CAR)Cl(CO)(PPh_3)_2]$ (A = S, Se, or Te), and consequently it was thought useful to examine the reactivity of the Group 6 metal carbyne complexes $[M(\equiv CR)L_2(\eta\text{-}C_5H_5)]$ [R = alkyl or aryl; L = CO or $P(OMe)_3$] towards the chalcogens.

Results and Discussion

Reaction of elemental sulphur (S_8) with $[Mo(\equiv CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ in tetrahydrofuran (thf) led to a smooth reaction (15 min), and the formation (57% yield) of a purple crystalline complex (1), which on the basis of elemental analysis, mass spectroscopy, and n.m.r. spectroscopy can be formulated as a 2 : 1 adduct of sulphur and the carbyne. Examination of the ^1H n.m.r. spectrum showed that the neopentyl group was still intact; also the $^{31}P\text{-}\{^1H\}$ spectrum contained only a single resonance with a chemical shift characteristic of a co-ordinated trimethyl phosphite, implying a possible molecular plane of symmetry. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum showed a resonance at δ 214.6 p.p.m., which was not coupled to a ^{31}P nucleus, and which was at higher field than the carbyne-carbon resonance (299.8 p.p.m.) [1] of the parent complex $[Mo(\equiv CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$, suggesting that the reaction with S_8 involved the carbyne carbon.

Similar, but slower, reactions occurred between S_8 and the dicarbonyl-molybdenum and -tungsten carbyne complexes $[Mo(\equiv CCH_2Bu^t)(CO)_2(\eta\text{-}C_5H_5)]$[5] and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$[6] affording orange and purple crystalline 2 : 1 adducts (2) and (3), respectively. These compounds were also characterised by analysis, and by n.m.r. and i.r. spectroscopy. Both complexes showed two terminal carbonyl bands in the i.r., which was consistent with the appearance in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of resonances at 252.2 [for (2)] and 240.2 p.p.m. [for (3)] typical of co-ordinated carbon monoxide. The ^{13}C spectra also showed low-field resonances at 247.5 [for (2)] and 228.9 p.p.m. [for (3)] similar to that observed (214.6 p.p.m.) in the corresponding spectrum of (1), suggesting that all three compounds were isostructural.

Elemental selenium also reacted with the dicarbonyl carbyne complexes $[M(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (M = Mo, R = CH_2Bu^t; M = W, R = $C_6H_4Me\text{-}4$) to form related 2 : 1 adducts (4) and (5), respectively, which were isolated as crystalline materials. The ^1H and $^{13}C\text{-}\{^1H\}$ spectra of (4) were particularly revealing in that the CH_2Bu^t resonance showed ^{77}Se satellites [$J(SeH)$ 12 Hz], and the low-field ^{13}C resonance at δ 251.9 p.p.m. showed $^{77}Se\text{–}^{13}C$ coupling of 88 Hz, suggesting the presence of a $Se_2C\text{–}CH_2Bu^t$ fragment in the compound. In agreement, the $^{77}Se\text{-}\{^1H\}$ n.m.r. spectrum showed a single resonance at δ −126.5 p.p.m. implying identical environments for the two selenium nuclei. Unfortunately, the low solubility of complex (5) precluded the observation of similar spectral features.

In order to define the molecular structures of these molecules, single-crystal *X*-ray diffraction studies were carried out on both (2) and (3). The molecular structure of the neopentyl molybdenum complex (2) is shown in Figure 1, and that of the *p*-tolyl tungsten complex (3) in Figure 2, each with its crystallographic numbering. Bond distances and angles for corresponding molecular parameters are listed side-by-side for easy comparison in Table 1.

Interest centres on the $(\eta\text{-}C_5H_5)(CO)_2MS_2C$ moiety (M =

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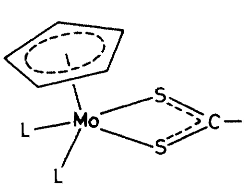
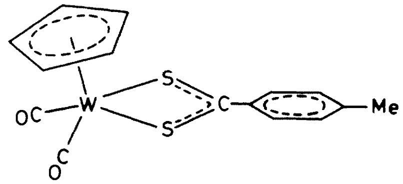
† Dicarbonyl(η-cyclopentadienyl)(3,3-dimethyldithiobutanoato-*SS′*)molybdenum and dicarbonyl(η-cyclopentadienyl)(dithio-*p*-toluato-*SS′*)tungsten.

Supplementary data available (No. SUP 23909, 44 pp.): H-atom co-ordinates, thermal parameters, complete bond lengths and angles, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.



(1) L = P(OMe)$_3$
(2) L = CO



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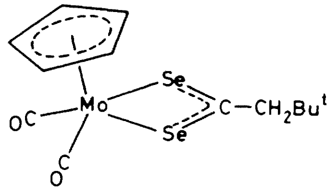

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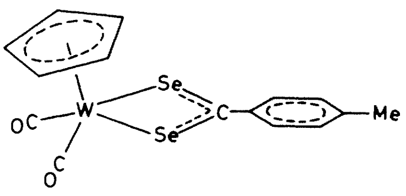


(5)

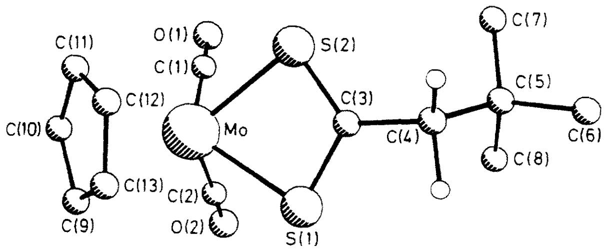


Figure 1. Molecular structure of [Mo{η^2-($S_2CCH_2Bu^t$)}$(CO)_2$(η-C_5H_5)] (2) viewed parallel to approximate molecular mirror plane: atoms are drawn as spheres of arbitrary radius. Methyl and cyclopentadienyl hydrogens are omitted for clarity

Mo or W). As might be expected, the two species are virtually identical in their molecular dimensions. The molecules adopt a 'four-legged piano stool' geometry,[7] in which the metal atoms can be regarded as being formally seven-co-ordinate with the cyclopentadienyl ligands occupying three co-ordination sites. This can be readily appreciated from Figure 3 which shows a projection of the structure of (2) onto the approximate plane of the cyclopentadienyl ligand and also shows, incidentally, that the molybdenum complex possesses almost exact mirror symmetry (excluding the cyclopentadienyl ring). In both structures the MS_2C four-membered ring is planar, with M–S and C–S bond lengths of *ca.* 2.47 and *ca.* 1.68 Å, respectively, indicating extensive delocalisation.

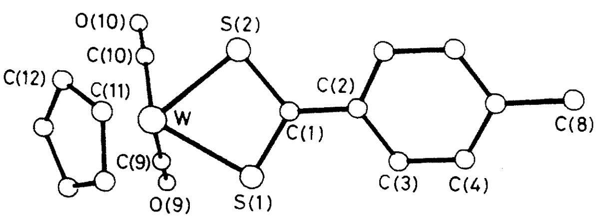


Figure 2. Molecular structure of [W{η^2-($S_2CC_6H_4Me$-4)}$(CO)_2$(η-C_5H_5)] (3) viewed parallel to approximate molecular mirror plane: atoms are drawn as spheres of arbitrary radius. Tolyl and cyclopentadienyl hydrogens are omitted for clarity

Table 1. Comparative bond lengths (Å) and angles (°) with estimated standard derivations in parentheses for the complexes [Mo{η^2-($S_2CCH_2Bu^t$)}$(CO)_2$(η-C_5H_5)] (2) and [W{η^2-($S_2CC_6H_4$-Me-4)}$(CO)_2$(η-C_5H_5)] (3)

Complex (2)		Complex (3)	
(*i*) (η-C_5H_5)M$(CO)_2S_2C$ moiety			
Mo-C(12)	2.356(6)	W-C(11)	2.378(10)
Mo-C(13)	2.374(6)	W-C(15)	2.386(11)
Mo-C(9)	2.326(5)	W-C(14)	2.337(11)
Mo-C(10)	2.281(5)	W-C(13)	2.295(11)
Mo-C(11)	2.301(7)	W-C(12)	2.297(11)
Mo-C(1)	1.956(5)	W-C(10)	1.977(11)
C(1)-O(1)	1.152(6)	C(10)-O(10)	1.162(14)
Mo-C(2)	1.961(5)	W-C(9)	1.980(10)
C(2)-O(2)	1.158(6)	C(9)-O(9)	1.152(13)
C(13)-C(12)	1.372(9)	C(15)-C(11)	1.43(2)
C(12)-C(11)	1.411(9)	C(11)-C(12)	1.46(2)
C(11)-C(10)	1.399(8)	C(12)-C(13)	1.37(2)
C(10)-C(9)	1.400(8)	C(13)-C(14)	1.41(2)
C(9)-C(13)	1.373(7)	C(14)-C(15)	1.40(2)
Mo-S(1)	2.477(1)	W-S(1)	2.473(3)
S(1)-C(3)	1.674(4)	S(1)-C(1)	1.702(9)
Mo-S(2)	2.469(1)	W-S(2)	2.471(3)
S(2)-C(3)	1.684(4)	S(2)-C(1)	1.689(9)
(*ii*) Neopentyl ligand		*p*-Tolyl ligand	
C(3)-C(4)	1.491(6)	C(1)-C(2)	1.463(14)
C(4)-C(5)	1.546(7)	C(2)-C(3)	1.415(14)
C(5)-C(6)	1.528(6)	C(3)-C(4)	1.385(15)
C(5)-C(7)	1.517(8)	C(4)-C(5)	1.38(2)
C(5)-C(8)	1.522(7)	C(5)-C(6)	1.37(2)
		C(6)-C(7)	1.42(2)
		C(5)-C(8)	1.51(2)
S(1)-Mo-S(2)	67.7(1)	S(1)-W-S(2)	67.8(1)
S(1)-Mo-C(2)	81.3(1)	S(1)-W-C(9)	79.7(3)
S(2)-Mo-C(1)	81.0(1)	S(2)-W-C(10)	81.5(3)
C(2)-Mo-C(1)	75.8(2)	C(9)-W-C(10)	77.4(4)
Mo-C(1)-O(1)	176.4(4)	W-C(10)-O(10)	177.1(9)
Mo-C(2)-O(2)	176.6(4)	W-C(9)-O(9)	178.9(8)
Mo-S(1)-C(3)	90.8(1)	W-S(1)-C(1)	91.4(3)
Mo-S(2)-C(3)	90.9(1)	W-S(2)-C(1)	91.7(3)
S(1)-C(3)-C(4)	124.1(3)	S(1)-C(1)-C(2)	125.3(7)
S(2)-C(3)-C(4)	125.7(3)	S(2)-C(1)-C(2)	125.9(7)

The S–M–S angle is *ca.* 68°, and the S–C–S angle is *ca.* 110°. This geometry is closely similar to that found[8] in the compound [Mo$(S_2CMe)_4$], although the mean Mo–S bond distance established therein was 2.526(2) Å, some 0.05 Å longer than in (2) and (3). Three possible causes of this difference immediately suggest themselves: (*i*) in tetrakis(dithioacetato)molybdenum(IV) the entire co-ordination polyhedron comprises sulphur atoms, whereas in (2) and (3) the M–S bonds lie *trans* to a cyclopentadienyl ligand; (*ii*) the replacement of the methyl group in the thioacetato-ligands by a neopentyl or a *p*-tolyl group may affect the degree of delocalisation of the bonding; (*iii*) the change of co-ordination number from 8 to 7 may itself induce a change in the effective radius of the Mo atom. In complexes (2) and (3) the cyclopentadienyl rings are orientated as shown for the molybdenum complex in Figure 3, with one of the five carbon atoms lying close to the plane which bisects the angle between the Mo–CO bonds. This carbon atom is closer to the metal, and the two opposite carbon atoms further away, than are the intermediate pair [Mo–C(10) 2.281(5), W–C(13) 2.295(11) Å], showing some degree of 'slippage.' The geometry of the *p*-tolyl and neopentyl ligands is as expected. In the *p*-tolyl ligand there is a twist of some 11° in the plane of the C_6 ring relative to that of the WS_2C ring, while the torsion angles in the neopentyl group are such as to preserve near-mirror symmetry for the molecule as a whole.

The formation of the complexes (1)—(5) from the carbyne metal complexes is without precedent, and contrasts with the reaction of $[Os(\equiv CPh)Cl(CO)(PPh_3)_2]$ with S, Se, and Te, where only one chalcogen atom is incorporated.[4] It is, therefore, interesting to consider briefly how these complexes are formed.

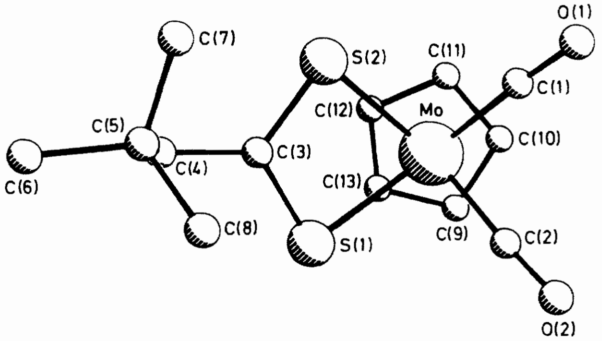
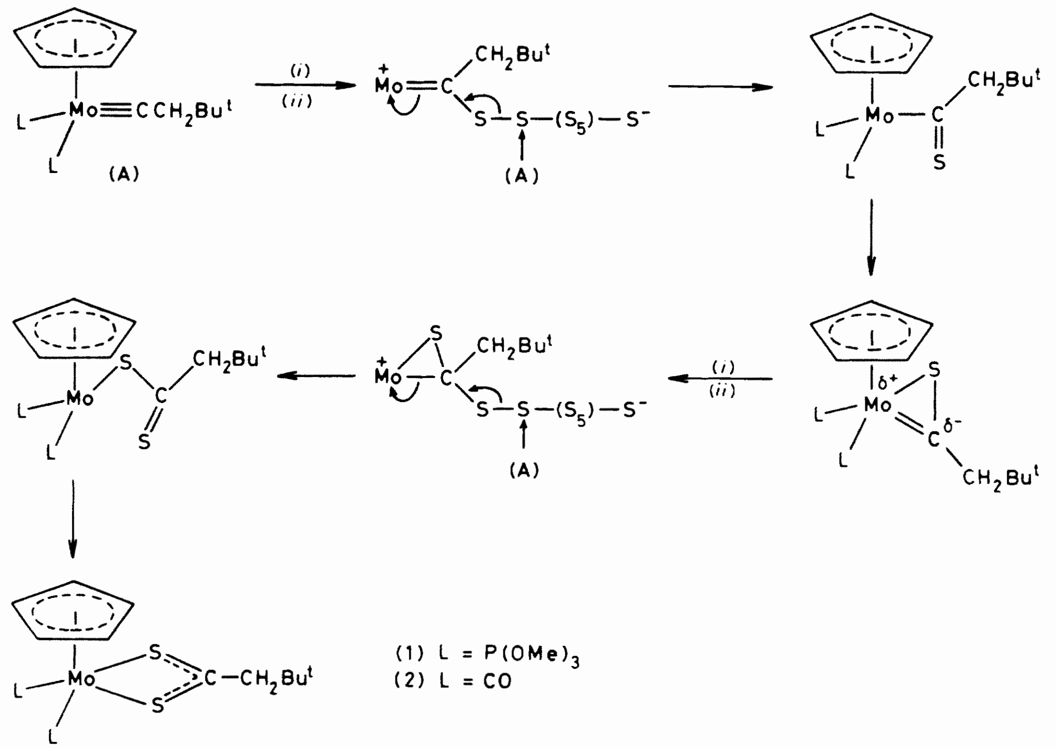


Figure 3. Molecular structure of complex (2) viewed perpendicular to the cyclopentadienyl ligand plane

As mentioned in the introduction, calculations show that the h.o.m.o. of the carbyne complexes $[M(\equiv CR)L_2(\eta\text{-}C_5H_5)]$ (M = Mo or W, L = CO or phosphite ligand) is sited largely on the metal. There is also considerable charge separation in the $\overset{\delta+}{M}\equiv\overset{\delta-}{C}$ triple bond. Thus, if the reaction of, for example, $[Mo(\equiv CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ with S_8 were frontier-orbital-controlled, then attack by sulphur would be expected to occur at the metal centre. It would then be difficult to envisage how the product (1) could be formed. However, if the reaction were charge controlled then electrophilic attack by S_8 on the carbyne carbon could establish a carbon-to-sulphur bond. Then, modelling the subsequent reactions on the reaction path[9] followed when triphenylphosphine reacts with S_8, the reaction sequence illustrated in the Scheme can be envisaged. Important steps are first attack on a dipolar intermediate by a second molecule (A) of the nucleophilic carbyne complex, and secondly the collapse of a 16-electron σ-thioacyl species to form an 18-electron η^2-thioacyl containing a polar molybdenum–carbon double bond, which provides a site for further electrophilic attack by S_8 thus introducing the second chalcogen atom. Interestingly, with the osmium complex $[Os(\equiv CPh)Cl(CO)(PPh_3)_2]$,[4] reaction with sulphur does not proceed beyond an η^2-thioacyl complex.

Experimental

The ^1H, $^{13}C\text{-}\{^1H\}$, $^{31}P\text{-}\{^1H\}$, and $^{77}Se\text{-}\{^1H\}$ n.m.r. spectra were recorded on JEOL FX 90Q or FX 200 spectrometers, as appropriate. Data given are for room-temperature measurements unless otherwise indicated, and coupling constants are in Hz.



Scheme. (*i*) + S_8; (*ii*) nucleophilic attack by the carbyne (A), ligands omitted for clarity

Table 2. Atomic positional parameters (fractional co-ordinates) for $[Mo\{\eta^2-(S_2CCH_2Bu^t)\}(CO)_2(\eta-C_5H_5)]$ (2) and $[W\{\eta^2-(S_2CC_6H_4Me-4)\}-(CO)_2(\eta-C_5H_5)]$ (3)

Atom	*x*	*y*	*z*
Mo	0.280 48(6)	0.204 88(6)	0.161 18(1)
S(1)	0.286 70(13)	0.431 94(18)	0.082 11(4)
S(2)	0.181 65(13)	0.026 11(18)	0.079 86(4)
O(1)	0.448 5(4)	−0.215 2(6)	0.176 9(2)
O(2)	0.602 7(4)	0.327 2(7)	0.176 7(2)
C(1)	0.383 3(5)	−0.062 6(7)	0.169 8(2)
C(2)	0.482 3(5)	0.287 1(7)	0.169 9(2)
C(3)	0.203 1(4)	0.246 2(6)	0.044 3(2)
C(4)	0.157 0(5)	0.274 0(9)	−0.012 9(2)
C(5)	0.251 8(5)	0.171 6(9)	−0.052 7(2)
C(6)	0.192 6(7)	0.240 4(10)	−0.107 9(2)
C(7)	0.247 2(6)	−0.067 0(9)	−0.049 3(2)
C(8)	0.405 1(5)	0.248 3(11)	−0.042 0(2)
C(9)	0.226 2(6)	0.427 4(9)	0.229 5(2)
C(10)	0.226 7(6)	0.218 2(9)	0.247 0(2)
C(11)	0.114 1(7)	0.112 9(11)	0.218 6(2)
C(12)	0.045 3(6)	0.261 4(11)	0.183 8(2)
C(13)	0.114 8(6)	0.450 6(10)	0.191 4(2)

Atom	*x*	*y*	*z*
W	0.336 16(2)	0.332 79(6)	0.568 42(2)
S(1)	0.186 0(2)	0.432 8(4)	0.562 9(2)
S(2)	0.246 8(2)	0.018 9(4)	0.597 4(2)
C(1)	0.160 0(6)	0.176 4(15)	0.592 0(6)
C(2)	0.076 3(7)	0.106 0(15)	0.610 3(7)
C(3)	0.005 6(7)	0.243(2)	0.589 9(7)
C(4)	−0.072 9(7)	0.176(2)	0.609 8(7)
C(5)	−0.085 8(7)	−0.025(2)	0.647 6(6)
C(6)	−0.017 5(8)	−0.159(2)	0.664 3(8)
C(7)	0.065 0(7)	−0.095(2)	0.648 1(8)
C(8)	−0.172 3(9)	−0.098(3)	0.666 5(9)
C(9)	0.320 2(7)	0.488(2)	0.451 6(7)
O(9)	0.310 4(7)	0.575 1(14)	0.383 0(6)
C(10)	0.380 2(7)	0.123(2)	0.485 1(8)
O(10)	0.409 1(6)	0.005 6(15)	0.435 9(6)
C(11)	0.381 1(9)	0.333(2)	0.725 6(7)
C(12)	0.449 9(8)	0.274(2)	0.673 5(8)
C(13)	0.467 7(7)	0.451(2)	0.624 2(8)
C(14)	0.411 7(8)	0.622(2)	0.638 9(7)
C(15)	0.358 4(8)	0.551(2)	0.701 0(8)

Carbon-13 chemical shifts are relative to $SiMe_4$, ^{31}P shifts are relative to 85% H_3PO_4 (external), and ^{77}Se shifts are relative to $SeMe_2$, with positive values to high frequency of the reference. Tris(acetylacetonato)chromium(III) was added to reduce ^{13}C relaxation times. Infrared spectra were recorded on a Perkin-Elmer 257 spectrophotometer. Molecular weights were determined by mass spectroscopy. All reactions were carried out in Schlenk tubes under an atmosphere of dry oxygen-free nitrogen, using freshly distilled solvents.

Reaction of Sulphur.—(*a*) *With* $[Mo(\equiv CCH_2Bu^t)\{P(OMe)_3\}_2(\eta-C_5H_5)]$. Elemental sulphur (0.03 g, 0.95 mmol) was added to a stirred solution of $[Mo(\equiv CCH_2Bu^t)\{P(OMe)_3\}_2(\eta-C_5H_5)]$ (0.23 g, 0.47 mmol) in thf (10 cm^3) at −78 °C. The reaction mixture was allowed to warm to room temperature, with a change in colour from yellow through orange to purple. After 15 min at room temperature, solvent was removed *in vacuo* and the residue extracted with hexane. Chromatography on an alumina-packed column and elution with hexane afforded a purple band, which was collected and recrystallised (−78 °C) from hexane to give purple *crystals* of $[Mo\{\eta^2-(S_2CCH_2Bu^t)\}\{P(OMe)_3\}_2(\eta-C_5H_5)]$ (1) (0.15 g, 57%) (Found: C, 39.1; H, 6.7. $C_{17}H_{34}MoP_2S_2$ requires C, 38.9; H, 6.5%). N.m.r.: ^1H (C_6D_6), δ 4.92 [d, 5 H, C_5H_5, J(PH) 1], 3.42 [apparent t, 18 H, POMe, J(PH) + J(P′H) 11.5], 2.85 [t, 2 H, CH_2, J(PH) 1], and 1.14 (s, 9 H, Bu^t); $^{13}C-\{^1H\}$ (C_6D_6), δ 214.6 (CS_2), 87.8 (C_5H_5), 67.0 (CH_2), 50.9 ($POCH_3$), 30.3 $[C(CH_3)_3]$, and 30.0 $[C(CH_3)_3]$; $^{31}P-\{^1H\}$ (C_6D_6), δ 212.7 p.p.m. (POMe).

(*b*) $[Mo(\equiv CCH_2Bu^t)(CO)_2(\eta-C_5H_5)]$. Elemental sulphur (0.07 g, 2.2 mmol) was added to a stirred solution of $[Mo(\equiv CCH_2Bu^t)(CO)_2(\eta-C_5H_5)]$ (0.22 g, 0.73 mmol) in thf (room temperature). After 12 h the solvent was removed *in vacuo* and the residue extracted with hexane. Chromatography on alumina and elution with hexane afforded an orange band which was collected. Recrystallisation (−78 °C) from hexane gave orange *crystals* of $[Mo\{\eta^2-(S_2CCH_2Bu^t)\}(CO)_2(\eta-C_5H_5)]$ (2) (0.19 g, 72%) (Found: C, 43.0; H, 4.8; S, 18.2%; *M* 364. $C_{13}H_{16}MoO_2S_2$ requires C, 42.9; H, 4.4; S, 17.6%; *M* 364); $\nu_{max.}$(CO) at 1 976s and 1 910m cm^{-1} (hexane). N.m.r.: ^1H (C_6D_6), δ 4.68 (s, 5 H, C_5H_5), 2.47 (s, 2 H, CH_2), and 0.93 (s, 9 H, Bu^t); $^{13}C-\{^1H\}$ (C_6D_6), δ 252.2 (CO), 247.5 (CS_2), 92.6 (C_5H_5), 69.9 (CH_2), 32.3 $[C(CH_3)_3]$, and 29.7 p.p.m. $[C(CH_3)_3]$.

(*c*) $[W(\equiv CC_6H_4Me-4)(CO)_2(\eta-C_5H_5)]$. A solution of $[W(\equiv CC_6H_4Me-4)(CO)_2(\eta-C_5H_5)]$ (0.41 g, 1.0 mmol) and elemental sulphur (0.096 g, 3.0 mmol) in CH_2Cl_2 (10 cm^3) was stirred at room temperature for 24 h. Removal of the solvent *in vacuo* followed by chromatography on alumina afforded, on elution with CH_2Cl_2–hexane (3 : 1), unreacted carbyne followed by a purple band which after removal of solvent *in vacuo* gave dark purple *microcrystals* of $[W\{\eta^2-(S_2CC_6H_4Me-4)\}(CO)_2(\eta-C_5H_5)]$ (3) (0.27 g, 58%) (Found: C, 37.6; H, 2.5; S, 13.7%; *M* 472. $C_{15}H_{12}O_2S_2W$ requires C, 38.1; H, 2.5; S, 13.6%; *M* 472); $\nu_{max.}$(CO) at 1 965s and 1 897m cm^{-1} (methylcyclohexane). N.m.r.: ^1H ($CDCl_3$), δ 7.6—7.2 [(AB)$_2$ system, 4 H, C_6H_4, J(AB) 8], 5.5 (s, 5 H, C_5H_5), and 2.3 (s, 3 H, Me-4); $^{13}C-\{^1H\}$ ($CDCl_3$), δ 240.2 (CO), 228.9 (CS_2), 143.6, 142.2, 128.7, 121.1 (C_6H_4), 91.3 (C_5H_5), and 21.6 p.p.m. (Me-4).

Reaction of Selenium.—(*a*) *With* $[Mo(\equiv CCH_2Bu^t)(CO)_2(\eta-C_5H_5)]$. Elemental selenium (0.16 g, 2.0 mmol) was added to a stirred solution of $[Mo(\equiv CCH_2Bu^t)(CO)_2(\eta-C_5H_5)]$ (0.15 g, 0.5 mmol) in thf (10 cm^3). After 24 h at room temperature the reaction mixture had changed colour from yellow to red. The solvent was removed *in vacuo* and the residue extracted with hexane. The hexane extracts were chromatographed on alumina. Elution with diethyl ether gave a red band, which was collected and recrystallised (−78 °C) from hexane to give red *crystals* of $[Mo\{\eta^2-(Se_2CCH_2Bu^t)\}(CO)_2(\eta-C_5H_5)]$ (4) (0.18 g, 78%) (Found: C, 34.5; H, 3.7%; *M* 458. $C_{13}H_{16}MoO_2Se_2$ requires C, 34.0; H, 3.5%; *M* 458); $\nu_{max.}$(CO) at 1 969s and 1 905m cm^{-1} (hexane). N.m.r.: ^1H (C_6D_6), δ 4.68 (s, 5 H, C_5H_5), 2.49 [s, 2 H, CH_2, J(^{77}SeH) 12], and 0.95 (s, 9 H, Bu^t); $^{13}C-\{^1H\}$ (C_6D_6), δ 251.9 [CSe_2, J(^{77}Se–C) 88], 250.6 (CO), 91.7 (C_5H_5), 75.9 (CH_2), 30.0 $[C(CH_3)_3]$, and 29.8 $[C(CH_3)_3]$; $^{77}Se-\{^1H\}$ (C_6D_6), δ −126.5 p.p.m. (CSe_2).

(*b*) $[W(\equiv CC_6H_4Me-4)(CO)_2(\eta-C_5H_5)]$. Elemental selenium (0.23 g, 3.0 mmol) was added to a stirred solution of $[W(\equiv CC_6H_4Me-4)(CO)_2(\eta-C_5H_5)]$ (0.41 g, 1.0 mmol) in thf (10 cm^3). After 4 d at room temperature the solvent was removed *in vacuo*. Chromatography on alumina and elution with dichloromethane-hexane (3 : 1) gave a blue band which after removal of solvent *in vacuo* gave dark blue *microcrystals* of $[W\{\eta^2-(Se_2CC_6H_4Me-4)\}(CO)_2(\eta-C_5H_5)]$ (5) (0.53 g, 94%) (Found: C, 31.9; H, 2.2%; *M* 566. $C_{15}H_{12}O_2Se_2W$ requires C, 31.8; H, 2.1%; *M* 566); $\nu_{max.}$(CO) at 1 949s and 1 875m cm^{-1} (CH_2Cl_2). N.m.r.: ^1H ($CDCl_3$), δ 7.70—7.06 [(AB)$_2$ system, 4 H, C_6H_4, J(AB) 8], 5.63 (s, 5 H, C_5H_5), and 2.11 (s, 3 H, Me-4); ^{13}C-{^1H} (CH_2Cl_2–CD_2Cl_2), δ 239.6 (CO), 230.4 (CSe_2), 148.9, 142.6, 129.8, 120.1 (C_6H_4), 90.9 (C_5H_5), and 22.1 p.p.m. (Me-4).

Crystal-structure Determinations.—Complex (2). Crystals of (2) were grown as red needles from a hexane solution cooled to −30 °C. Diffracted intensities were collected at 293 K from a small crystal on a Nicolet *P*3*m* four-circle diffractometer. Of the 3 100 reflections measured for $2.9 \leqslant 2\theta \leqslant 55°$ there were 2 165 with $I \geqslant 2.0\sigma(I)$ and only these were used. No correction for *X*-ray absorption was made.

Crystal data. $C_{13}H_{16}MoO_2S_2$, M = 364.2, monoclinic, a = 9.392(3), b = 6.344(1), c = 25.412(8) Å, β = 94.79(2)°, Z = 4, D_c = 1.60 g cm^{-3}, U = 1 508.7(7) Å^3, F(000) = 736, space group $P2_1/c$ (no. 14), Mo-K_α *X*-radiation (graphite monochromator), λ = 0.710 69 Å, μ(Mo-K_α) = 11.1 cm^{-1}.

The structure was solved by heavy-atom methods and refined by full-matrix blocked-cascade least squares, with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were incorporated at calculated 'riding' positions (C–H 0.960 Å) apart from those of the methylene group [H(4A) and H(4B)], which were freely refined. Individual weights were ascribed according to the scheme $w = [\sigma^2(F_o) + g|F_o|^2]^{-1}$, with g = 0.0005. Refinement converged at R 0.033, R' 0.033.

Complex (3). Crystals of (3) were grown as dark red columns from thf. Diffracted intensities were collected at 293 K from a crystal of dimensions 0.05 × 0.15 × 0.35 mm. Of the 4 056 reflections measured for $2.9 \leqslant 2\theta \leqslant 55°$, 2 382, satisfying the criterion $I \geqslant 2.5\sigma(I)$ and corrected for Lorentz, polarisation, and *X*-ray absorption effects, were used in the solution and refinement of the structure. An analytical absorption correction assuming faces {001}, {010}, and {100} was used. There was no significant crystal decay.

Crystal data. $C_{15}H_{12}O_2S_2W$, M = 472.2, monoclinic, a = 16.001(6), b = 6.161(1), c = 14.932(3) Å, β = 96.32(2)°, Z = 4, D_c = 2.14 g cm^{-3}, U = 1 463.2(6) Å^3, F(000) = 896, space group $P2_1/c$ (no. 14), μ(Mo-K_α) = 83.4 cm^{-1}.

The structure was solved as for (2), except all the hydrogen atoms were located on electron-density difference maps, and were refined isotropically without positional constraints. Individual weights were ascribed according to the scheme $w = [\sigma^2(F_o) + g|F_o|^2]^{-1}$, with g = 0.0004. Refinement converged at R 0.042, R' 0.038.

Scattering factors and corrections for anomalous dispersion were taken from ref. 10. All calculations were carried out within the laboratory on an 'Eclipse' Data General Minicomputer with the SHELXTL system of programs.[11] Atomic positional parameters for (2) and (3) are given in Table 2.

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