Distortions in Six-co-ordinate Complexes of Molybdenum(II) and Tungsten(II). Crystal Structures of *mer*-[Mo($SC_6H_2Pr^i_3$-2,4,6)$_2$(CO)$_3$(PMePh$_2$)], *cis,cis,cis*-[W($SC_6H_2Me_3$-2,4,6)$_2$(CO)$_2$(PMe$_2$Ph)$_2$] and [W($SeC_6H_3Pr^i_2$-2,6)$_2$(CO)$_2$(PMe$_2$Ph)$_2$]†

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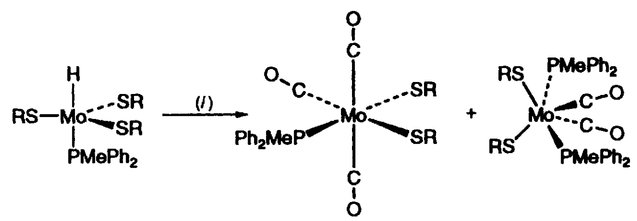
The red, diamagnetic complexes *mer*-[Mo($SC_6H_2Pr^i_3$-2,4,6)$_2$(CO)$_3$(PMePh$_2$)] **1** and [Mo($SC_6H_2Pr^i_3$-2,4,6)$_2$(CO)$_2$(PMePh$_2$)$_2$] **2** have been prepared by reaction of [MoH($SC_6H_2Pr^i_3$-2,4,6)$_3$(PMePh$_2$)] with CO in tetrahydrofuran. The crystal structure of **1** shows it to have a distorted octahedral geometry with *mer*-CO ligands [*d*(Mo–S) 2.380(1) and 2.366(1); *d*(Mo–C) 2.030(5), 2.026(4) and 2.066(5); *d*(Mo–P) 2.561(1) Å; large S–Mo–S angle of 116.0°]. Reaction of CO with [WH($SC_6H_2Me_3$-2,4,6)$_3$(PMe$_2$Ph)$_2$] in toluene gives green, distorted octahedral *cis,cis,cis*-[W($SC_6H_2Me_3$-2,4,6)$_2$(CO)$_2$(PMe$_2$Ph)$_2$] **3** [*d*(W–S) 2.379(2) and 2.385(2); *d*(W–C) 1.967(7) and 1.991(8); *d*(W–P) 2.556(2) and 2.507(2) Å]. Reaction with [WH($SeC_6H_3Pr^i_2$-2,6)$_3$(PMe$_2$Ph)$_2$] gives burgundy, trigonal prismatic [W($SeC_6H_3Pr^i_2$-2,6)$_2$(CO)$_2$(PMe$_2$Ph)$_2$] **4** [*d*(W–Se) 2.506(1) and 2.583(1); *d*(W–C) 1.942(8) and 1.943(8); *d*(W–P) 2.467(2) and 2.471(2) Å]. The physical properties of **1**–**4** and the structures of **1**, **3** and **4** are discussed in terms of their distortions from regular octahedral or trigonal-prismatic geometries. A method of classifying such structures is proposed.

In a continuation of our studies of thiolato- or selenolato-hydride complexes of molybdenum and tungsten,[1] we report here the reaction of carbon monoxide gas with the five-co-ordinate complex [MoH($SC_6H_2Pr^i_3$-2,4,6)$_3$(PMePh$_2$)] and the six-co-ordinate complexes [WH($SC_6H_2Me_3$-2,4,6)$_3$(PMe$_2$Ph)$_2$] and [WH($SeC_6H_3Pr^i_2$-2,6)$_3$(PMe$_2$Ph)$_2$]. Both reactions result in the loss of thiol or selenol with reduction of the metal to give the new carbonyl complexes described below. The products of the reactions are distorted six-co-ordinate, d^4 complexes. Hoffmann and co-workers[2–4] have classified such structures in terms of the variation of the angles between *cis*-donor and *cis*-acceptor ligands in the equatorial plane of the idealised octahedron. The compounds we have prepared provide further examples of the types of distortions analysed by Hoffmann and co-workers[2–4] and our compounds are conveniently separated into three classes.

Results and Discussion

Preparation and Structure of the Molybdenum Complexes.— The hydride complex [MoH($SC_6H_2Pr^i_3$-2,4,6)$_3$(PMePh$_2$)][1] was treated in thf (tetrahydrofuran) solution with carbon monoxide gas giving an immediate change from green to red. Addition of cold methanol afforded a mixture of dark red rectangular prisms and a minority of bright red plates, in a ratio of 4:1. The two sets of crystals were separated manually. The dark red prisms were characterised as *mer*-[Mo($SC_6H_2Pr^i_3$-2,4,6)$_2$(CO)$_3$(PMePh$_2$)] **1** and the red plates as [Mo($SC_6H_2Pr^i_3$-2,4,6)$_2$(CO)$_2$(PMePh$_2$)$_2$] **2** as follows.

The attack of the strong π-acid carbonyls results in the



1 2

Scheme 1 R = $C_6H_2Pr^i_3$-2,4,6. (*i*) CO + PMePh$_2$ − HSR

reductive elimination of thiol from the five-co-ordinate hydride to give the tricarbonyl **1** as the main product (Scheme 1). However, the presence of free phosphine in the reaction solution results in the formation of a small amount of the dicarbonylbis(phosphine) complex **2**. This complex becomes the dominant product when 1 equivalent of PMePh$_2$ is provided in the reaction solution (see Experimental section). It is not known at this stage whether **2** is produced by reaction of **1** with PMePh$_2$ or by reaction of a precursor to **1**.

mer-[Mo($SC_6H_2Pr^i_3$-2,4,6)$_2$(CO)$_3$(PMePh$_2$)] **1**. The molecular structure of complex **1** is shown in Fig. 1 and the crystallographic results are in Tables 1 and 2. Selected spectroscopic properties of this and the other complexes described in this paper are in Table 3.

Complex **1** has a distorted octahedral geometry with meridional carbonyls. The *trans* arrangement of the phosphine ligand, P(6), and the benzenethiolate ligand, S(2), is distorted from the vertical axis of an ideal octahedron with a P(6)–Mo–S(2) angle of 157.6°. The P(6)–Mo–C(5) [79.1(1)°] and S(1)–Mo–S(2) [116.0°] angles serve to classify the distortion, which is primarily electronic in orgin, as class 1 (see

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Final atomic coordinates (fractional $\times 10^4$) for *mer*-$[Mo(SC_6H_2Pr^i_3\text{-}2,4,6)_2(CO)_3(PMePh_2)]\cdot 0.5thf$ **1** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo	983.2(1)	−275.9(3)	3645.8(2)	C(262)	−451(3)	−2302(10)	1705(5)
S(1)	1944.5(4)	374(1)	4041.0(5)	C(263)	−505(3)	−4251(7)	2340(6)
C(11)	2138(2)	475(4)	5015(2)	C(3)	820(2)	−528(4)	4665(3)
C(12)	2266(2)	1634(3)	5328(2)	O(3)	690(2)	−752(3)	5208(2)
C(121)	2327(2)	2752(3)	4871(2)	C(4)	1135(2)	−199(4)	2614(2)
C(122)	2884(2)	2742(5)	4586(3)	O(4)	1215(2)	−163(3)	2035(2)
C(123)	2272(2)	3951(4)	5255(3)	C(5)	102(2)	−352(4)	3365(3)
C(13)	2372(2)	1711(4)	6082(2)	O(5)	−383(1)	−453(3)	3266(2)
C(14)	2371(2)	716(4)	6527(2)	P(6)	737.5(4)	1986(1)	3487.7(6)
C(141)	2451(2)	869(4)	7346(2)	C(61a)	746(2)	2953(4)	4285(2)
C(142)	2839(3)	−77(5)	7752(3)	C(62a)	717(2)	4210(4)	4219(3)
C(143)	1884(3)	909(8)	7592(3)	C(63a)	710(2)	4937(4)	4819(3)
C(15)	2285(2)	−416(4)	6207(2)	C(64a)	725(2)	4431(5)	5492(3)
C(16)	2178(2)	−567(3)	5453(2)	C(65a)	749(2)	3197(5)	5562(3)
C(161)	2167(2)	−1843(4)	5145(2)	C(66a)	758(2)	2459(4)	4966(2)
C(162)	1861(2)	−2757(4)	5547(3)	C(61b)	29(2)	2278(4)	2946(2)
C(163)	2772(3)	−2243(5)	5138(3)	C(62b)	−439(2)	2497(4)	3265(3)
S(2)	840.7(4)	−2403(1)	3539.6(5)	C(63b)	−976(2)	2638(5)	2846(3)
C(21)	935(2)	−3083(3)	2693(2)	C(64b)	−1045(2)	2557(5)	2116(3)
C(22)	1482(2)	−3371(4)	2567(2)	C(65b)	−591(2)	2332(5)	1779(3)
C(221)	2028(2)	−3069(4)	3097(2)	C(66b)	−50(2)	2189(5)	2199(3)
C(222)	2441(3)	−2346(7)	2748(3)	C(67)	1212(2)	2787(4)	2983(2)
C(223)	2301(3)	−4224(6)	3437(4)				
C(23)	1527(2)	−3996(4)	1934(2)	The disordered solvent molecule			
C(24)	1060(2)	−4341(4)	1428(2)	C(70)*	5116(19)	4638(40)	5615(19)
C(241)	1135(2)	−5054(4)	753(2)	C(71)*	4528(16)	4234(35)	4729(21)
C(242)	921(3)	−6342(5)	786(3)	C(74)*	4961(13)	3843(25)	5175(16)
C(243)	854(3)	−4420(6)	59(3)	C(75)*	4947(54)	3989(87)	4695(57)
C(25)	527(2)	−4045(4)	1567(2)	C(76)*	5731(29)	4652(83)	5099(45)
C(26)	446(2)	−3421(4)	2187(2)	C(77)*	5533(26)	5538(47)	4732(29)
C(261)	−159(2)	−3127(5)	2291(3)	C(78)*	5384(21)	4381(36)	5301(21)

* Site occupancy factor 0.5.

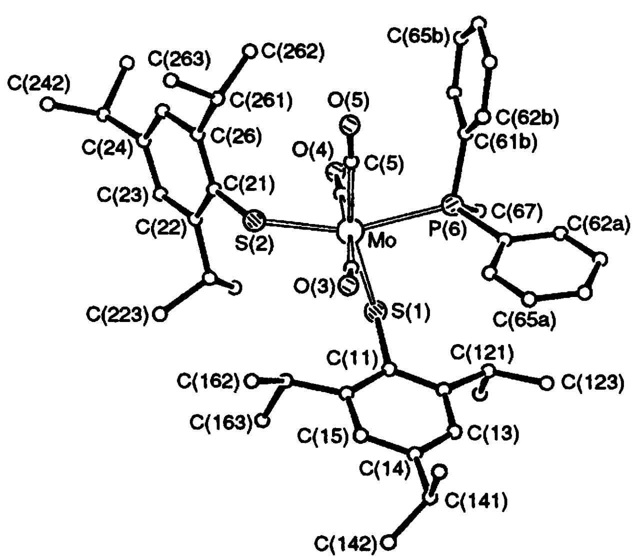


Fig. 1 Molecular structure of $[Mo(SC_6H_2Pr^i_3\text{-}2,4,6)_2(CO)_3(PMePh_2)]$ **1**

below). The complex *cis*-$[Mo(SBu^t)_2(CNBu^t)_4]$ **5**[4] has a very similar geometry with corresponding angles for C–Mo–C [73.7(4)°] and S–Mo–S [115(3)°].

In complex **1** the two metal–thiolate bond distances, [2.380(1) and 2.366(1) Å] are in the range observed in other six-co-ordinate molybdenum(II) thiolate complexes,[5,6] *e.g.* $[Mo(SBu^n)_2(Ph_2PCH_2CH_2PPh_2)_2]$[6] has *d*(Mo–S) 2.361(1) Å and *cis*-$[Mo(SBu^t)_2(CNBu^t)_4]$[4] has *d*(Mo–S) 2.374(3) and 2.372(3) Å. The carbonyl bond distances are as expected for a molybdenum(II) complex.[5]

There are few examples of tricarbonyl thiolate complexes. The molybdenum(II) tricarbonyl complex $[Mo(CO)_3(C_5H_4NS)_2]$,[7] the compound $[Mo(CO)_3(S_2CNMe_2)_2]$,[8] and the complexes $[W(CO)_3(S_2CNMe_2)(C_5H_5)]$ and $[Mo(CO)_2(S_2CNMe_2)(C_5H_5)]$[9] have been prepared but have not been characterised by X-ray crystallography. The tricarbonyl species $[PPh_4][Mo(CO)_3(SC_6H_2Pr^i_3\text{-}2,4,6)_3]$ is known to exist at saturation pressures of carbon monoxide, but has not been isolated due to the equilibrium being much more in favour of the dicarbonyl species $[PPh_4][Mo(CO)_2(SC_6H_2Pr^i_3\text{-}2,4,6)_3]$.[10]

The dark red crystals of complex **1** showed three CO stretching bands at 2040, 1990 and 1917 cm^{-1} in their infrared spectrum, the band at lowest wavenumber being the most intense. This is characteristic of a meridional tricarbonyl geometry.

The ^1H NMR spectrum of the complex shows two sets of overlapping methine septets in the range δ 3–4, corresponding to the isopropyl methine groups of two inequivalent triisopropylbenzenethiolate ligands, and the $^{31}P\text{-}\{^1H\}$ NMR spectrum shows the expected single resonance at δ −127.7. The proton-coupled spectrum is also a singlet, precluding the presence of a hydride ligand.

The absence of a hydride stretching frequency in the infrared spectrum or any proton coupling in the phosphorus NMR spectrum indicates the product is not hydride-containing. The hydride ligand in the starting material must therefore have been lost in the reaction by reductive elimination of thiol to produce a diamagnetic molybdenum(II) complex, this being a typical reaction of thiolatohydride complexes.[5]

$[Mo(SC_6H_2Pr^i_3\text{-}2,4,6)_2(CO)_2(PMePh_2)_2]$ **2**. The minor product of the reaction (Scheme 1) of $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMePh_2)]$ with carbon monoxide was isolated as bright red crystals. Elemental microanalysis of the product is consistent with the formulation $[Mo(SC_6H_2Pr^i_3\text{-}2,4,6)_2\text{-}$

Table 2 Selected molecular dimensions (lengths in Å, angles in °) in *mer*-[Mo(SC$_6$H$_2$Pr$^i_3$-2,4,6)$_2$(CO)$_3$(PMePh$_2$)]·0.5thf **1** with e.s.d.s in parentheses

(*a*) About the Mo atom			
Mo–S(1)	2.380(1)	Mo – C(4)	2.026(4)
Mo–S(2)	2.366(1)	Mo – C(5)	2.066(5)
Mo–C(3)	2.030(5)	Mo – P(6)	2.561(1)
S(1)–Mo–S(2)	116.0*	C(3)–Mo–C(5)	83.0(2)
S(1)–Mo–C(3)	94.8(1)	C(4)–Mo–C(5)	96.0(2)
S(2)–Mo–C(3)	84.0(1)	S(1)–Mo–C(5)	86.0*
S(1)–Mo–C(4)	87.7(1)	S(2)–Mo–P(6)	157.6*
S(2)–Mo–C(4)	90.5(1)	C(3)–Mo–P(6)	99.4(1)
C(3)–Mo–C(4)	174.5(2)	C(4)–Mo–P(6)	85.7(1)
S(1)–Mo–C(5)	164.3(1)	C(5)–Mo–P(6)	79.1(1)
S(2)–Mo–C(5)	79.4(1)		
(*b*) In the thiolate ligands			
S(1)–C(11)	1.799(4)	Mo–S(1)–C(11)	112.9(1)
S(2)–C(21)	1.800(4)	Mo–S(2)–C(21)	116.5(1)
(*c*) In the carbonyl ligands			
C(3)–O(3)	1.139(6)	Mo–C(3)–O(3)	173.3(4)
C(4)–O(4)	1.132(6)	Mo–C(4)–O(4)	179.3(4)
C(5)–O(5)	1.140(6)	Mo–C(5)–O(5)	173.8(4)
(*d*) In the phosphine ligand			
P(6)–C(61a)	1.828(4)	P(6)–C(67)	1.822(5)
P(6)–C(61b)	1.831(4)		
Mo–P(6)–C(61a)	120.1(1)	Mo–P(6)–C(67)	112.3(2)
Mo–P(6)–C(61b)	113.7(1)	C(61a)–P(6)–C(67)	103.0(2)
C(61a)–P(6)–C(61b)	103.0(2)	C(61b)–P(6)–C(67)	102.8(2)

* E.s.d. is less than 0.05°.

Table 3 Spectroscopic properties of the carbonyl complexes

Complex	^{31}P NMR [a]	^{77}Se NMR [b]	$\tilde{\nu}$(CO)/cm^{-1}
1	−127.7 (s)		2040m [c] 1990m 1917s
2	−121.3 (s)		1935s [c] 1852s
3	−157.7 (d, $^2J_{PP}$ 7.3, $^1J_{PW}$ 205) −162.4 (d, $^2J_{PP}$ 7.5, $^1J_{WP}$ 142)		1940s [d] 1866s
4	−138.5 (s, $^1J_{PW}$ 107)	425 (br) 590 (br)	1918s [c] 1830s

[a] δ in ppm relative to P(OMe)$_3$, *J* in Hz. [b] δ in ppm relative to SeMe$_2$. [c] In KBr disc. [d] In cyclohexane solution.

(CO)$_2$(PMePh$_2$)$_2$] **2**. The infrared spectrum of this complex showed two strong CO stretching bands at 1935 and 1852 cm^{-1} corresponding to a *cis*-dicarbonyl product. The ^{1}H NMR spectrum shows four overlapping methine resonances in the region δ 2–4. These signals are due to two inequivalent sets of isopropyl groups in two inequivalent environments and therefore correspond to *cis*-triisopropylbenzenethiolate ligands. The ^{31}P NMR spectrum is a singlet resonance at δ −121.3. No ^{13}C carbonyl resonances could be detected.

The spectroscopic data for complex **2** show a striking similarity to those for the analogous complexes [M(SC$_6$H$_2$Pr$^i_3$-2,4,6)$_2$(CO)$_2$(PMe$_2$Ph)$_2$] **6** (M = Mo or W), formed by reductive elimination of thiol from the six-co-ordinate hydride complexes [MH(SC$_6$H$_2$Pr$^i_3$-2,4,6)$_3$(PMe$_2$Ph)$_2$] by carbon monoxide.[5] Thus **6** (M = Mo) exhibits two carbonyl stretches in its infrared spectrum (KBr disc) at 1935 and 1850 cm^{-1} and a singlet in the ^{31}P NMR spectrum at δ −107.9. The similarities between **2** and **6** (M = Mo or W) extend to the ^{1}H NMR spectrum in which the methine region shows two broad resonances which resolve at reduced temperature to four overlapping multiplets corresponding to two *cis*-triisopropylbenzenethiolate ligands.

The crystal structures of red complexes **6** revealed[5] identical distorted trigonal-prismatic geometries for both complexes. The two thiolate ligands occupy one edge (the ridge) of the prism; in the approximately rectangular base plane (formed from the other two edges), the two carbonyl ligands are at opposite corners, with the two phosphines in the other pair of opposite corners. The core of compounds **6** is shown in Fig. 2, which emphasises the angles important in the classification of the distortion as class 3 trigonal prismatic (*TPR*) (see below). It is very likely that complex **2** shows the same core geometry.

Preparation and Structures of the Tungsten Complexes.—The reaction of the hydride complexes [WH(ER)$_3$(PMe$_2$Ph)$_2$][11] with carbon monoxide resulted in the reductive elimination of HER and formation of [W(CO)$_2$(ER)$_2$(PMe$_2$Ph)$_2$] (ER = SC$_6$H$_2$Me$_3$-2,4,6 **3** or SeC$_6$H$_3$Pr$^i_2$-2,6 **4**), reaction (1). In the

$$[WH(ER)_3(PMe_2Ph)_2] + 2CO \longrightarrow [W(ER)_2(CO)_2(PMe_2Ph)_2] + HER \quad (1)$$

case of the selenolate complex, this reaction had to be carefully monitored by ^{31}P NMR spectroscopy in order to judge when to halt it, by flushing with N$_2$, to prevent the formation of the complex [W(CO)$_4$(PMe$_2$Ph)$_2$] (δ_P −165.7)[12] *via* the competing reaction (2). The dicarbonyl species was produced before the

$$[WH(SeC_6H_3Pr^i_2)_3(PMe_2Ph)_2] + 4CO \longrightarrow [W(CO)_4(PMe_2Ph)_2] + HSeC_6H_3Pr^i_2 + (SeC_6H_3Pr^i_2)_2 \quad (2)$$

tetracarbonyl species; thus the yield of the side product could be minimised.

The products from reaction (1) had properties that were dependent on the ligand used. With the more bulky isopropyl-containing ligand, the products were red, whereas with 2,4,6-trimethylbenzenethiolate, the product was green. This reflects the different structures found for these complexes.

[W(SC$_6$H$_2$Me$_3$-2,4,6)$_2$(CO)$_2$(PMe$_2$Ph)$_2$] **3**. In a previous publication[5] we discussed the possible structures of the green complexes [M(SC$_6$H$_2$Me$_3$-2,4,6)$_2$(CO)$_2$(PMe$_2$Ph)$_2$] **3** (M = Mo or W) on the basis of their spectroscopic properties. We proposed that their structures have C_1 symmetry so that only one of five possible octahedral isomers or two of eleven trigonal-prismatic isomers are possible candidates for the structure in the absence of distortion.

The actual structure which we now report for **3** (M = W) (Fig. 3 and Tables 4 and 5) has the predicted C_1 symmetry and lies between octahedral and *TPR*. The two triangles P(1),O(2), S(2) and P(2),O(1),S(1) (Fig. 4) are twisted away from the eclipsed *TPR* stereochemistry by an average twist angle[2,13] (θ) of 35° toward the regular octahedral twist angle of 60° (see Figs. 5 and 6 and discussion below). The W–S distances are equal at 2.379(2) and 2.385(2) Å, in contrast to the corresponding distances in the red isomers [M(SC$_6$H$_2$Pr$^i_3$-2,4,6)$_2$(CO)$_2$(PMe$_2$Ph)$_2$] **6** [M = Mo, 2.464(1) and 2.395(1); M = W, 2.460(2) and 2.395(2) Å].[5] The W–P distances are greater for **3** [2.556(2) and 2.507(2) Å] than for **6** [M = Mo, 2.459(2) and 2.463(2); M = W, 2.472(2) and 2.470(2) Å]. The W–C bond lengths are similar to those of the red isomers **6**. The angles at the metal, particularly the C(1)–W–C(2) angle [102.5(3)°], define the structural distortion as class 2 (see below).

[W(SeC$_6$H$_3$Pr$^i_2$-2,6)$_2$(CO)$_2$(PMe$_2$Ph)$_2$] **4**. This compound forms burgundy crystals whose crystal structure is shown in Fig. 7. Crystallographic details are listed in Tables 6 and 7. The structure is very similar to that of the red isomers **6**, being close to *TPR*. Complex **4** as well as the red isomers has the same average twist angle of 12° (see Fig. 6) where each of the two triangles defining the twist contains one S (or Se), one P and one O atom of a carbonyl. The only difference in bond distances is, as expected, in the W–Se bonds [2.506(1) and 2.583(1) Å] compared to M–S distances in the range 2.380–2.464 Å for **3** and **6**.

Complex **4** has two CO absorptions in the infrared as would be expected regardless of the geometry (Table 3). The $^{31}P-\{^1H\}$ NMR spectrum is a singlet at δ −138.5, whereas the ^{77}Se NMR spectrum shows two broad resonances at δ 425 and 590 which can be explained by a rapid interconversion of two conformations of the complex. The conformations must have similar ^{31}P frequencies, to allow averaging, but well separated ^{77}Se frequencies; clearly the ^{77}Se resonances are quite different in this complex (Table 3). The ^1H NMR spectrum of **4** is as expected for fluxionality; for example, the methine protons show a single septet at δ 3.65. A variable-temperature ^1H NMR study of compounds **6** showed them to be fluxional as well.[5]

The Six-co-ordinate, d^4, *Complexes*.—Kubácek and Hoffmann[3] undertook a general theoretical analysis of deformations in d^4 six-co-ordinate complexes with C_{2v} geometry. By considering subunits of the molecule, the effects could be subdivided. The carbonyl ligands are preferentially *cis* because their strong π acidity makes the *trans* arrangement unfavourable. Calculations of the energy of compounds having a *cis* carbonyl pair, as shown in Fig. 5, indicate that there is a double minimum in energy, with α either less than 90° (class 1) or greater than 90° (class 2 or 3). When a *cis* group of π-donor ligands is *trans* to the carbonyls, and α is less than 90°, then β will be close to 90°, whereas if α is greater than 90°, then β will be less than 90°. Last, considering a set of σ-donor ligands (neither strongly π-accepting nor -donating) *trans* to the carbonyls, if α is less than 90°, γ will be about 180°, but if α is greater than 90°, then γ will be less than 180° (see Fig. 5).

Kubácek and Hoffmann[3] considered two classes of distortions retaining the C_{2v} symmetry from a regular octahedron, but we have grouped our structures (which do not have that symmetry) with α greater than 90° either into class 2 structures, which are distorted about half-way between octahedral and *TPR*, or into class 3 structures, which are distorted almost all the way to *TPR*. Therefore the class 2 structure has an average twist angle θ of *ca.* 30° while the class 3 structures have an average twist angle close to 0°.

Fig. 6 provides examples of these classes of distorted six-co-ordinate complexes. The angle α for deep red complex **1** is defined as P(6)–Mo–C(5) [79.1(1)°] so that the π-donating thiolate groups are in the equatorial plane according to the model in Fig. 5. Therefore **1** is a distorted, octahedral, class 1 complex very similar to the green complex *cis*-[$Mo(SBu^t)_2(CNBu^t)_4$] **5**, which has an angle of 73.7(4)° between the

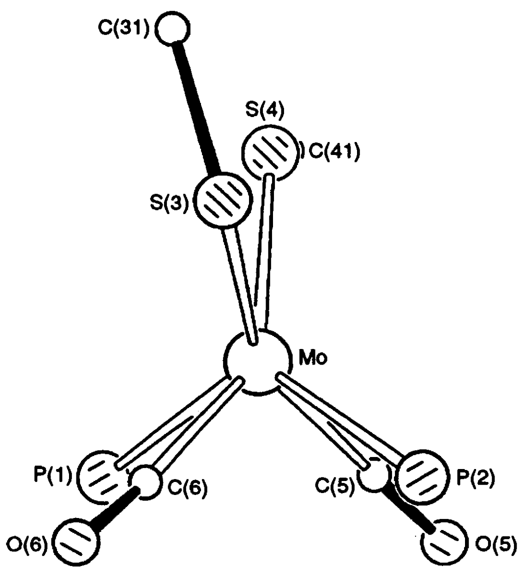


Fig. 2 Core structure of [$Mo(SC_6H_2Pr^i_3$-2,4,6$)_2(CO)_2(PMe_2Ph)_2$] **6** (M = Mo)[5]

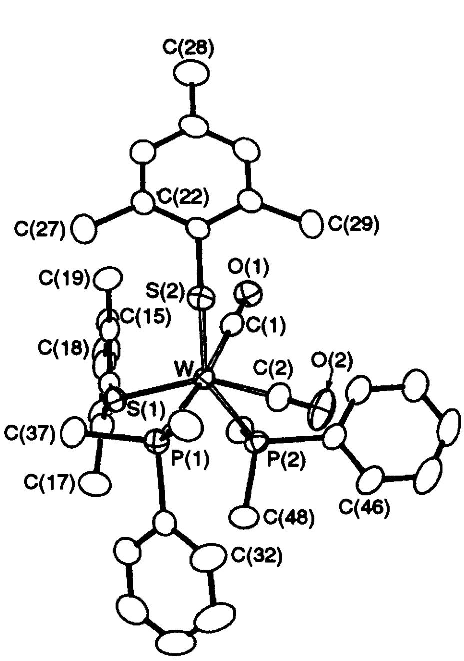


Fig. 3 Molecular structure of [$W(SC_6H_2Me_3$-2,4,6$)_2(CO)_2(PMe_2Ph)_2$] **3**

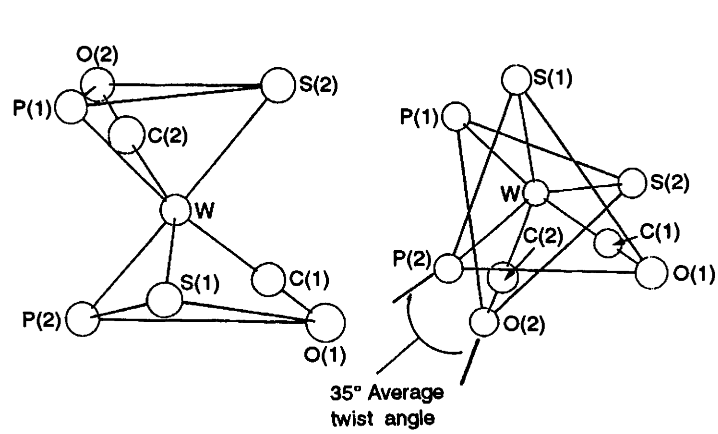


Fig. 4 Core structure of [$W(SC_6H_2Me_3$-2,4,6$)_2(CO)_2(PMe_2Ph)_2$] **3**, emphasising the atoms used to define the two triangles which are related by a twist angle θ = 35°

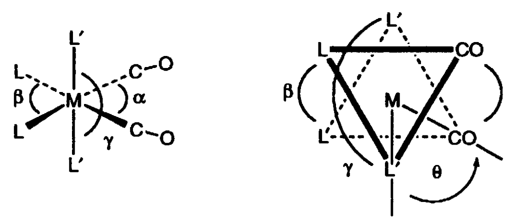
Table 4 Final atomic coordinates (fractional × 10^4) for $[W(SC_6H_2Me_3\text{-}2,4,6)_2(CO)_2(PMe_2Ph)_2]\cdot C_6H_5Me$ **3** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	6500(1)	5699(1)	6972(1)	C(28)	4228(6)	7759(4)	8770(4)
S(1)	7317(1)	5166(1)	7608(1)	C(29)	4608(5)	7148(4)	6924(3)
S(2)	6469(1)	6854(1)	7035(1)	C(31)	8332(4)	5230(4)	6173(3)
P(1)	7916(1)	5885(1)	6569(1)	C(32)	8286(7)	5226(5)	5648(3)
P(2)	5942(1)	4636(1)	6651(1)	C(33)	8565(8)	4718(7)	5366(4)
O(1)	4824(3)	5631(3)	7555(2)	C(34)	8903(8)	4175(7)	5630(6)
O(2)	5993(4)	6041(3)	5836(2)	C(35)	8978(6)	4176(5)	6147(5)
C(1)	5446(5)	5649(3)	7342(2)	C(36)	8687(5)	4694(4)	6418(4)
C(2)	6147(5)	5909(4)	6257(3)	C(37)	8744(5)	6043(4)	7019(3)
C(11)	6821(4)	4694(3)	8085(3)	C(38)	7967(5)	6594(4)	6151(3)
C(12)	6975(5)	4013(4)	8103(3)	C(41)	5061(5)	4674(4)	6215(3)
C(13)	6569(6)	3638(4)	8461(3)	C(42)	4313(6)	4872(5)	6391(4)
C(14)	6019(6)	3895(4)	8810(3)	C(43)	3630(6)	4888(7)	6078(4)
C(15)	5909(5)	4563(4)	8814(3)	C(44)	3684(7)	4683(6)	5593(4)
C(16)	6312(4)	4969(3)	8462(3)	C(45)	4421(8)	4479(6)	5400(4)
C(17)	7600(6)	3713(4)	7749(4)	C(46)	5101(6)	4470(4)	5715(3)
C(18)	5532(7)	3472(5)	9181(4)	C(47)	5539(5)	4098(3)	7149(3)
C(19)	6219(5)	5691(3)	8526(3)	C(48)	6665(5)	4118(4)	6312(3)
C(21)	5818(4)	7124(3)	7542(3)	C(1S)	8532(6)	7981(4)	5197(3)
C(22)	6146(4)	7244(3)	8034(3)	C(2S)	9062(5)	7502(5)	5014(4)
C(23)	5619(5)	7440(3)	8424(3)	C(3S)	8746(7)	6957(5)	4767(4)
C(24)	4785(5)	7532(3)	8337(3)	C(4S)	7900(8)	6890(5)	4702(4)
C(25)	4480(5)	7431(3)	7850(3)	C(5S)	7371(5)	7369(6)	4885(4)
C(26)	4986(4)	7229(3)	7449(3)	C(6S)	7687(6)	7914(5)	5132(4)
C(27)	7052(5)	7183(4)	8141(3)	C(7S)	8878(10)	8577(5)	5468(5)

Table 5 Selected molecular dimensions (lengths in Å, angles in °) in $[W(SC_6H_2Me_3\text{-}2,4,6)_2(CO)_2(PMe_2Ph)_2]\cdot C_6H_5Me$ **3** with e.s.d.s in parentheses

(*a*) About the W atom			
W–S(1)	2.385(2)	W–C(2)	1.991(8)
W–S(2)	2.379(2)	W–P(1)	2.556(2)
W–C(1)	1.967(7)	W–P(2)	2.507(2)
S(1)–W–S(2)	115.02(6)	S(2)–W–P(2)	152.06(7)
S(1)–W–C(1)	97.0(2)	C(1)–W–C(2)	102.5(3)
S(1)–W–C(2)	154.9(2)	C(1)–W–P(1)	172.7(2)
S(1)–W–P(1)	81.46(6)	C(1)–W–P(2)	78.6(2)
S(1)–W–P(2)	91.83(6)	C(2)–W–P(1)	81.1(2)
S(2)–W–C(1)	90.0(2)	C(2)–W–P(2)	76.9(2)
S(2)–W–C(2)	80.9(2)	P(1)–W–P(2)	108.63(6)
S(2)–W–P(1)	84.17(6)		
(*b*) In the thiolate ligands			
S(1)–C(11)	1.767(7)	C(11)–S(1)–W	118.9(2)
S(2)–C(21)	1.777(7)	C(21)–S(2)–W	112.0(2)
(*c*) In the carbonyl ligands			
O(1)–C(1)	1.152(8)	O(1)–C(1)–W	178.7(6)
O(2)–C(2)	1.152(8)	O(2)–C(2)–W	175.7(7)
(*d*) In the phosphine ligands			
P(1)–C(31)	1.821(7)	P(2)–C(41)	1.826(8)
P(1)–C(37)	1.811(7)	P(2)–C(47)	1.823(7)
P(1)–C(38)	1.817(7)	P(2)–C(48)	1.813(7)
W–P(1)–C(31)	117.0(2)	W–P(2)–C(41)	116.9(2)
W–P(1)–C(37)	115.5(3)	W–P(2)–C(47)	114.9(2)
W–P(1)–C(38)	113.9(3)	W–P(2)–C(48)	115.9(3)
C(31)–P(1)–C(37)	102.8(4)	C(41)–P(2)–C(47)	100.7(4)
C(31)–P(1)–C(38)	103.8(4)	C(41)–P(2)–C(48)	103.4(4)
C(37)–P(1)–C(38)	102.0(4)	C(47)–P(2)–C(48)	102.8(4)

equatorial π-acid isocyanide ligands.[4] Both these complexes have π-acid ligands in the axial positions with a *trans* angle of approximately 174°, near to the expected angle of 180°. Both have π-basic thiolate ligands with angles β [116.0(1) and 115.3(1)°] which are larger than the expected angle of 90°. A calculation on $[Mo(SH)_2(CNH)_4]$ gave a predicted angle β of 102.5°, closer to the observed angle for **5**.[4] As an alternative to the angles shown in Fig. 6, we could have chosen α as C(3)–Mo–C(5) [83.0(2)°], the smaller angle between *cis*-CO groups. This would give a β angle S(1)–Mo–C(4) of 87.7(1)°, which is close to the expected value of 90°. However, the γ angle S(2)–Mo–P(6) is then only 157.6°. Hence we prefer the orientation of **1** shown in Fig. 6. As expected from their similar geometries, **1** and **5** have similar θ values (48° and 50°, respectively; see Fig. 6). In the calculation of the twist angle each triangle always contained one sulfur atom.



class 1	class 2	class 3
α < 90°	α > 90°	α > 90°
β ≈ 90°	β < 90°	β < 90°
γ ≈ 180°	γ < 180°	γ < 180°
θ ≈ 60°	θ ≈ 30°	θ ≈ 0°

Fig. 5 Angles used to classify the molecular distortions

The green complex **3** is a distorted octahedral complex of class 2 with an angle α of greater than 90° and an average twist angle θ of 35°. The related green molybdenum complex $[Mo(SC_6H_2Me_3\text{-}2,4,6)_2(CO)_2(PMe_2Ph)_2]$ is also likely to have this structure.

The burgundy complex **4** is structurally similar to the red complexes **6**[5] as noted above. All of these complexes have wide C–M–C angles α and are rare examples of complexes with monodentate ligands which have nearly trigonal-prismatic stereochemistry. They are all of class 3 (Fig. 6).

All the complexes discussed and classified in Fig. 6 are formally 16-electron species. If the metal centre is to supplement its electron count, it could undergo donation of unpaired electrons from the thiolate lone-pairs. Such pπ-dπ donation to the metal is indicated by a shortening of the M–S bond length

Table 6 Final atomic coordinates (fractional × 10^4) for $[W(SeC_6H_3Pr^i{}_2\text{-}2,6)_2(CO)_2(PMe_2Ph)_2]$ **4** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	2529(1)	1993(1)	1349(1)	C(31)	1203(7)	2346(4)	−320(3)
Se(1)	1717(1)	2821(1)	466(1)	C(32)	1915(8)	2494(5)	−789(4)
Se(2)	2787(1)	3290(1)	1889(1)	C(33)	1515(12)	2208(7)	−1358(4)
P(1)	1611(2)	1583(1)	2248(1)	C(34)	485(14)	1779(7)	−1478(5)
P(2)	3834(2)	1245(1)	758(1)	C(35)	−224(10)	1644(6)	−1033(5)
O(1)	4754(5)	1548(3)	2326(3)	C(36)	106(8)	1934(5)	−436(4)
O(2)	923(6)	594(3)	916(3)	C(37)	3031(8)	3001(5)	−685(4)
C(1)	3902(8)	1693(4)	1950(4)	C(38)	4094(10)	2762(6)	−1028(5)
C(2)	1526(7)	1123(5)	1070(4)	C(39)	2672(10)	3820(5)	−831(5)
C(11)	−23(7)	1786(4)	2164(4)	C(40)	−783(8)	1864(5)	24(5)
C(12)	−475(10)	2405(7)	1886(7)	C(41)	−1693(9)	2511(6)	−56(5)
C(13)	−1698(10)	2605(7)	1848(7)	C(42)	−1474(9)	1123(6)	6(5)
C(14)	−2506(9)	2159(6)	2060(5)	C(51)	2765(7)	4159(4)	1346(3)
C(15)	−2080(10)	1514(7)	2321(5)	C(52)	1681(7)	4588(4)	1193(3)
C(16)	−859(9)	1318(6)	2374(5)	C(53)	1756(7)	5263(4)	879(4)
C(17)	1731(8)	576(5)	2423(4)	C(54)	2840(8)	5497(5)	698(4)
C(18)	2157(9)	2009(5)	2979(4)	C(55)	3863(8)	5055(4)	831(4)
C(21)	4621(9)	424(5)	1133(4)	C(56)	3845(7)	4378(4)	1139(3)
C(22)	3917(11)	−174(5)	1276(5)	C(57)	459(7)	4356(5)	1356(4)
C(23)	4470(16)	−816(7)	1552(7)	C(58)	54(9)	4839(8)	1849(5)
C(24)	5707(18)	−852(8)	1692(7)	C(59)	−548(8)	4360(6)	809(4)
C(25)	6404(14)	−268(8)	1557(6)	C(60)	5049(7)	3932(4)	1276(4)
C(26)	5876(10)	371(6)	1277(5)	C(61)	5731(8)	3892(5)	727(4)
C(27)	3176(9)	838(5)	34(4)	C(62)	5845(9)	4257(6)	1832(4)
C(28)	5066(8)	1821(5)	547(4)				

Table 7 Selected molecular dimensions (lengths in Å, angles in °) in $[W(SeC_6H_3Pr^i{}_2\text{-}2,6)_2(CO)_2(PMe_2Ph)_2]$, **4** with e.s.d.s in parentheses

(*a*) About the W atom			
W–Se(1)	2.506(1)	W–P(2)	2.467(2)
W–Se(2)	2.583(1)	W–C(1)	1.942(8)
W–P(1)	2.471(2)	W–C(2)	1.943(8)
Se(1)–W–Se(2)	81.2(1)	Se(2)–W–C(2)	150.5(3)
Se(1)–W–P(1)	131.4(1)	P(1)–W–C(1)	74.5(3)
Se(1)–W–P(2)	93.8(1)	P(1)–W–C(2)	75.2(3)
Se(1)–W–C(1)	148.5(3)	P(1)–W–P(2)	127.6(1)
Se(1)–W–C(2)	95.2(2)	P(2)–W–C(1)	76.3(3)
Se(2)–W–P(1)	85.2(1)	P(2)–W–C(2)	75.7(3)
Se(2)–W–P(2)	133.6(1)	C(1)–W–C(2)	110.7(3)
Se(2)–W–C(1)	84.3(2)		
(*b*) In the selenolate ligands			
Se(1)–C(31)	1.945(8)	W–Se(1)–C(31)	118.3(2)
Se(2)–C(51)	1.950(7)	W–Se(2)–C(51)	114.9(2)
(*c*) In the carbonyl ligands			
O(1)–C(1)	1.191(10)	W–C(1)–O(1)	176.5(7)
O(2)–C(2)	1.169(10)	W–C(2)–O(2)	178.5(8)
(*d*) In the phosphine ligands			
P(1)–C(11)	1.819(8)	P(2)–C(21)	1.829(9)
P(1)–C(17)	1.823(9)	P(2)–C(27)	1.813(9)
P(1)–C(18)	1.812(8)	P(2)–C(28)	1.811(9)
W–P(1)–C(11)	111.9(3)	W–P(2)–C(21)	117.2(3)
W–P(1)–C(17)	115.7(3)	W–P(2)–C(27)	119.6(3)
W–P(1)–C(18)	118.6(3)	W–P(2)–C(28)	110.6(3)
C(11)–P(1)–C(17)	104.7(4)	C(21)–P(2)–C(27)	101.1(4)
C(11)–P(1)–C(18)	101.9(4)	C(21)–P(2)–C(28)	103.9(4)
C(17)–P(1)–C(18)	102.2(4)	C(27)–P(2)–C(28)	102.4(4)

and the opening up of the M–S–C angle.[14] This is not easily demonstrated in the presence of considerable steric effects within complexes such as the present ones. The essentially trigonal-prismatic complexes **6** have unequal M–S bond lengths, with the longer one at approximately 2.46 Å being associated with a smaller M–S–C angle of about 117°, while the shorter M–S distance of 2.395(1) Å goes with a larger angle of 121–123°. Complex **4** shows the same trend, with a shorter W–Se(1) at 2.506(1) Å having a W–Se(1)–C(31) angle of 118.3(2)°, whilst the longer W–Se(2) at 2.583(1) Å has the smaller angle W–Se(2)–C(51) of 114.9(2)°. However, although complex **1** shows this trend, complexes **2** and **3** have fairly equal Mo–S or W–S bond lengths with quite different angles. Therefore it is not certain that the opening of the M–S–C angle is entirely electronic in origin; it would in fact be rather surprising if these angles were unaffected by the steric bulk of the thiolate ligands.

As pointed out by Hoffman and co-workers,[2–4] the distortions we have classified in Fig. 6 are a consequence of the d^4 configuration of **1**–**6** and their analogues. It is known that complexes of this general formulation having a d^6 configuration display essentially regular octahedral geometry, *e.g.* in *trans*,*trans*,*trans*-$[Os(SC_6F_5)_2(CO)_2(PEt_2Ph)_2]$.[15]

Conclusion

We have shown that reaction of the unsaturated thiolatohydrides $[MoH(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(PMePh_2)_2]$ and $[WH(ER)_3(PMe_2Ph)_2]$ (ER = $SC_6H_2Me_3$-2,4,6 or $SeC_6H_3Pr^i{}_2$-2,6) with carbon monoxide results in the reductive elimination of thiol (or selenol) and formation of the new six-co-ordinate, d^4, carbonyl species *mer*-$[Mo(SC_6H_2Pr^i{}_3\text{-}2,4,6)_2(CO)_3(PMePh_2)]$ **1**, $[Mo(SC_6H_2Pr^i{}_3\text{-}2,4,6)_2(CO)_2(PMePh_2)_2]$ **2**, $[W(SC_6H_2Me_3\text{-}2,4,6)_2(CO)_2(PMe_2Ph)_2]$ **3** and $[W(SeC_6H_3Pr^i{}_2\text{-}2,6)_2(CO)_2(PMe_2Ph)_2]$ **4**. Their structures show distortions from regular octahedral or trigonal-prismatic geometries which are predominantly electronic in origin, and can be conveniently classified into three general types by analysis of the angular properties of subunits of their structures.

Experimental

All operations were performed under an atmosphere of dinitrogen. The carbonyl complexes in both the solution and solid-state were not very sensitive to exposure to air. All solvents were dried and degassed before use. The molybdenum–phosphine starting materials,[16–18] the tungsten starting materials,[1,5,11] complex **3**[5] and the thiols[10] were prepared by literature methods. Spectroscopic measurements were made

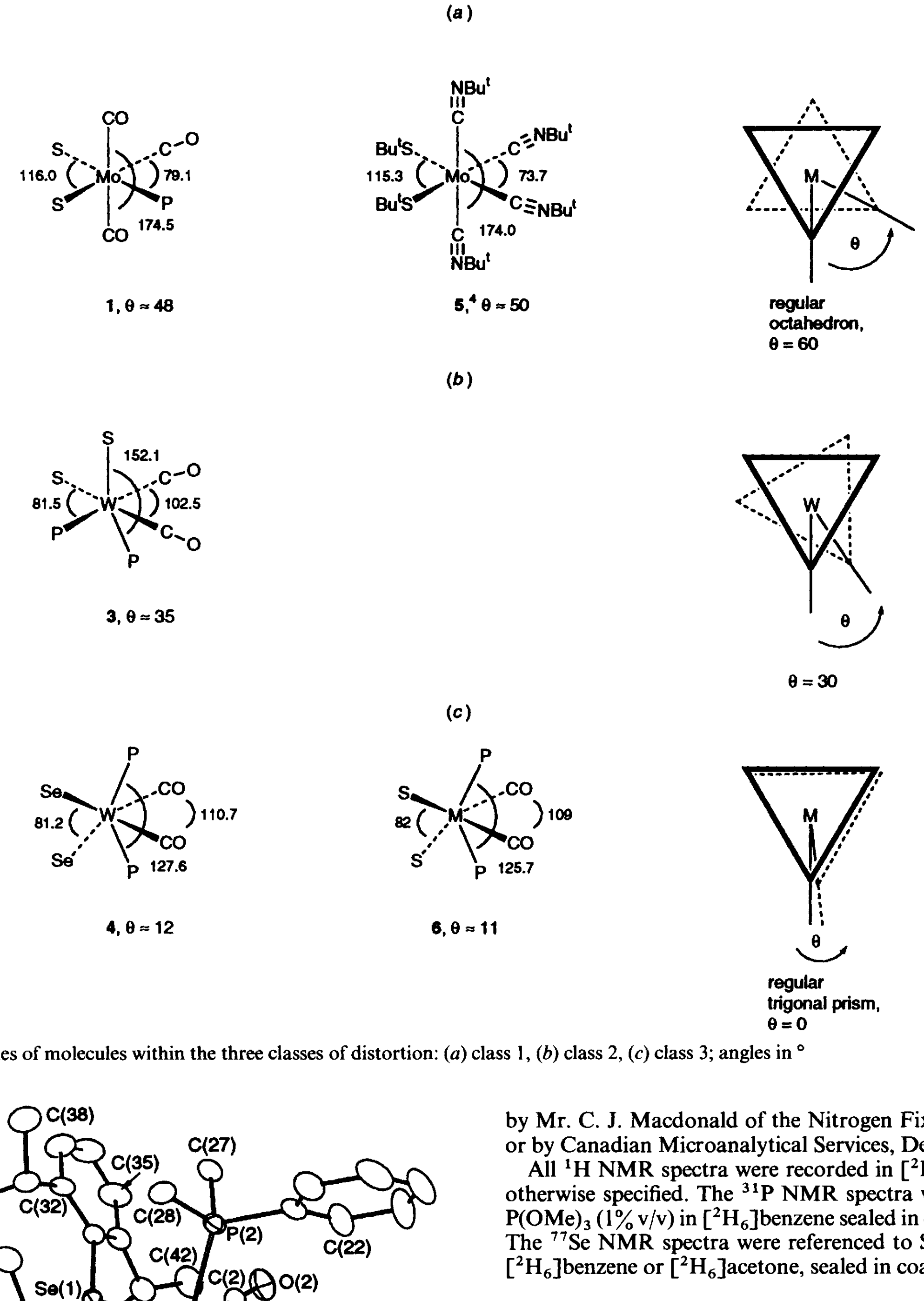


Fig. 6 Examples of molecules within the three classes of distortion: (*a*) class 1, (*b*) class 2, (*c*) class 3; angles in °

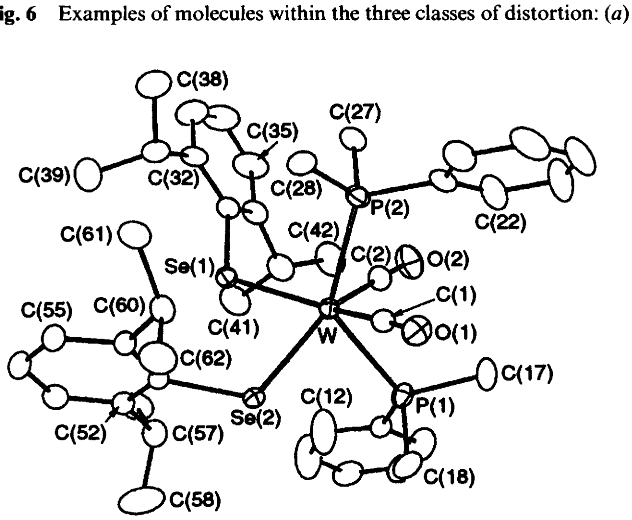


Fig. 7 Molecular structure of $[W(SeC_6H_3Pr^i_2\text{-}2,6)_2(CO)_2(PMe_2Ph)_2]$ **4**

with JEOL GX270 (NMR), Perkin-Elmer SP3–200 (IR), Nicolet 5DX (FTIR) and VG70–250S [fast atom bombardment (FAB) mass spectra] instruments. Matrices used for the FAB mass spectra were *o*-nitrophenyl octyl ether (npoe), *m*-nitrobenzyl alcohol (nba) or benzene–nba. The largest peak of the isotopic envelope is reported. Microanalyses were determined by Mr. C. J. Macdonald of the Nitrogen Fixation Laboratory or by Canadian Microanalytical Services, Delta, B.C.

All ^1H NMR spectra were recorded in $[^2H_6]$benzene unless otherwise specified. The ^{31}P NMR spectra were referenced to $P(OMe)_3$ (1% v/v) in $[^2H_6]$benzene sealed in coaxial capillaries. The ^{77}Se NMR spectra were referenced to $SeMe_2$ (1% v/v) in $[^2H_6]$benzene or $[^2H_6]$acetone, sealed in coaxial capillaries.

Preparations.—mer-*Tricarbonyl(methyldiphenylphosphine)bis(2,4,6-triisopropylbenzenethiolato)molybdenum*(II) **1**. Dry carbon monoxide gas was bubbled through a cold, stirred solution of $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMePh_2)]$ in thf under dinitrogen to produce an instant change from green to red. After stirring for 30 min the volume of the reaction solution was reduced to a minimum in a vacuum. Slow precipitation of the product with cold methanol afforded a mixture of red *crystals* in a ratio of 4:1 which were then collected by filtration and washed with methanol. The major product was separated by hand (60% yield) (Found: C, 64.1; H, 7.1; S, 7.3. $C_{46}H_{59}MoO_3PS_2$ requires: C, 64.9; H, 6.9; S, 7.5%).

Dicarbonylbis(methyldiphenylphosphine)bis(2,4,6-triisopropylbenzenethiolato)molybdenum(II) **2**. The compounds $[MoH_4(PMePh_2)_4]$ (0.42 g, 0.44 mmol) and $HSC_6H_2Pr^i_3\text{-}2,4,6$ (0.3 cm^3) were reacted in cold thf solution (30 cm^3) for 4 h to produce $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMePh_2)]$. Carbon monoxide gas was then bubbled through this reaction mixture for

Table 8 Summary of crystal data, details of intensity collection and least-squares refinement parameters

Compound	1	3	4
Empirical formula	$C_{46}H_{59}MoO_3PS_2 \cdot 0.5C_4H_8O$	$C_{36}H_{44}O_2P_2S_2W \cdot C_7H_8$	$C_{42}H_{56}O_2P_2Se_2W$
Crystal colour, size/mm	Dark red-brown prism, 0.14 × 0.24 × 0.52	Green needle, 0.25 × 0.35 × 0.30	Burgundy block, 0.20 × 0.15 × 0.18
Crystal mounting	In glass capillary	Sealed in epoxy resin	Sealed in epoxy resin
M	887.1	910.76	996.6
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$ (equiv. to no. 14)	$P2_12_12_1$ (no. 19)	$P2_1/n$ (equiv. to no. 14)
a/Å	23.747(3)	16.245(2)	11.018(1)
b/Å	10.998(1)	20.544(2)	17.677(4)
c/Å	18.694(3)	25.956(2)	22.193(4)
β/°	100.303(10)	90.00	98.26(1)
U/Å^3	4803.3(11)	8662.5(15)	4277(2)
Z	4	8	4
D_c/g cm^{-3}	1.227	1.397	1.547
$F(000)$	1872	3696	1984
μ(Mo-Kα)/mm^{-1}	0.42	2.870	4.509
ω scan width/°	$0.7 + 0.35 \tan\theta$	$0.60 + 0.35 \tan\theta$	$0.70 + 0.35 \tan\theta$
θ range/°	1.5–23 ($h,k,\pm l$)	1.57–26.98 (h,k,l)	1.15–25.0 ($\pm h,k,l$)
Absorption correction: min, max. transmission	0.99, 1.00	0.3747, 0.8089	0.4091, 0.7184
Total no. of reflections recorded	7677	9429	8079
No. of unique reflections	6656	9429	7512
R_{int}	0.031	—	0.094
No. of 'observed' reflections	4457 ($I > 2\sigma_I$)	5156 ($I > 2\sigma_I$)	4549 ($I > 3\sigma_I$)
No. of reflections used in refinement	6656	9429	4549
Refinement method	Large-block-matrix least-squares on F	Full-matrix least-squares on F^2	Full-matrix least-squares on F
Final R indices[a]	$R = 0.067$, $R' = 0.048$ (all data)	$R = 0.116$, $wR2 = 0.115$ (all data)[b]	$R = 0.034$, $R' = 0.041$ ($I > 3\sigma_I$)
Weighting scheme	$w = (\sigma_F^2 + 0.000\,20F^2)^{-1}$	$w = 1/[\sigma^2(F_o) + (0.0472P)^2 + 18.0331P]$[c]	$w = 1/[\sigma^2(F_o) + 0.0008(F_o)^2]$
Largest, mean Δ/σ	0.54, 0.02	0.09, 0.02	0.01, 0.00
Parameters refined	682	402	327
Max., min. electron density in final difference map/e Å^{-3}	0.45, −0.50	1.03, −0.52	0.72, −0.55

[a] Definition of indices: $R = \Sigma(F_o - F_c)/\Sigma F_o$; $R' = [\Sigma w(F_o - F_c)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$. [b] For observed data only: $R = 0.037$, $wR2 = 0.091$. [c] Where $P = (F_o^2 + 2F_c^2)/3$.

30 min, producing a red solution. Reduction of the reaction solution volume followed by slow precipitation of the product with cold methanol yielded red *crystals* (0.08 g, 17%) (Found: C, 67.0; H, 7.6; S, 5.7. $C_{58}H_{72}MoO_2P_2S_2$ requires: C, 68.0; H, 7.1; S, 6.3%).

Dicarbonylbis(2,6-*diisopropylbenzeneselenolato*)*bis*(*dimethylphenylphosphine*)*tungsten*(II) **4**. The complex $[WH(SeC_6H_3\text{-}Pr^i_2\text{-}2,6)_3(PMe_2Ph)_2]$ (0.430 g, 0.363 mmol) was dissolved in toluene (10 cm^3). The mixture was then flushed with CO by three evacuate-backfill cycles. The Schlenk flask (total volume of about 50 cm^3) was sealed off and the solution was left stirring. Within minutes, the solution had turned redder and after 1 h the solution was deep red. The flask was purged with argon by two evacuate-backfill cycles and left stirring for 2 h. The toluene was removed *in vacuo*, the residue taken up in toluene (*ca.* 2 cm^3), layered with methanol (10 cm^3) and stored at −30 °C for 20 h. The burgundy microcrystalline *powder* was filtered off, washed with methanol and dried *in vacuo*. Yield: 0.162 g (16.2%). NMR: ^1H δ (fluxional) 7.52 (m, 6 H, $SeC_6H_3Pr^i_2$, PMe_2Ph), 7.2 (m, 10 H, $SeC_6H_3Pr^i_2$, PMe_2Ph), 3.65 [sept, 4 H, $SeC_6H_3(CHMe_2)_2$], 1.65 (d, 12 H, PMe_2Ph), 1.2 [overlapping, 24 H, $SeC_6H_3(CHMe_2)_2$]; $^{31}P\text{-}\{^1H\}$ δ −138.5 (s, $^1J_{PW}$ = 107, $^2J_{SeP}$ not observed); $^{77}Se\text{-}\{^1H\}$ δ 425 (br), 590 (br). FAB mass spectrum: *m*/*z* 996 (M^+), 968 (M^+ − CO), 858 (M^+ − PMe_2Ph), 830 (M^+ − CO − PMe_2Ph), 802 (M^+ − 2CO − PMe_2Ph), 757 (M^+ − $SeC_6H_3Pr^i_2$), 699 (M^+ − $SeC_6H_3Pr^i_2$ − 2CO), 561 (M^+ − $SeC_6H_3Pr^i_2$ − 2CO − PMe_2Ph), 479 ($Pr^i_2H_3C_6SeSeC_6H_3Pr^i_2$) (Found: C, 50.9; H, 5.6. $C_{42}H_{56}O_2P_2Se_2W$ requires C, 50.6; H, 5.7%).

Crystal Structure Analyses.—Crystal data and experimental details are summarised in Table 8.

Following very similar procedures, intensity measurements were recorded on Enraf-Nonius CAD4 diffractometers with monochromated Mo-Kα radiation (λ = 0.710 69 Å) at room temperature. An ω–θ or ω–2θ scan technique was used, with variable scan speeds. There was little or no crystal deterioration noted from the measurements of the intensity control reflections.

Diffraction intensities were corrected for Lorentz-polarisation effects, slight deterioration (in **1** only), absorption (by semi-empirical ψ scan methods) and (for **1**) to eliminate negative net intensities (by Bayesian statistical methods). For the three structures, the metal atoms were located by the Patterson method, and remaining non-hydrogen atoms were located in successive Fourier and Fourier-difference syntheses. All non-hydrogen atoms (except those in the solvent molecules in **1** and **3**) were refined with anisotropic thermal parameters. Hydrogen atoms of phenyl and methine groups were included in idealised positions, riding on the parent carbon atoms; those in methyl groups were refined with geometrical constraints. In **1**, a thf molecule is disordered (and not fully resolved) about a centre of symmetry; in **3**, a toluene molecule was included as a rigid group with fixed geometry. Refinement was by least-squares methods, details of which are in Table 8.

Scattering factor curves for neutral atoms were from ref. 19. Computer programs used in the analyses include SHELX[20] and others listed in ref. 21 (using a DEC MicroVAX II computer) and SHELXTL PC[22] and SHELXL 93[23] (on a 486–66 personal computer).

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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