Journal of Organometallic Chemistry, 341 (1988) 373–380
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Iron–molybdenum and iron–tungsten sulphido clusters containing hydrazido(2 –) ligands. The synthesis and X-ray crystal and molecular structure of $[\{Fe(CO)_3(\mu_3\text{-}S)\}_2Mo(NNMe_2)_2(PPh_3)](\mathit{Fe\text{–}Fe}) \cdot CH_2Cl_2$ *

Peter T. Bishop, Jonathan R. Dilworth*, Stephen Morton,

Department of Chemistry and Biological Chemistry, University of Essex, Colchester, CO4 3SQ (Great Britain)

and Jon A. Zubieta

Chemistry Department, State University of New York at Albany, Albany, N.Y. 12222 (U.S.A.)

(Received November 6th, 1987)

Abstract

Treatment of $[MCl(NNRR')_2(PPh_3)_2]Cl$ (M = Mo or W; R,R' = Me_2 or Me, Ph) with $[\{Fe(CO)_3(\mu_2\text{-}SLi)\}_2](\mathit{Fe\text{-}Fe})$ gives the trinuclear clusters $[\{Fe(CO)_3(\mu_3\text{-}S)\}_2M(NNRR')_2(PPh_3)](\mathit{Fe\text{-}Fe})$ in good yield. The X-ray crystal structure of $[\{Fe(CO)_3(\mu_3\text{-}S)\}_2Mo(NNMe_2)_2(PPh_3)] \cdot CH_2Cl_2$ (space group $P2_12_12_1$,; *a* 15.089(4), *b* 15.569(5), *c* 16.983(4) Å; $Z = 4$; $R = 0.061$ for 1915 observed reflections) confirms the absence of iron–molybdenum bonding, and the complexes generally show similar Mössbauer parameters. Analogous coordination environments at molybdenum are obtained in $[Mo(NNMePh)_2(C_7H_6S_2)(PPh_3)]$ ($C_7H_6(SH)_2$ = 3,4-dimercaptotoluene) and in the dimeric species $[\{Mo(NNMePh)_2(\mu_2\text{-}S)(PPh_3)\}_2]$. These are prepared by reaction of $[MoCl(NNMePh)_2(PPh_3)_2]Cl$ with 3,4-dimercaptotoluene and $S(SiMe_3)_2$, respectively.

Introduction

As an iron-molybdenum-sulphido cluster is involved at the active site in the enzyme nitrogenase, there is considerable interest in the chemistry of these species. However, none of the clusters reported to date contain ligands such as dinitrogen (N_2), diazenide (N_2R), or hydrazide(2 –) (NNR_2). Since such ligands are proven intermediates in the protonation and alkylation reactions of dinitrogen at a

---

* Dedicated to Professor C. Eaborn on the occasion of his 65th birthday.

Table 1

Spectroscopic properties of the complexes

Complex		Mössbauer [a]		^{31}P NMR [b]	^{1}H NMR [b]	
		δ (mm s^{-1})	Δ (mm s^{-1})	(δ(ppm))	(δ(ppm))	
$[\{Fe(CO)_3(\mu_3\text{-}S)\}_2Mo(NNMe_2)_2(PPh_3)]$	**(1)**	0.033(3)	0.800(4)	35.4	7–8(m,15H)	3.1(s,12H)
$[\{Fe(CO)_3(\mu_3\text{-}S)\}_2Mo(NNMePh)_2(PPh_3)]$	**(2)**	0.064(3)	0.752(5)	30.9	6.6–8(m,25H)	3.3(s,6H)
$[\{Fe(CO)_3(\mu_3\text{-}S)\}_2W(NNMe_2)_2(PPh_3)]$	**(3)**	0.033(5)	0.771(8)	36.4	7–8(m,15H)	3.2(s,12H)
$[\{Fe(CO_3(\mu_3\text{-}S)\}_2W(NNMePh)_2(PPh_3)]$	**(4)**	0.090(6)	0.786(10)	36.4	6.6–8(m,25H)	3.3(s,6H)
$[Mo(NNMePh)_2(PPh_3)(C_7H_6S_2)]$	**(5)**	–			6.6–7.7(m,18H)	3.4(s,6H) 2.3 (s,3H)
$[\{Mo(NNMePh)_2(PPh_3)(\mu_2\text{-}S)\}_2]$	**(6)**	–		39.8	6.7–7.9(m,25H)	3.4(d,6H; ^{5}J(PH) 0.5 Hz)
$[\{Fe(CO)_3(\mu_3\text{-}S)\}_2Mo(NNMe_2)_2(PMe_3)]$	**(7)**	0.060(1)	0.707(2)	1.1	3.3(s,12H)	1.4(d,9H; ^{2}J(PH 6.6 Hz)

[a] At 78 K. [b] In $CDCl_3$; $\delta(^{31}P)$ relative to 85% H_3PO_4; $\delta(^{1}H)$ relative to $SiMe_4$.

molybdenum site, we have now extended previous studies of complexes of such ligands [1–3] to the synthesis of the first reported iron–molybdenum and iron–tungsten sulphido-bridged clusters containing hydrazido(2 −) ligands.

It has previously been shown that $[\{Fe(CO)_3(\mu_2\text{-}SLi)\}_2]$, prepared from $[Fe_2S_2(CO)_6]$ and $Li[BHEt_3]$ in tetrahydrofuran (thf), reacts with a variety of metal and non-metal dihalides, L_nMX_2, to give clusters of the general type $[\{Fe(CO)_3(\mu_3\text{-}S)\}_2ML_n]$ [3–9], and this provides a convenient starting point for our synthesis.

Results and discussion

The dilithium salt $[\{Fe(CO)_3(\mu_2\text{-}SLi)\}_2]$ reacts with the hydrazido(2 −) complexes $[MCl(NNRR')_2(PPh_3)_2]Cl$ (M = Mo or W; R,R′ = Me_2 or Me, Ph) in tetrahydrofuran to give the air-stable light-brown clusters $[\{Fe(CO)_3(\mu_3\text{-}S)\}_2M(NNRR')_2(PPh_3)](\textit{Fe-Fe})$ (**1–4**), with the elimination of PPh_3. The reaction proceeds in high yield (ca. 70%) for M = Mo, but the yield is lower (ca. 50%) for M = W, probably because substitution at the less labile tungsten centre is slower and competing reactions become significant.

The ^1H NMR spectra (Table 1) confirm the presence of the hydrazido(2 −) ligand and a single tertiary phosphine ligand, the latter giving the expected singlet in the $^{31}P\{^1H\}$ NMR spectra. The infrared spectra (CH_2Cl_2 solution) of the carbonyl region show bands characteristic of the $Fe_2(CO)_6$ unit (1960sh, 1973s, 2004s, and 2046s cm^{-1}), which do not vary significantly from one complex to another. Similarly, the Mössbauer parameters for the complexes, although distinct from those for $[\{Fe(CO)_3(\mu_2\text{-}S)\}_2]$ (δ 0.068, Δ 1.088 mm s^{-1} at 77 K [10]; δ 0.08 Δ 1.11 mm s^{-1} at 4.2 K [11]), do not show much influence of M or R,R′ on the iron. Indeed, parameters obtained by us for $[\{Fe(CO)_3(\mu_3\text{-}S)\}_2Ni(Ph_2PCH_2CH_2PPh_2)]$ [5,11] (δ 0.051, Δ 0.723 mm s^{-1}) suggest that the nature of the bridging group, ML_n, has little effect on the iron environment.

A single crystal X-ray structure of $[\{Fe(CO)_3(\mu_3\text{-}S)\}_2Mo(NNMe_2)_2(PPh_3)] \cdot CH_2Cl_2$ (**1** $\cdot$ CH_2Cl_2) (Fig. 1) confirms the absence of iron–molybdenum bonding. Bond lengths and bond angles for **1** are given in Table 2.

In many respects the structure of **1** resembles that of $[(S_2MoS_2)Mo(NNMe_2)_2(PPh_3)]$ [3]. In both cases, the central molybdenum atom has approximately trigonal bipyramidal coordination, with the disulphide ligand spanning one axial and one equatorial site. However, whereas $[MoS_4]^{2-}$ has a bite angle of 94.1(3)°, the $\{Fe(CO)_3S\}_2$ unit has a bite angle of only 74.0(2)°, resulting in considerable distortion from the pure trigonal bipyramidal geometry. In particular, S(1) is considerably removed from its expected axial site. As in the tetrathiomolybdate complex, the equatorial Mo–S bond is markedly shorter than the axial Mo–S bond, although the difference is not as great in **1** as in $[(S_2MoS_2)Mo(NNMe_2)_2(PPh_3)]$. All M–L bonds are marginally longer in the present complex than in the tetrathiomolybdate analogue. Both complexes show one linear (Mo–N–N 178.2(1.5), 178.2(3.0)°) and one slightly bent (Mo–N–N 159.4(1.4), 165.0(3.0)°) hydrazide ligand. The causes of these distortions are not clear, but they do not appear to be electronic in origin.

The structure of the $\{Fe(CO)_3S\}_2$ subunit in **1** reflects the breaking of the S–S bond, with the sulphur–sulphur distance increasing from 2.007(5) Å [13] in $\{Fe(CO)_3S\}_2$ to 2.972 Å in **1**. This may be compared to the values in $[\{Fe(CO)_3\text{-}$

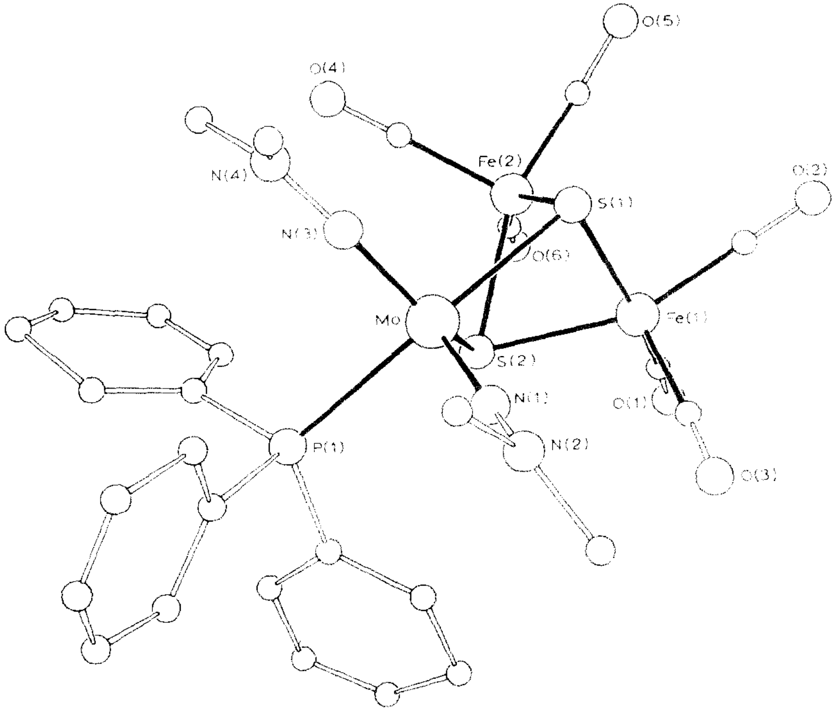

Fig. 1. An ORTEP view of the structure of $[Mo(NNMe_2)_2(PPh_3)\{S_2Fe_2(CO)_6\}]$ showing the atom-labelling scheme.

Table 2

Selected bond lengths and angles for **1**

(a) Bond lengths (Å)			
Mo–P	2.540(5)	Mo–S(1)	2.459(5)
Mo–S(2)	2.478(4)	Mo–N(1)	1.825(15)
Mo–N(3)	1.758(17)	Fe(1)–Fe(2)	2.520(4)
Fe(1)–S(1)	2.304(5)	Fe(1)–S(2)	2.302(5)
Fe(2)–S(1)	2.287(5)	Fe(2)–S(2)	2.296(6)
Fe–C(av)	1.772	C–O(av)	1.145
N(1)–N(2)	1.30(2)	N(3)–N(4)	1.34(3)
(b) Bond angles (°)			
P–Mo–S(1)	158.9(2)	P–Mo–S(2)	85.5(1)
S(1)–Mo–S(2)	74.0(2)	P–Mo–N(1)	91.6(5)
S(1)–Mo–N(1)	101.7(4)	S(2)–Mo–N(1)	117.0(5)
P–Mo–N(3)	90.9(5)	S(1)–Mo–N(3)	98.9(5)
S(2)–Mo–N(3)	130.7(5)	N(1)–Mo–N(3)	112.3(7)
Fe(2)–Fe(1)–S(1)	56.4(1)	Fe(2)–Fe(1)–S(2)	56.6(2)
Fe(1)–Fe(2)–S(1)	57.0(1)	Fe(1)–Fe(2)–S(2)	56.9(1)
S(1)–Fe(1)–S(2)	80.4(2)	S(1)–Fe(2)–S(2)	80.9(1)
Fe(1)–S(1)–Fe(2)	66.6(2)	Fe(1)–S(2)–Fe(2)	66.5(2)
Mo–S(1)–Fe(1)	93.3(2)	Mo–S(1)–Fe(2)	91.1(2)
Mo–S(2)–Fe(1)	92.9(2)	Mo–S(2)–Fe(2)	90.4(2)
Mo–N(1)–N(2)	159.4(14)	Mo–N(3)–N(4)	178.2(15)

SEt}$_2$] (2.932 Å) [14] and [{Fe(CO)$_2$(tipt)}$_2$] (2.806 Å) [15] (tiptH = 2,4,6-tri(isopropyl)thiophenol). The S–Fe–S bond angles in **1** are S(1)–Fe(2)–S(2), 80.9(2)°, S(1)–Fe(1)–S(2), 80.4(2)°, and S(1)–Mo–S(2), 74.0(2)°, respectively, so that the Fe_2S_2 butterfly does not appear to open significantly to allow for a larger bite angle at molybdenum. The {Fe(CO)$_3$(μ_3-S)}$_2$Mo unit in the present structure resembles one previously observed in the $[MoOFe_5S_6(CO)_{12}]^-$ anion [4].

In view of the wide range apparently possible for the S–Mo–S bond angle, it was anticipated that other bidentate dianionic sulphur donors should form complexes of this type, and this is indeed the case. Treatment of [MoCl(NNMePh)$_2$(PPh$_3$)$_2$]Cl with the lithium salt of 3,4-dimercaptotoluene results in the formation of [Mo(NNMePh)$_2$(3,4-S$_2$C$_6$H$_3$Me)(PPh$_3$)] (**5**). Treatment of [MoCl(NNMePh)$_2$(PPh$_3$)$_2$]Cl with S(SiMe$_3$)$_2$ results in the formation of the symmetrical dimer [{Mo(NNMePh)$_2$(μ_2-S)(PPh$_3$)}$_2$] (**6**). In the latter complex, the methyl resonance in the ^{1}H NMR spectrum was observed as a close doublet (Table 1). Since none of the hydrazido-carbon atoms show any splitting in the ^{13}C{^{1}H} spectrum, it was concluded that this was a small, but finite, ^5J(PH) splitting and not due to inequivalence of the methyl groups.

The triphenylphosphine ligands in the complexes **1**–**4** are fairly labile. Thus treatment of **1** with an excess of more basic trimethylphosphine results in replacement of PPh$_3$ by PMe$_3$ without any other changes in the molecule.

In view of the small bite angle of the $[Fe_2(CO)_6S_2]^{2-}$ unit, it is not surprising that we have so far been unable to put two such subunits onto one molybdenum atom, for instance by metathesis with [MoCl$_4$(NNR$_2$)].

Experimental

All reactions were carried out in an atmosphere of dioxygen-free dinitrogen using dried, degassed solvents.

[{Fe(CO)$_3$S}$_2$] [5,16], [MoCl(NNMe$_2$)$_2$(PPh$_3$)$_2$]Cl [1], and [MoCl(NNMePh)$_2$(PPh$_3$)$_2$]Cl [1] were prepared by the literature methods.

^{1}H, ^{31}P and ^{13}C NMR spectra were recorded on a Bruker WP80 spectrometer in CDCl$_3$ solution, infrared spectra as Nujol mulls, and Mössbauer spectra of powdered samples were recorded in aluminium holders on a constant acceleration spectrometer, previously described [17]. The source was ca. 25 mCi of ^{57}Co in rhodium (obtained from the Radiochemical Centre, Amersham) at 20 °C. The source was moved with a saw-tooth wave form, and the spectra were computer-fitted. The velocity was calibrated, and the linearity of the waveform monitored, by reference spectra of 10 mg cm^{-2} iron foil, to which isomer shifts are referred. All spectra were recorded twice.

Crystal structure of complex [{Fe(Co)$_3$(μ_3-S)}$_2$Mo(NNMe$_2$)$_2$(PPh$_3$)] · CH$_2$Cl$_2$. Crystals of **1** · CH$_2$Cl$_2$ were grown from dichloromethane/diethyl ether at −30 °C. A crystal of **1** · CH$_2$Cl$_2$ of dimensions 0.30 × 0.25 × 0.30 mm, located in a thin walled glass capillary, was mounted on the Nicolet R3m diffractometer.

Crystal data for complex 1. $C_{28}H_{27}Fe_2MoN_4O_6P \cdot CH_2Cl_2$, M = 818.25, orthorhombic, space group $P2_12_12_1$, a 15.089(4), b 15.569(5), c 16.983(4) Å, V 3984.3 Å^3, $Z = 4$, $F(000) = 1688$, D_{calc} 1.362 g cm^{-3} Mo-K_α radiation (λ 0.71073 Å) μ 12.31 cm^{-1}.

Data collection. Data were collected using the ω–2θ scan mode for $2 < 2\theta < 45°$. No absorption correction was applied, but data were corrected for Lorentz and polarisation effects for 3008 reflections collected. 1915 reflections with $I > 3\sigma(I_0)$ were used in the structure analysis.

Structure solution and refinement. The iron and molybdenum atoms were located on a Patterson map, all other non-hydrogen atoms on subsequent Fourier difference syntheses. Anisotropic least-squares refinement with weights of $w = 1/\{\sigma^2(F_0) + 0.001(F_0)^2\}$ and fixed contributions from hydrogen atoms led finally to $R = 0.061$ and $R_w = 0.062$, with a goodness of fit (GOF) of 1.307. All calculations were performed on a General Nova computer using local versions of the Nicolet SHELXTL package. The atomic coordinates are given in Table 3.

*General method for the synthesis of compounds **1–4***

$[\{Fe(CO)_3(\mu_2\text{-}S)\}_2]$ (ca. 0.5 mmol) was dissolved in thf (10 cm^3) and cooled to −78 °C. Two equivalents of a 1.0 *M* solution of Li[BHEt$_3$] in thf were added to the solution, which was then stirred for 15 min at −78 °C. The solution was then warmed to room temperature, evaporated to dryness and the $[\{Fe(CO)_3(\mu_2\text{-}SLi)\}_2]$ redissolved in dry MeCN (25 cm^3). This solution was then cannulated into a solution of $[MCl(NNRR')_2(PPh_3)_2]Cl$ in MeCN (20 cm^3) and the mixture stirred for 3 h. After evaporating to dryness, the crude product was treated with MeOH (10 cm^3), filtered, washed with two further portions (5 cm^3) of MeOH, and dried. This product was then recrystallised from CH_2Cl_2/Et_2O.

The following complexes were prepared in this manner, using the quantities shown.

*Bis{dimethylhydrazido(2 −)}{di-μ_3-sulphidohexacarbonyldiiron(I)}(triphenylphosphine)molybdenum(VI)(Fe-Fe) (**1**).* $[\{Fe(CO)_3S\}_2]$ (0.507 g, 1.47 mmol), Li[BHEt$_3$] (3.05 cm^3, 3.05 mmol), and $[MoCl(NNMe_2)_2(PPh_3)_2]Cl$ (1.21 g, 1.50 mmol) yield 0.437 g, 69.4%. Analysis. Found: C, 41.3; H, 2.9; N, 6.8. $C_{28}H_{27}Fe_2MoN_4O_6PS_2$ calcd.: C, 41.1; H, 43.3; N, 6.9%.

*Bis{methylphenylhydrazido(2 −)}{di-μ_3-sulphidohexacarbonyldiiron(I)}(triphenylphosphine)molybdenum(VI)(Fe-Fe) (**2**).* $[\{Fe(CO)_3S\}_2]$ (0.173 g, 0.503 mmol), Li[BHEt$_3$] (1.01 cm^3, 1.01 mmol), and $[MoCl(NNMePh)_2(PPh_3)_2]Cl$ (0.471 g, 0.506 mmol) yield 0.360 g, 75.9%. Analysis. Found: C, 48.2; H, 3.0; N, 6.0. $C_{38}H_{31}Fe_2MoN_4O_6PS_2$ calcd.: C, 48.4; H, 3.3; N, 6.0%.

*Bis{dimethylhydrazido(2 −)}{di-μ_3-sulphidohexacarbonyldiiron(I)}(triphenylphosphine)tungsten(VI)(Fe-Fe) (**3**).* $[\{Fe(CO)_3S\}_2]$ (0.174 g, 0.506 mmol), Li[BHEt$_3$] (1.05 cm^3, 1.05 mmol), and $[WCl(NNMe_2)_2(PPh_3)_2]Cl$ (0.456 g, 0.509 mmol) yield 0.258 g, 56%. Analysis. Found: C, 37.5; H, 3.0; N, 5.9%. $C_{28}H_{27}Fe_2N_4O_6PS_2W$ calcd.: C, 37.1; H, 3.0; N, 6.2%.

*Bis{methylphenylhydrazido(2 −)}{di-μ_3-sulphidohexacarbonyldiiron(I)}(triphenylphosphine)tungsten(VI)(Fe-Fe) (**4**).* $[\{Fe(CO)_3S\}_2]$ (0.177 g, 0.515 mmol), Li[BHEt$_3$] (1.10 cm^3, 1.10 mmol), and $[WCl(NNMePh)_2(PPh_3)_2]Cl$ (0.525 g, 0.515 mmol) yield 0.20 g, 37.7%. Analysis. Found: C, 44.6; H, 3.1; N, 5.2. $C_{38}H_{31}Fe_2N_4O_6PS_2W$ calcd.: C, 44.3; H, 3.0; N, 5.3%.

*Bis{methylphenylhydrazido(2 −)}(2,3-toluenedithiolato)(triphenylphosphine)molybdenum(VI) (**5**).* A solution of 3,4-dimercaptotoluene (0.180 g, 1.15 mmol) in thf (10 cm^3) was treated with butyllithium (1.55 *M*; 1.50 cm^3, 2.33 mmol). A solution of $[MoCl(NNMePh)_2(PPh_3)_2]Cl$ (1.008 g, 1.08 mmol) in MeCN (25 cm^3) was added

Table 3

Atomic coordinates ($\times 10^4$) for $\mathbf{1} \cdot CH_2Cl_2$

Atom	*x*	*y*	*z*
Mo	2473(1)	1291(1)	1508(1)
Fe(1)	417(2)	524(2)	2087(2)
Fe(2)	667(2)	2073(2)	2455(2)
P	3862(3)	1030(3)	2319(3)
S(1)	901(3)	1554(3)	1212(3)
S(2)	1657(3)	999(3)	2746(3)
N(1)	2714(9)	371(10)	877(9)
N(2)	2992(13)	−62(14)	271(11)
N(3)	2919(10)	2251(12)	1135(9)
N(4)	3286(13)	2978(13)	858(10)
O(1)	−286(10)	−187(12)	3560(9)
O(2)	−1361(8)	610(12)	1431(10)
O(3)	1012(12)	−1071(11)	1379(12)
O(4)	1695(11)	3632(9)	2622(11)
O(5)	−931(12)	2909(12)	1849(10)
O(6)	33(14)	1860(13)	4070(8)
C(1)	19(13)	55(12)	2988(11)
C(2)	−659(12)	576(13)	1672(11)
C(3)	756(14)	−441(14)	1655(12)
C(4)	1318(14)	3040(13)	2544(14)
C(5)	−309(13)	2559(12)	2101(11)
C(6)	327(15)	1983(15)	3436(14)
C(7)	2849(17)	−1006(13)	225(15)
C(8)	3495(15)	343(16)	−336(15)
C(9)	3561(18)	2985(16)	86(15)
C(10)	3329(20)	3634(18)	1367(19)
C(11)	4105(12)	1916(11)	2952(11)
C(12)	3537(15)	2187(15)	3513(14)
C(13)	3661(19)	2846(17)	4017(17)
C(14)	4481(16)	3315(16)	3970(14)
C(15)	5082(18)	3119(16)	3437(14)
C(16)	4893(16)	2369(14)	2909(14)
C(17)	4908(12)	839(11)	1768(10)
C(18)	5568(12)	338(13)	2037(12)
C(19)	6332(16)	264(15)	1602(15)
C(20)	6411(15)	665(14)	942(13)
C(21)	5838(16)	1155(15)	605(15)
C(22)	4969(15)	1261(15)	1067(13)
C(23)	3809(13)	98(12)	2984(11)
C(24)	4202(15)	112(15)	3706(12)
C(25)	4121(15)	−568(15)	4211(14)
C(26)	3672(15)	−1277(16)	3956(14)
C(27)	3296(15)	−1370(16)	3220(14)
C(28)	3368(14)	−589(14)	2742(14)
Cl(2)	3446(23)	6313(21)	385(23)
Cl(1)	2393(26)	6790(23)	1643(24)
Cx [a]	2737(61)	6205(54)	964(54)

[a] Cx = carbon atom of dichloromethane.

and the reaction allowed to stir for 2 h. The solution was filtered, the solvent evaporated in vacuo, and the residue treated with MeOH (15 cm^3), filtered and dried. The product was recrystallised from dichloromethane/diethyl ether. Yield: 0.50 g, 57.6%. Analysis. Found: C, 62.7; H, 5.3; N, 6.90. $C_{39}H_{37}MoN_4PS_2$ calcd.: C, 62.2, H, 5.93, N, 7.4%.

Tetrakis{methylphenylhydrazido(2 −)}(di-μ_2*-sulphido)bis(triphenylphosphine)dimolybdenum(VI) (6).* A solution of hexamethyldisilylsulphide was prepared in situ by reduction of elemental sulphur (0.12 g, 3.74 mmol) with $Li[BHEt_3]$ (7.50 cm^3, 7.50 mmol) in thf (25 cm^3) followed, after 1 h, by addition of Me_3SiCl (0.94 g, 8.63 mmol) at −78 °C. The solution was heated under reflux for 1.5 h, cooled to room temperature, and a solution of $[MoCl(NNMePh)_2(PPh_3)_2]Cl$ (3.14 g, 3.37 mmol) in CH_2Cl_2 (30 cm^3) added. After stirring for 18 h, the solution was evaporated to dryness, the residue extracted in CH_2Cl_2 and filtered, and the product isolated by addition of toluene. Yield: 0.77 g, 36.2%. Analysis. Found: C, 60.7; H, 4.8; N, 8.9. $C_{64}H_{62}Mo_2N_8P_2S_2$ calcd.: C, 61.0; H, 5.0; N, 8.9%.

Bis{dimethylhydrazido(2 −)}{di-μ_3*-sulphidohexacarbonyldiiron(I)}(trimethylphosphine)molybdenum(VI)(Fe-Fe) (7).* A solution of **1** (0.215 g, 0.267 mmol) in dichloromethane (5 cm^3) was treated with PMe_3 (ca. 0.25 g, 3.3 mmol). After stirring at room temperature for 3 h, MeOH (15 cm^3) was added, and the volume reduced to about half under vacuum to initiate precipitation. The product was recrystallised from CH_2Cl_2/hexane. Yield: 0.078 g, 47.0%. Analysis. Found: C, 24.6; H, 3.4; N, 8.6. $C_{13}H_{21}FeMoN_4O_6PS_2$ calcd.: C, 24.7; H, 3.4; N, 8.9%.

References

1 J. Chatt, B.A.L. Crichton, J.R. Dilworth, P. Dahlstrom, R. Gutkoska and J.A. Zubieta, Inorg. Chem., 21 (1982) 2383.
2 J.R. Dilworth, J.A. Zubieta and J.R. Hyde, J. Am. Chem. Soc., 104 (1982) 365.
3 J.R. Dilworth and J.A. Zubieta, J. Chem. Soc. Chem. Commun., (1981) 13.
4 K.S. Rose, P.E. Lamberty, J.E. Kovacs, E. Sinn and B. Averill, Polyhedron, 5 (1986) 393.
5 D. Seyferth, R.S. Henderson and L.-C. Song, Organometallics, 1 (1982) 125.
6 V.W. Day, D.A. Lesch and T.B. Rauchfuss, J. Am. Chem. Soc., 104 (1982) 1290.
7 P. Braunstein, A. Tiripicchio and E. Sappa, Inorg. Chem., 20 (1981) 358.
8 P.D. Williams, M.D. Curtis, D.N. Duffy and W.M. Butler, Organometallics, 2 (1983) 165.
9 J.A. Kovacs, J.K. Boshkin and R.H. Holm, J. Am. Chem. Soc., 107 (1985) 1784.
10 J.R. Dilworth, S. Morton, M. O'Connor and J. Silver, Inorg. Chim. Acta, 127 (1987) 91.
11 G.L. Lilley, E. Sinn and B.A. Averill, Inorg. Chem., 25 (1986) 107.
12 D. Seyferth, R.S. Henderson and M.K. Gallagher, J. Organomet. Chem., 193 (1980) C75.
13 C.H. Wei and L.F. Dahl, Inorg. Chem., 4 (1965) 1.
14 L.F. Dahl and C.H. Wu, Inorg. Chem., 2 (1963) 328.
15 P.T. Bishop, J.R. Dilworth and J.A. Zubieta, unpublished results.
16 W. Hüber and J.A. Gruber, Z. Anorg. Allg. Chem., 296 (1958) 91.
17 M.Y. Hamed, R.C. Hider and J. Silver, Inorg. Chim. Acta, 66 (1982) 13.