The Addition of Isonitriles to $[\{M(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (M = Mo or W). Syntheses and Properties of $[M_2(\mu\text{-}\eta^2\text{-}CNR)(CO)_4(\eta\text{-}C_5H_5)_2]$ (M = Mo or W, R = Me or Bu^t) and $[\{Mo(CNR)(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (R = Me or Bu^t). *X*-Ray Crystal Structures of $[Mo_2(\mu\text{-}\eta^2\text{-}CNBu^t)(CO)_4(\eta\text{-}C_5H_5)_2]$ and $[\{Mo(CNBu^t)(CO)_2(\eta\text{-}C_5H_5)\}_2]$†

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Addition of CNR (R = Me or Bu^t) to the M≡M complex $[\{M(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (M = Mo or W) results in addition of one isonitrile across the M≡M bond and the formation of $[M_2(\mu\text{-}\eta^2\text{-}CNR)(CO)_4(\eta\text{-}C_5H_5)_2]$. The Bu^t molybdenum derivative crystallises as black platey needles [orthorhombic, *a* = 31.75(3), *b* = 8.171(11), *c* = 15.722(17) Å; *R* converged to 0.0357 for 1 775 independent reflections for which $I/\sigma(I) > 3.0$]. The molecule consists of two $Mo(CO)_2(\eta\text{-}C_5H_5)$ groups linked by a Mo–Mo single bond and bridged by the CNBu^t group in a $\mu\text{-}\eta^2$ four-electron donor fashion. The bonding is viewed as donation of the carbon lone pair to one molybdenum atom and donation of CN π-electron density to the second. Prolonged reaction times of $[Mo_2(\mu\text{-}\eta^2\text{-}CNR)(CO)_4(\eta\text{-}C_5H_5)_2]$ with excess CNR results in cleavage of the CN–Mo π-donor interaction and formation of the symmetrically disubstituted complexes $[\{Mo(CNR)(CO)_2(\eta\text{-}C_5H_5)\}_2]$. The Bu^t derivative crystallises as dark red prisms [monoclinic, *a* = 10.354(7), *b* = 11.672(5), *c* = 10.793(5) Å, β = 103.68(4)°; *R* converged to 0.0519 for 1 102 independent reflections for which $I/\sigma(I) > 3.0$]. The molecule consists of two $Mo(CNBu^t)(CO)_2(\eta\text{-}C_5H_5)$ groups linked through a Mo–Mo single bond with a crystallographically imposed centre of symmetry midway along the Mo–Mo bond. Decarbonylation by thermolysis of this compound results in the formation of $[Mo_2(CNBu^t)(\mu\text{-}\eta^2\text{-}CNBu^t)(CO)_3(\eta\text{-}C_5H_5)_2]$, containing one terminal and one bridging isonitrile. Reductive cleavage of $[\{Mo(CNR)(CO)_2(\eta\text{-}C_5H_5)\}_2]$ with sodium amalgam gives the anions $[Mo(CNR)(CO)_2(\eta\text{-}C_5H_5)]^-$ which react with $SnPh_3Cl$ to give the tin complexes $[Mo(SnPh_3)(CNR)(CO)_2(\eta\text{-}C_5H_5)]$, as mixtures of *cis* and *trans* isomers.

In connection with our research on carbene chemistry we required a good source of isonitrile anions $[M(CNR)(CO)_2(\eta\text{-}C_5H_5)]^-$ (M = Mo or W). Literature methods for their syntheses involve the sodium amalgam reduction of a halide (X) species $[MX(CNR)(CO)_2(\eta\text{-}C_5H_5)]$.[1] In our hands, these particular reductions do not proceed in very high yield and, in addition, the syntheses and purifications of the halides are a little tedious. At the outset of this work we were well aware of the ease by which two-electron ligands, L (such as CO and PR_3), add across the Mo≡Mo bond of the readily available $[\{Mo(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (**1**),[2] forming $[\{MoL(CO)_2(\eta\text{-}C_5H_5)\}_2]$.[3] We reasoned that an isonitrile would also add across the Mo≡Mo bond to form $[\{Mo(CNR)(CO)_2(\eta\text{-}C_5H_5)\}_2]$. These molecules would then be sources of $[Mo(CNR)(CO)_2(\eta\text{-}C_5H_5)]^-$ by sodium amalgam cleavage of the metal–metal bond.

Results and Discussion

Addition of one equivalent of CNR (R = Bu^t or Me) to a toluene solution of $[\{Mo(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (**1**)[2] at ambient temperature results in a fast colour change from deep red-brown to maroon. During this time the i.r. bands in the carbonyl region associated with (**1**) are replaced by new bands corresponding to the single isolated products, characterised as $[Mo_2(\mu\text{-}\eta^2\text{-}CNR)(CO)_4(\eta\text{-}C_5H_5)_2]$ [R = Bu^t (**2**) or Me (**3**) respectively] (Scheme 1). These compounds are reasonably air stable. Since the start of this work a report[4] has appeared giving the i.r., ^1H and ^{13}C n.m.r. spectroscopic properties of (**2**) and (**3**) and we find essentially identical results (Table 1). We do have some additional comments concerning the fluxional properties of (**3**). The ^1H n.m.r. spectrum at ambient temperature in $CDCl_3$ (Table 1) and xylene [δ 4.99 (s, 5 H, C_5H_5), 4.93 (s, 5 H, C_5H_5), 3.06 (s, 3 H, Me)] show two sharp cyclopentadienyl resonances. On warming, the signals in xylene broaden and start to coalesce. Coalescence is not complete at 120 °C, our experimental limit. The signals sharpen up again on cooling back to ambient temperature. This is interpreted as an oscillation of the CNMe group as indicated in Scheme 2. The n.m.r. data put a minimum $\Delta G^\ddagger$ for this process at 87 kJ mol^{-1}. We note that the C_5Me_5 analogue of (**3**) is known but prepared by a different process and that it is also fluxional.[5] Similar studies on (**2**) were frustrated by partial decomposition upon warming.

The nature of the isonitrile bonding was confirmed by an *X*-ray crystal-structure analysis of (**2**). The structure of the related molecule $[Mo_2(\mu\text{-}\eta^2\text{-}CNPh)(CO)_4(\eta\text{-}C_5H_5)_2]$ (**4**)[4] is very similar to that of (**2**). The structure of (**2**) is illustrated in Figure 1 together with the atom labelling. Bond lengths, angles, details of planar fragments, and atomic positional parameters are gathered in Tables 2, 3, and 4. The molecule is bimetallic and contains two $Mo(CO)_2(\eta\text{-}C_5H_5)$ fragments linked by a single Mo–Mo bond [3.215 2(10) Å]. The bimetal system is bridged by the CNBu^t group such that the carbon C(15) lone pair binds to Mo(1) through a σ bond while the CN π system is bound in a

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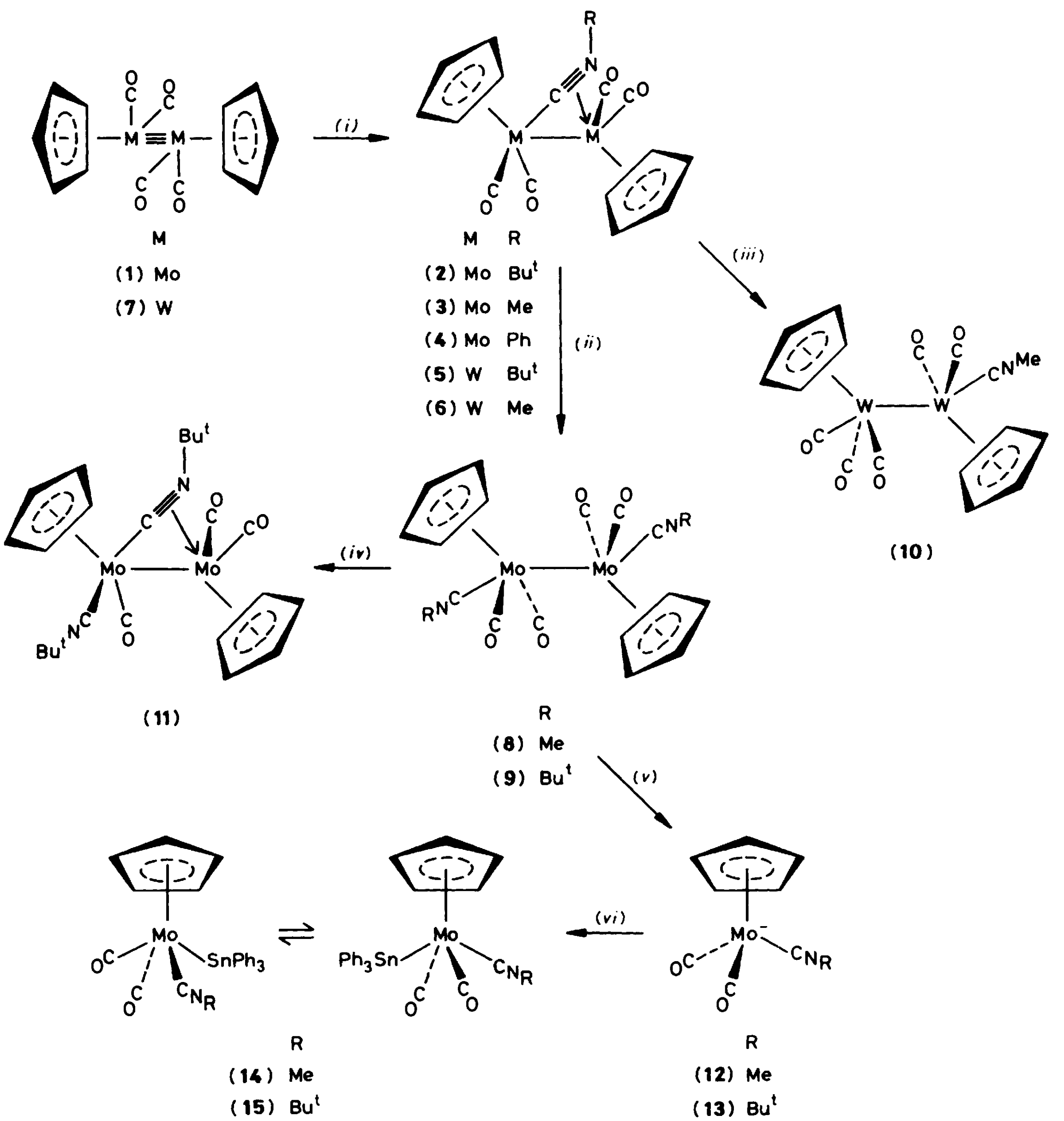
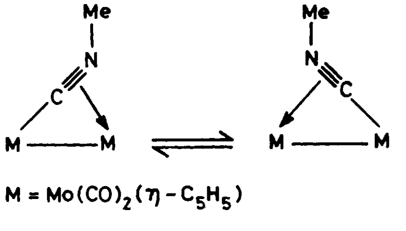
† μ-(σ:η²-t-Butyl isocyanide) bis[dicarbonyl(η-cyclopentadienyl)molybdenum] (*Mo–Mo*) and bis[dicarbonyl(η-cyclopentadienyl)(t-butyl isocyanide)molybdenum] (*Mo–Mo*) respectively.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.



Scheme 1. (*i*) 1 equiv. CNR, toluene; (*ii*) excess CNR, toluene; (*iii*) (**6**), excess CNMe, toluene; (*iv*) (**9**), heat; (*v*) Na–Hg, thf; (*vi*) SnPh$_3$Cl, thf



Scheme 2. Proposed fluxional process for [Mo$_2$(μ-η^2-CNMe)(CO)$_4$(η-C$_5$H$_5$)$_2$] (**3**)

η^2 fashion to Mo(2). The angle at the donor isonitrile carbon is 168° and there is a quite pronounced bend at the nitrogen (136°). These bends are not coplanar or cumulative [the torsion angle about N(1)–C(15) is +120.5°]. The CNPh system[4] in (**4**) has similar features. The CN π system is not quite symmetrically

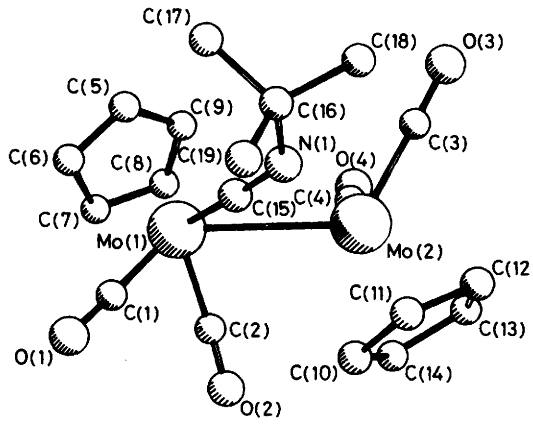


Figure 1. Molecular structure of [Mo$_2$(μ-η^2-CNBu^t)(CO)$_4$(η-C$_5$H$_5$)$_2$] (**2**) with atom labelling. Atom Mo(2) is linked to the bridging isonitrile group *via* a π-donor bond from N(1)–C(15)

Table 1. I.r.[a] and n.m.r.[b] data for the complexes

Compound	I.r./cm^{-1}	$\delta(^1H)$/p.p.m.	$\delta(^{13}C)$/p.p.m.
(**2**)	1 965m, 1 923vs, 1 894s, 1 850s, 1 700w ($CNBu^t$)	5.34 (s, 5 H, C_5H_5), 5.33 (s, 5 H, C_5H_5), 1.38 (s, 9 H, Bu^t)	[c]247.3 (CO), 245.7 (CO), 235.0 (CO), 234.8 (CO), 206.2 (CN), 95.4 (C_5H_5), 95.3 (C_5H_5), 60.5 ($\mathit{C}Me_3$), 29.8 (Me)
(**3**)	1 968m, 1 927vs, 1 897s, 1 854s, 1 731w (CNMe)	5.33 (s, 5 H, C_5H_5), 5.32 (s, 5 H, C_5H_5), 3.60 (s, 3 H, Me)	[d]246.8 (CO), 245.7 (CO), 235.6 (CO), 234.3 (CO), 206.2 (CN), 95.4 (C_5H_5), 93.1 (C_5H_5), 40.8 (Me)
(**5**)	1 961m, 1 917vs, 1 885s, 1 837s, 1 677w ($CNBu^t$)	[e]5.47 (s, 5 H, C_5H_5), 5.39 (s, 5 H, C_5H_5), 1.25 (s, 9 H, Bu^t)	[f]236.9 (CO), 233.2 (CO), 221.4 (CO), 221.3 (CO), 198.2 (CN), 93.6 (C_5H_5), 91.2 (C_5H_5), 58.3 ($\mathit{C}Me_3$), 29.2 (Me)
(**6**)	[g]1 957m, 1 909vs, 1 873s, 1 817s, 1 709w (CNMe)	5.49 (s, 5 H, C_5H_5), 5.43 (s, 5 H, C_5H_5), 3.66 (s, 3 H, Me)	[h]234.4 (CO), 231.8 (CO), 219.7 (CO), 219.2 (CO), 193.8 (CN), 91.8 (C_5H_5), 89.3 (C_5H_5), 37.9 (Me)
(**8**)	[i]2 109m,br (CNMe), 1 943w, 1 922w, 1 891w, 1 880w, 1 865s, 1 840(sh)	5.07 (s, 10 H, C_5H_5), 3.58 (s, 6 H, Me)	[j]231.9 (CO), 183.2 (CN), 91.4 (C_5H_5), 30.4 (Me)
(**9**)	[i]2 107m,br ($CNBu^t$), 1 944w, 1 922w, 1 880w, 1 871w, 1 866s, 1 840w	5.05 (s, 10 H, C_5H_5), 1.49 (s, 18 H, Bu^t)	[k]223.2 (CO), 183.3 (CN), 91.7 (C_5H_5), 58.3 ($\mathit{C}Me_3$), 30.7 (Me)
(**10**)	[g]2 137m,br (CNMe), 1 965s, 1 901s, 1 877vs	5.30 (s, C_5H_5), 5.15 (s, C_5H_5), 3.70 (s, Me)	
(**11**)	2 090w,br ($CNBu^t$), 1 917s, 1 878s, 1 835s, 1 680w,br ($CNBu^t$)	4.95 (s, 5 H, C_5H_5), 4.89 (s, 5 H, C_5H_5), 1.29 (s, 9 H, Bu^t), 1.04 (9 H, Bu^t)	[l]248.7 (CO), 248.0 (CO), 240.9 (CO), 207.7 (μ-CN), 171.9 (terminal CN), 93.4 (C_5H_5), 90.9 (C_5H_5), 58.2, ($\mathit{C}Me_3$), 58.0 ($\mathit{C}Me_3$), 30.3 (Me), 30.1 (Me)
(**14**)	[g]2 164m (CNMe), 2 145(sh) (CNMe), 1 944m, 1 928m, 1 861s	7.62, 7.55, 7.31 (3 × m *cis* + *trans* Ph), 5.21 [s, 5 H, C_5H_5, *cis*-(**14**)], 5.08 [s, 5 H, C_5H_5, *trans*-(**14**)], 3.53 [s, 3 H, Me, *trans*-(**14**)], 2.78 [s, 3 H, Me, *cis*-(**14**)]	[m]238.8 [CO, *cis*-(**14**)], 233.2 [CO, *cis*-(**14**)], 230.0 [CO, *trans*-(**14**)], 164.5 [CN, *cis*-(**14**)], 164.0 [CN, *trans*-(**14**)], 144.6 [C_i, *cis*-(**14**)], 144.2 [C_i, *trans*-(**14**)], 136.6 (C_o), 127.8 (C_m), 125.7 (C_p), 88.2 (C_5H_5), 31.1 (Me)
(**15**)	[g]2 125m (CNMe), 2 113m (CNMe), 1 936m, 1 928m, 1 865s	7.60, 7.55, 7.30 (3 × m, *cis* + *trans* Ph), 5.21 [s, 5 H, C_5H_5, *cis*-(**15**)], 5.07 [s, 5 H, C_5H_5, *trans*-(**15**)], 1.53 [s, 9 H, Bu^t, *trans*-(**15**)], 0.97 [s, 9 H, Bu^t, *cis*-(**15**)]	[m]229.4 (CO), 144.2 (C_p), 136.6 (C_o), 127.7 (C_m), 125.7 (C_p), 88.3 (C_5H_5), 88.1 (C_5H_5), 58.1 [$\mathit{C}Me_3$, *trans*-(**15**)], 57.6 [$\mathit{C}Me_3$, *cis*-(**15**)], 30.6 [Me, *trans*-(**15**)], 29.7 [Me, *cis*-(**15**)]

[a] Recorded in light petroleum unless specified otherwise. [b] Recorded in $CDCl_3$ at ambient temperature unless specified otherwise. [c] In acetone, 0 °C. [d] In acetone, −60 °C. [e] In acetone. [f] In acetone, −70 °C. [g] In CH_2Cl_2. [h] In acetone, −50 °C. [i] In toluene. [j] In toluene, −80°C. [k] In toluene, −90 °C. [l] In CD_2Cl_2, −50 °C. [m] In $CDCl_3$, −50 °C.

bound to Mo(2), with the Mo–C distances 0.03—0.04 Å longer than the Mo–N distance in both (**2**) and the CNPh analogue (**4**).

The $Mo_2(CO)_4(\eta\text{-}C_5H_5)_2$ core structures of (**2**) and (**4**) are very reminiscent of other Mo_2 systems of general formula $[Mo_2(\mu\text{-}L)(CO)_4(\eta\text{-}C_5R_5)_2]$ in which L acts as a four-electron donor, *e.g.* R = H, L = MeCHO,[6] R^1R^2CS,[7] R^1CCR^2,[8] $MeCO^+$,[9] CN^-,[10] $H_2C{=}C{=}CH_2$,[11] or $NCNMe_2$;[12] R = Me, L = CNMe[5] or $N{=}N{=}CMe_2$.[13]

The previously unreported tungsten analogues (**5**) and (**6**) are formed in reactions of $[\{W(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (**7**) with $CNBu^t$ or CNMe respectively. The tungsten compounds are a little more air stable and they are orange. The spectroscopic data for these compounds are very similar to those of the molybdenum analogues (Table 1). The carbonyls and isonitrile carbon appear as signals to lower frequency than those of the corresponding molybdenum analogues. This is often the case for tungsten and molybdenum compounds.[14] Again, there are two cyclopentadienyl resonances in the ^1H n.m.r. spectra at ambient temperature, suggesting the lack of any CNR oscillation on this time-scale.

All the complexes (**2**)—(**6**) have a weak to medium intensity band in the region 1 677—1 731 cm^{-1}. This is attributed to a ν(CN) absorption, well below ν(CN) of free CNR as a consequence of the diminution in bond order as electron density is transferred to a Mo or W atom.

All the reactions leading to (**2**), (**3**), (**5**), and (**6**) are complete within a few minutes at ambient temperature. These compounds are the sole products with these short reaction times.

However, if excess CNMe is used in the reaction of (**1**) and stirring prolonged at ambient temperature further changes in the i.r. spectrum of the reaction mixture result. The ν(CO) stretching bands of (**3**) are replaced by a broad envelope of i.r. bands centred around 1 860 cm^{-1} in addition to other weak absorptions. The only compound isolated from this reaction is deep maroon and whose spectroscopic properties suggest the formulation $[\{Mo(CNMe)(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (**8**). Excess $CNBu^t$ similarly reacts with (**2**), this time to form $[\{Mo(CNBu^t)(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (**9**). This reaction is slower and it is necessary to concentrate the reaction mixture in order for the reaction to proceed at a reasonable rate. These reactions must be executed at ambient temperature since the products are thermally unstable. Both (**8**) and (**9**) are new compounds and constitute the first examples of products formed by cleavage of the CN–molybdenum π interaction.

Table 2. Bond lengths (Å) and angles (°), with estimated standard deviations in parentheses, for $[Mo_2(\mu\text{-}\eta^2\text{-}CNBu^t)(CO)_4(\eta\text{-}C_5H_5)_2]$ (**2**)

Mo(1)–Mo(2)	3.215 2(10)	Mo(1) · · · C(4)	3.251(8)
Mo(1)–C(1)	1.937(9)	Mo(2)–C(3)	1.959(9)
O(1)–C(1)	1.171(12)	O(3)–C(3)	1.147(12)
Mo(1)–C(2)	1.953(9)	Mo(2)–C(4)	1.949(8)
O(2)–C(2)	1.145(12)	O(4)–C(4)	1.168(10)
Mo(1)–C(5)	2.353(13)	Mo(2)–C(10)	2.381(9)
Mo(1)–C(6)	2.315(12)	Mo(2)–C(11)	2.381(10)
Mo(1)–C(7)	2.312(13)	Mo(2)–C(12)	2.326(10)
Mo(1)–C(8)	2.292(14)	Mo(2)–C(13)	2.304(9)
Mo(1)–C(9)	2.319(15)	Mo(2)–C(14)	2.327(10)
C(5)–C(6)	1.321(18)	C(10)–C(11)	1.384(14)
C(6)–C(7)	1.360(18)	C(11)–C(12)	1.423(14)
C(7)–C(8)	1.350(19)	C(12)–C(13)	1.377(13)
C(8)–C(9)	1.302(21)	C(13)–C(14)	1.429(13)
C(9)–C(5)	1.299(20)	C(14)–C(10)	1.399(13)
Mo(1)–C(15)	1.953(7)	Mo(2)–N(1)	2.205(7)
N(1)–C(15)	1.212(10)	Mo(2)–C(15)	2.237(7)
N(1)–C(16)	1.497(11)	C(16)–C(18)	1.359(22)
C(16)–C(17)	1.425(20)	C(16)–C(19)	1.415(24)

Mo(2)–Mo(1)–C(1)	110.2(3)	Mo(1)–Mo(2)–C(3)	117.3(3)
Mo(2)–Mo(1)–C(2)	79.6(3)	Mo(1)–Mo(2)–C(4)	73.5(2)
Mo(2)–Mo(1)–C(15)	43.2(2)	Mo(1)–Mo(2)–C(15)	36.7(2)
C(1)–Mo(1)–C(2)	79.4(4)	C(3)–Mo(2)–C(4)	74.5(4)
C(1)–Mo(1)–C(15)	85.4(3)	C(3)–Mo(2)–C(15)	106.5(3)
C(2)–Mo(1)–C(15)	109.3(3)	C(4)–Mo(2)–C(15)	103.3(3)
Mo(1)–C(15)–N(1)	168.1(6)	Mo(1)–Mo(2)–N(1)	68.1(2)
C(15)–N(1)–C(16)	136.3(7)	C(3)–Mo(2)–N(1)	87.9(3)
N(1)–C(16)–C(17)	107.8(9)	C(4)–Mo(2)–N(1)	123.4(3)
N(1)–C(16)–C(18)	111.7(11)	C(15)–Mo(2)–N(1)	31.7(3)
N(1)–C(16)–C(19)	106.6(11)	C(17)–C(16)–C(19)	106.1(13)
C(17)–C(16)–C(18)	109.2(13)	C(18)–C(16)–C(19)	115.2(14)
Mo(1)–C(1)–O(1)	178.9(8)	Mo(2)–C(3)–O(3)	177.0(8)
Mo(1)–C(2)–O(2)	175.3(8)	Mo(2)–C(4)–O(4)	172.7(7)
C(9)–C(5)–C(6)	107.8(13)	C(14)–C(10)–C(11)	107.5(8)
C(5)–C(6)–C(7)	108.6(12)	C(10)–C(11)–C(12)	108.6(9)
C(6)–C(7)–C(8)	105.0(12)	C(11)–C(12)–C(13)	108.3(9)
C(7)–C(8)–C(9)	108.5(13)	C(12)–C(13)–C(14)	107.1(8)
C(8)–C(9)–C(5)	110.1(14)	C(13)–C(14)–C(10)	108.6(8)

The ^1H n.m.r. spectra of (**8**) and (**9**) at ambient temperature each consist of just two lines with respective relative intensities 10:6 and 10:18, clearly showing that they contain two incorporated CNR molecules per Mo_2 unit. The ^1H n.m.r. spectrum of (**9**) at low temperature is very complex, the cyclopentadienyl region containing ten resolved lines of various intensities. The ^{13}C n.m.r. spectrum at 193 K in $C_6D_5CD_3$ is similarly complex, there being several overlapping signals in each of the regions associated with cyclopentadienyl, methyl, and Bu^t. However only single carbonyl and CN resonances are observed; this may be because the signal-to-noise ratio is not adequate to observe other, weak signals in these areas. The solubility of (**8**) is too low for low-temperature n.m.r. work. The complexity of the n.m.r. spectra for (**9**) is attributed to a number of isomers. Isomerism arises as a result of staggered rotamers about the metal–metal bond as well as the various possibilities for the isonitrile ligands being situated *cis* or *trans* to the Mo–Mo bond. We have not investigated this in detail for (**9**) but this phenomenon is related to the fluxional properties of $[\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$[15] and $[Mo_2(CNMe)(CO)_5(\eta\text{-}C_5H_5)_2]$[16] which have been examined in some depth.

The structure (**9**) is confirmed by the results of an *X*-ray crystallographic study. The molecular structure is illustrated in Figure 2 while bond lengths, angles, details of planar fragments, and atomic positional parameters are listed in Tables 5, 6, and 7. Again, the molecule consists of two $Mo(CO)_2(\eta\text{-}C_5H_5)$ fragments linked by a Mo–Mo bond [3.221(3) Å]. Each Mo

Table 3. Details of planar fragments for $[Mo_2(\mu\text{-}\eta^2\text{-}CNBu^t)(CO)_4(\eta\text{-}C_5H_5)_2]$ (**2**). Equations of mean planes are of the form $pX + qY + rZ = d$ where *p*, *q*, and *r* are direction cosines referred to orthogonal crystal axes *a*, *b*, *c*. Deviations (Å) of atoms from mean planes are shown in parentheses

	p	*q*	*r*	*d*
Plane A: C(5)—C(9) [root mean square (r.m.s.) deviation 0.006 Å]	−0.5949	0.7258	0.3454	2.2709
[C(5) 0.007, C(6) −0.009, C(7) 0.008, C(8) −0.004, C(9) −0.002, Mo(1) −2.024]				
Plane B: C(10)—C(14) (r.m.s. deviation 0.003 Å)	0.5334	−0.5034	−0.6798	2.9475
[C(10) −0.004, C(11) 0.005, C(12) −0.003, C(13) 0.001, C(14) 0.002, Mo(2) −2.016]				
Plane C: Mo(1), Mo(2), C(15)	−0.0021	0.7536	0.6574	2.0986
[N(1) 0.196, C(16) 0.523, C(17) 1.410, C(18) 1.122, C(19) −0.677]				
Plane D: Mo(1), O(1), O(2), C(1), C(2) (r.m.s. deviation 0.011 Å)	−0.8954	0.3929	−0.2094	−1.8167
[Mo(1) 0.009, O(1) 0.002, O(2) 0.012, C(1) −0.004, C(2) −0.019, Mo(2) −2.905]				
Plane E: Mo(2), O(3), O(4), C(3), C(4) (r.m.s. deviation 0.024 Å)	0.8044	0.0648	−0.5905	3.1339
[Mo(2) 0.017, O(3) −0.001, O(4) 0.027, C(3) 0.000, C(4) −0.043, Mo(1) −2.524]				

Selected interplanar angles (°):

A—B	156.6	B—E	37.1
A—D	41.8	C—E	109.9
C—D	80.8	B—C	145.8
A—C	39.2		

Torsion angle (°): Mo(1)–C(15)–N(1)–C(16) +120.5

Table 4. Atomic positional parameters, with estimated standard deviations in parentheses, for $[Mo_2(\mu\text{-}\eta^2\text{-}CNBu^t)(CO)_4(\eta\text{-}C_5H_5)_2]$ (**2**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Mo(1)	0.065 12(2)	0.137 89(8)	0.121 32(5)
Mo(2)	0.166 35(2)	0.131 49(8)	0.125 78(5)
O(1)	0.030 04(24)	−0.210 7(9)	0.086 3(5)
O(2)	0.082 35(22)	0.094 1(11)	−0.071 1(4)
O(3)	0.210 09(22)	0.351 1(10)	0.260 6(5)
O(4)	0.144 86(22)	0.495 0(7)	0.086 3(5)
N(1)	0.138 72(20)	−0.012 6(8)	0.230 4(4)
C(1)	0.043 4(3)	−0.079 9(11)	0.100 2(6)
C(2)	0.077 5(3)	0.114 6(11)	0.000 3(5)
C(3)	0.194 3(3)	0.266 3(11)	0.212 0(6)
C(4)	0.150 1(3)	0.356 2(10)	0.100 3(5)
C(5)	0.034 7(4)	0.277 6(18)	0.236 8(8)
C(6)	0.003 9(3)	0.221 2(15)	0.188 4(9)
C(7)	0.005 4(4)	0.298 9(17)	0.112 0(8)
C(8)	0.039 1(5)	0.399 4(13)	0.117 2(10)
C(9)	0.055 7(4)	0.383 8(17)	0.192 5(12)
C(10)	0.168 5(3)	−0.084 1(12)	0.024 0(6)
C(11)	0.198 8(3)	−0.118 8(12)	0.084 5(7)
C(12)	0.229 2(3)	0.009 2(12)	0.084 2(7)
C(13)	0.217 9(3)	0.121 1(12)	0.022 8(6)
C(14)	0.179 9(3)	0.063 1(13)	−0.015 3(6)
C(15)	0.108 8(2)	0.027 5(9)	0.187 4(5)
C(16)	0.145 3(3)	−0.098 7(12)	0.313 5(5)
C(17)	0.112 4(5)	−0.049(3)	0.369 6(10)
C(18)	0.183 1(5)	−0.060(3)	0.348 7(11)
C(19)	0.138 8(10)	−0.267(2)	0.297 8(10)

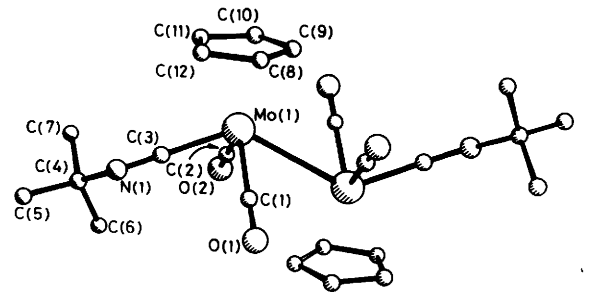


Figure 2. Molecular structure of $[\{Mo(CNBu^t)(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (**9**) with atom labelling. The molecule has a crystallographic inversion centre at the midpoint of the Mo–Mo bond

Table 5. Bond lengths (Å) and angles (°), with estimated standard deviations in parentheses, for $[\{Mo(CNBu^t)(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (**9**)*

Mo(1)–Mo(1^I)	3.221(3)	Mo(1)–C(8)	2.267(15)
Mo(1)–C(3)	1.997(23)	Mo(1)–C(9)	2.370(13)
N(1)–C(3)	1.215(27)	Mo(1)–C(10)	2.456(15)
N(1)–C(4)	1.436(25)	Mo(1)–C(11)	2.411(14)
C(4)–C(5)	1.514(29)	Mo(1)–C(12)	2.294(13)
C(4)–C(6)	1.463(37)	Mo(1)···C(1^I)	3.227(10)
C(4)–C(7)	1.469(40)	Mo(1)···C(2^I)	3.236(7)
Mo(1^I)–Mo(1)–C(1)	72.2(3)	C(3)–N(1)–C(4)	155.8(19)
Mo(1^I)–Mo(1)–C(2)	72.5(2)	N(1)–C(4)–C(5)	107.6(16)
Mo(1^I)–Mo(1)–C(3)	128.0(7)	N(1)–C(4)–C(6)	108.4(19)
C(1)–Mo(1)–C(2)	105.0(4)	N(1)–C(4)–C(7)	108.2(20)
C(1)–Mo(1)–C(3)	84.2(7)	C(5)–C(4)–C(6)	110.1(19)
C(2)–Mo(1)–C(3)	70.0(7)	C(5)–C(4)–C(7)	108.7(20)
Mo(1)–C(3)–N(1)	168.3(19)	C(6)–C(4)–C(7)	113.6(22)
Constrained bond lengths and angles			
Mo(1)–C(carbonyl)	1.987	Mo(1)–C–O(carbonyl)	180.0
C–O(carbonyl)	1.147	C–C–C(cp)	108.0
C–C(cp)	1.420		

* Symmetry operation I is $-x$, $-y$, $-z$; cp = cyclopentadienyl.

atom carries a terminally bound $CNBu^t$ ligand. The molecule possesses a crystallographically imposed centre of inversion at the midpoint of the Mo–Mo bond. The co-ordination geometry about each Mo is a square-based pyramidal system with the cyclopentadienyl group occupying an apical position ('four-legged piano stool') and the Mo–Mo bond one of the four basal vertices. The two carbonyls are mutually *trans* at opposite corners of the square base. Molybdenum–carbon distances suggest neither of the two carbonyls to be semi-bridging although any small bending of the two carbonyls is obscured by the necessary imposed geometrical constraints. The $CNBu^t$ group is terminally bound with bond angles at the carbon of 168° and at the nitrogen of 156°. The bends in the molybdenum–isonitrile linkage are coplanar and cumulative, the torsion angle about N(1)–C(3) is −0.3°. The molybdenum atom is 2.019 Å away from the constrained plane of the cyclopentadienyl ligand, which is tilted so that atom C(10) is the most remote from the metal atom.

The geometry of the $M_2L_6(\eta\text{-}C_5H_5)_2$ core of this compound is comparable to that of related molecules including $[\{M(CO)_3(\eta\text{-}C_5H_5)\}_2]$ (M = Mo or W),[15] $[(\eta\text{-}C_5H_5)(OC)_3MoW\{=\overline{C(CH_2)_3O}\}(CO)_2(\eta\text{-}C_5H_5)]$,[17] and $[Mo(CNMe)(CO)_5(\eta\text{-}C_5H_5)_2]$.[16]

Table 6. Details of planar fragments for $[\{Mo(CNBu^t)(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (**9**). Equations of mean planes are of the form $pX + qY + rZ = d$ where p, q, and r are direction cosines referred to orthogonal crystal axes a, b, c^*. Deviations (Å) of atoms from mean planes are shown in parentheses

	p	q	r	d
Plane A: C(8)—C(12) (r.m.s. deviation 0.000 Å)				
	−0.7359	−0.0173	0.6769	2.8067
[Mo(1) −2.019]				
Plane B: Mo(1), O(1), O(2), C(1), C(2) (r.m.s. deviation 0.000 Å)				
	−0.6811	−0.0786	−0.7280	−1.3965
[C(8) 0.283, C(9) 1.260, C(10) 0.582, C(11) −0.814, C(12) −0.999]				
Plane C: N(1), C(3), C(4)				
	−0.4249	−0.3001	0.8541	1.1572
[Mo(1) −0.002, C(5) 0.126, C(6) −1.267, C(7) 1.180]				

Selected angles (°) between planes:

A—B	89.4
A—C	26.4

Torsion angle (°): Mo(1)–C(3)–N(1)–C(4) −0.3

Table 7. Atomic positional parameters, with estimated standard deviations in parentheses, for $[\{Mo(CNBu^t)(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (**9**)*

Atom	X/a	Y/b	Z/c
Mo(1)	0.072 26(12)	0.007 47(23)	0.149 28(12)
O(1)	0.156 6(16)	0.223 4(8)	0.014 8(16)
O(2)	0.195 1(11)	−0.201 2(6)	0.034 8(12)
N(1)	0.381 8(14)	−0.031 9(15)	0.271 4(14)
C(1)	0.125 7(10)	0.144 4(5)	0.064 0(10)
C(2)	0.150 1(7)	−0.124 8(4)	0.076 7(7)
C(3)	0.266 3(17)	−0.004 6(28)	0.230 3(13)
C(4)	0.494 3(17)	−0.107 4(19)	0.294 4(18)
C(5)	0.610 1(17)	−0.044 8(22)	0.379 5(18)
C(6)	0.524 6(26)	−0.134 6(32)	0.172 0(27)
C(7)	0.462 9(31)	−0.208 5(26)	0.362 8(38)
C(8)	−0.068 2(15)	0.087 8(10)	0.256 7(14)
C(9)	−0.141 0(8)	−0.006 7(16)	0.192 8(8)
C(10)	−0.075 8(15)	−0.108 7(11)	0.245 8(14)
C(11)	0.037 2(12)	−0.077 2(14)	0.342 5(11)
C(12)	0.041 9(11)	0.044 3(14)	0.349 2(10)

* The estimated standard deviations of the carbonyl and cyclopentadienyl atoms are derived from those of the group parameters which were used to refine them.

Curiously, the tungsten analogues of (**8**) and (**9**) are not formed in analogous reactions of CNR with either (**5**) or (**6**). Thus addition of excess CNMe to $[W_2(\mu\text{-}\eta^2\text{-}CNMe)(CO)_4(\eta\text{-}C_5H_5)_2]$ (**6**) gives only a low (15%) yield of $[(\eta\text{-}C_5H_5)(OC)_3W\text{-}W(CNMe)(CO)_2(\eta\text{-}C_5H_5)]$ (**10**) and none of a tungsten analogue of (**8**). The ν(CN) stretch for (**10**) is clearly observable at 2 137 cm^{-1}, typical for a terminal isonitrile. The ^1H n.m.r. properties of (**10**) are complex and again attributed to interconverting isomers; they are qualitatively rather similar to those of the molybdenum analogue $[Mo_2(CNMe)(CO)_5(\eta\text{-}C_5H_5)_2]$[15] discussed elsewhere. The mechanism of formation of (**10**) is clearly complex, requiring a CO migration from an intermolecular source.

Heating $[\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ in toluene while purging the solution with N_2 is known to form the Mo≡Mo complex (**1**).[2] We performed a similar reaction using (**9**), to see whether an isonitrile-substituted analogue of (**1**) would form. This is not the case. Thermolysis in toluene results in a reasonable yield of $[Mo_2(CNBu^t)(\mu\text{-}\eta^2\text{-}CNBu^t)(CO)_3(\eta\text{-}C_5H_5)_2]$ (**11**) as the only isolated product. The presence of a bridging $CNBu^t$ is inferred from the i.r. and n.m.r. data (Table 1). The i.r. spectrum shows a weak broad band at 1 680 cm^{-1} that we attribute to ν(CN) of the bridging CNBu^t group, together with a band at 2 090 cm^{-1} assigned to the terminal CNBu^t group. The ^{13}C n.m.r. spectrum at −90 °C contains two CN signals in addition to three distinct carbonyl resonances. Inspection of the ^{13}C n.m.r. data (Table 1) for the other molybdenum complexes shows that bridging CNR groups are manifested by signals around δ 206 while terminal groups give resonances around δ 183. On this basis, the signal at δ 207.7 is assigned as the bridging CNBu^t and that at δ 171.9 to the terminal CNBu^t. Assuming the same basic skeleton as (**2**), the terminal CNBu^t can adopt any one of four positions, we do not know which.

The original aim of this work was to provide a good synthesis of the anions $[M(CNR)(CO)_2(\eta\text{-}C_5H_5)]^-$ (M = Mo and W). Compounds (**8**) and (**9**) are indeed good precursors for the molybdenum anions $[Mo(CNR)(CO)_2(\eta\text{-}C_5H_5)]^-$ [R = Me (**12**) or Bu^t (**13**)]. Sodium amalgam reduction of (**8**) gives a pale yellow-green solution containing (**12**) whose i.r. spectrum is virtually identical to the published spectrum,[1] indicating successful cleavage. The anion was further characterised by its reaction with $SnPh_3Cl$ which proceeds to give high yields of the new compound $[Mo(SnPh_3)(CNMe)(CO)_2(\eta\text{-}C_5H_5)]$ (**14**). Compound (**14**) was characterised by elemental analysis, i.r., ^{1}H n.m.r., and ^{13}C n.m.r. spectroscopy. Partial data for the tungsten analogue of (**14**) have been reported, although it was prepared in a quite different fashion.[18] The i.r. spectrum of (**14**) indicates that it is present as a mixture of *cis* and *trans* isomers [*cis*-(**14**) and *trans*-(**14**)], which is further confirmed by the ^{1}H and ^{13}C n.m.r. spectra. The ^{1}H n.m.r. spectrum shows two cyclopentadienyl signals and two CNMe signals in the ratio 65:35. The ^{13}C n.m.r. spectrum is particularly informative. There are three CO signals, two of which are weak with equal intensities, while the third is unique and just over three times as intense. We assign the stronger signal to *trans*-(**14**) and the weaker signals to *cis*-(**14**). These data indicate *trans*-(**14**) to be more abundant. There is also a pairwise arrangement of signals for the CN, Me, and C_{ipso} carbons while the other phenyl signals and the cyclopentadienyl signals overlap for the two isomers.

The analogous anion (**13**) is similarly formed by sodium amalgam cleavage of dimer (**9**). We are not aware of any other reports of this anion although there is one brief mention of the tungsten analogue,[19] again prepared in a very different fashion. The i.r. spectrum of (**13**) is qualitatively very similar to that of (**12**) and it also reacts with $SnPh_3Cl$, this time to form high yields of the spectroscopically characterised $[Mo(SnPh_3)(CNBu^t)(CO)_2(\eta\text{-}C_5H_5)]$ (**15**). The derivative (**15**) is clearly very similar to (**14**) and exists as two isomers [*cis*-(**15**) and *trans*-(**15**)], except that the *trans*-(**15**):*cis*-(**15**) ratio is 60:40 by integration of the ^{1}H n.m.r. signals. The quality of the ^{13}C n.m.r. spectrum is insufficient to pick out all the carbonyls but the CNBu^t and cyclopentadienyl signals are each just resolved as pairs due to the *cis* and *trans* isomers.

Experimental

Infrared spectra were measured using a Perkin-Elmer 257 instrument, calibrated using the 1 601.4 cm^{-1} absorption of polystyrene film, or on a Perkin-Elmer 1710 Fourier-transform instrument linked to a Perkin-Elmer 4600 Data Station.

Proton n.m.r. spectra were recorded using Bruker WP-80SY (80 MHz), Perkin-Elmer R34 (220 MHz), or Bruker AM-250 (250 MHz) spectrometers. Carbon-13 spectra were obtained using JEOL PFT-100 (25.15 MHz) and Bruker AM-250 (62.9 MHz) instruments.

Mass spectra were recorded with an Kratos MS25 spectrometer operating at low resolution using the electron-impact or chemical-ionisation (NH_3) modes.

All reactions were performed under nitrogen or argon atmospheres using deoxygenated solvents dried with an appropriate agent: tetrahydrofuran (thf) from sodium-benzophenone and light petroleum (b.p. 40—60 °C throughout) from $LiAlH_4$. Alumina was Brockmann Activity I and deactivated with water (5% w/w throughout) or Brockmann Activity II used as supplied. The compounds CNMe,[20] CNBu^t,[21] $[\{M(CO)_3(\eta\text{-}C_5H_5)\}_2]$,[22] and $[\{M(CO)_2(\eta\text{-}C_5H_5)\}_2]$ [M = Mo (**1**) or W (**7**),[2] are available by literature methods.

$[Mo_2(\mu\text{-}\eta^2\text{-}CNBu^t)(CO)_4(\eta\text{-}C_5H_5)_2]$ (**2**).—The ligand CNBu^t (0.34 g, 4.1 mmol) was added to a solution of $[\{Mo(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (**1**) (4.1 mmol) in toluene (150 cm^3), prepared by thermolysis of $[\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ (2.00 g, 4.1 mmol). The brown solution was allowed to stir at room temperature (30 min) during which time the solution turned deep red. The toluene was removed and the residue chromatographed on a short alumina column (8 × 2 cm). Elution with light petroleum–dichloromethane (4:1) afforded a small amount of the starting material followed by $[Mo_2(\mu\text{-}\eta^2\text{-}CNBu^t)(CO)_4(\eta\text{-}C_5H_5)_2]$ (**2**) (1.27 g, 60%) as deep maroon crystals on crystallisation from light petroleum (m.p.: compound too dark to observe) (Found: C, 44.2; H, 3.7; N, 3.0%; M^+, 517. $C_{19}H_{19}Mo_2NO_4$ requires C, 44.1; H, 3.7; N, 2.7%; M^+, 517).

$[Mo_2(\mu\text{-}\eta^2\text{-}CNMe)(CO)_4(\eta\text{-}C_5H_5)_2]$ (**3**).—In a similar manner to the preparation of (**2**) above, complex (**3**) was synthesised in 71% yield by the reaction of a solution of $[\{Mo(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (**1**) (4.1 mmol) with CNMe (0.17 g, 4.1 mmol) and a reaction time of 100 min. The complex was isolated as maroon crystals upon crystallisation from a light petroleum–dichloromethane solution (m.p.: compound too dark to observe) (Found: C, 41.6; H, 3.3; N, 2.9%; $[M - CO]^+$, 447. $C_{16}H_{13}Mo_2NO_4$ requires C, 41.3; H, 2.8; N, 3.0%; M^+, 475).

$[W_2(\mu\text{-}\eta^2\text{-}CNBu^t)(CO)_4(\eta\text{-}C_5H_5)_2]$ (**5**).—A solution of $[\{W(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (**7**) (7.5 mmol), produced by the thermolysis of $[\{W(CO)_3(\eta\text{-}C_5H_5)\}_2]$ (5.00 g, 7.5 mmol) in xylene (200 cm^3), was treated with CNBu^t (0.68 g, 8.22 mmol) and stirred at room temperature (1 h). The solvent was removed and the dark orange residue chromatographed on an alumina column (8 × 2 cm), eluting with an increasing concentration of dichloromethane in light petroleum to yield $[W_2(\mu\text{-}\eta^2\text{-}CNBu^t)(CO)_4(\eta\text{-}C_5H_5)_2]$ (**5**) (3.12 g, 60%) as dark orange crystals, m.p. 135—137 °C (Found: C, 33.3; H, 2.8; N, 1.9%; $[M - CNBu^t]^+$, 608. $C_{19}H_{19}NO_4W_2$ requires C, 33.0; H, 2.8; N, 2.0%; M^+, 691).

$[W_2(\mu\text{-}\eta^2\text{-}CNMe)(CO)_4(\eta\text{-}C_5H_5)_2]$ (**6**).—In a similar manner to the preparation of (**5**) above complex (**6**) was synthesised in 38% yield through the treatment of a solution of $[\{W(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (**7**) (1.5 mmol) with CNMe (0.06 g, 1.5 mmol), m.p. 150 °C (decomp.) (Found: C, 29.1; H, 2.3; N, 1.8%; $[M - CNMe]^+$, 608. $C_{16}H_{13}NO_4W_2$ requires C, 29.6; H, 2.0; N, 2.2%; M^+, 649).

Reaction of $[W_2(\mu\text{-}\eta^2\text{-}CNMe)(CO)_4(\eta\text{-}C_5H_5)_2]$ (**6**) *with* CNMe.—A mixture of the bridged complex (**6**) (0.65 g, 1 mmol) and CNMe (0.16 g, 4 mmol) in toluene (100 cm^3) was stirred at room temperature (2 d) until the i.r. spectrum showed no bands of the starting material (**6**). Removal of solvent and chromatography on alumina (8 × 2 cm), eluting with an increasing concentration of dichloromethane in light petroleum gave $[W_2(CNMe)(CO)_5(\eta\text{-}C_5H_5)_2]$ (**10**) (0.10 g, 15%) as red crystals, m.p. 175—177 °C (Found: C, 30.1; H, 2.5; N, 1.7%; $[M + H]^+$, 680. $C_{17}H_{13}NO_5W_2$ requires C, 30.1; H, 1.9; N, 2.1%; M^+, 679).

$[Mo_2(CNBu^t)(\mu\text{-}\eta^2\text{-}CNBu^t)(CO)_3(\eta\text{-}C_5H_5)_2]$ (**11**).—A solution of $[Mo_2(\mu\text{-}\eta^2\text{-}CNBu^t)(CO)_4(\eta\text{-}C_5H_5)_2]$ (**2**) (2.0 g, 3.87 mmol) in toluene (50 cm^3) was treated with CNBu^t (0.64 g, 7.74 mmol), thus generating a solution of (**9**), and the mixture refluxed (1 h). After removal of solvent the residue was taken up in light petroleum and filtered through a short alumina column (8 × 2 cm) to give maroon crystals of $[Mo_2(CNBu^t)(\mu\text{-}\eta^2\text{-}CNBu^t)(CO)_3(\eta\text{-}C_5H_5)_2]$ (**11**) (1.08 g, 49%) on crystallisation from light petroleum, m.p. 138—140 °C (Found: C, 48.1; H, 5.0; N, 4.6%; $[M - CNBu^t]^+$, 489. $C_{23}H_{28}Mo_2N_2O_3$ requires C, 48.3; H, 4.9; N, 4.9%; M^+, 572).

$[\{Mo(CNMe)(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (**8**).—The isonitrile CNMe (0.39 g, 9.45 mmol) was added to a solution of $[\{Mo(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (**1**) (4.08 mmol) in toluene (150 cm^3) and the reaction mixture stirred at room temperature (24 h). After removal of the solvent and chromatography on alumina (8 × 2 cm), elution with light petroleum–dichloromethane (1:1) afforded $[\{Mo(CNMe)(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (**8**) (1.18 g, 56%) as maroon crystals after crystallisation from hexane–dichloromethane, m.p. 154—156 °C (Found: C, 42.0; H, 3.4; N, 5.2%; $[M - 3CO]^+$, 434. $C_{18}H_{16}Mo_2N_2O_4$ requires C, 41.9; H, 3.1; N, 5.4%; M^+, 516).

$[\{Mo(CNBu^t)(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (**9**).—The complex $[Mo_2(\mu\text{-}\eta^2\text{-}CNBu^t)(CO)_4(\eta\text{-}C_5H_5)_2]$ (**2**) was prepared by the addition of CNBu^t (0.34 g, 4.1 mmol) to a solution of $[\{Mo(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (**1**) (4.1 mmol) in toluene (150 cm^3). The maroon solution of (**2**) was then concentrated and excess CNBu^t (5.25 g, 63 mmol) added. The reaction was stirred at room temperature (3.5 h) during which time the colour became deep red. After removal of solvent and chromatography on alumina (8 × 2 cm), eluting with light petroleum–dichloromethane (1:1) yielded $[\{Mo(CNBu^t)(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (**9**) (1.71 g, 69%) as dark red crystals after crystallisation from hexane–dichloromethane, m.p. 143—145 °C (Found: C, 48.3; H, 4.9; N, 4.4%; $[M - CO]^+$, 572. $C_{24}H_{28}Mo_2N_2O_4$ requires C, 48.0; H, 4.7; N, 4.7%; M^+, 600).

$[Mo(SnPh_3)(CNMe)(CO)_2(\eta\text{-}C_5H_5)]$ (**14**).—A solution of $[\{Mo(CNMe)(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (**8**) (0.27 g, 0.52 mmol) in thf (40 cm^3) was treated with sodium amalgam (Hg, 4 cm^3; Na, 0.15 g, 7 mmol) and stirred at ambient temperature for 30 min, during which time the colour changed from maroon to pale yellow-green. Formation of $[Mo(CNMe)(CO)_2(\eta\text{-}C_5H_5)]^-$ (**12**) was indicated by the i.r. spectrum [ν(CO) at 1 765s, 1 717s; ν(CN) at 1 869s cm^{-1}]. Addition of $SnPh_3Cl$ (0.39 g, 1.0 mmol) and stirring (30 min) gave a pale yellow solution which was chromatographed after removal of solvent. Elution with dichloromethane gave $[Mo(SnPh_3)(CNMe)(CO)_2(\eta\text{-}C_5H_5)]$ (**14**) on crystallisation from light petroleum–dichloromethane (0.18 g, 30%), m.p. 133—135 °C (Found: C, 53.2; H, 4.0; N, 2.1%; M^+, 608. $C_{27}H_{23}MoNO_2Sn$ requires C, 53.5; H, 3.8; N, 2.3%; M^+, 608).

$[Mo(SnPh_3)(CNBu^t)(CO)_2(\eta\text{-}C_5H_5)]$ (**15**).—This was prepared in a similar manner to (**14**) above using (**9**) as starting material. The anion $[Mo(CNBu^t)(CO)_2(\eta\text{-}C_5H_5)]^-$ (**13**) is characterised by its i.r. spectrum [ν(CO) at 1 769s, 1 717s; ν(CN) at 1 873 cm^{-1}]. The final product $[Mo(SnPh_3)(CNBu^t)(CO)_2(\eta\text{-}C_5H_5)]$ (**15**) was isolated in 52% yield after crystallisation from light petroleum–dichloromethane, m.p. 135—137 °C (Found: C, 55.5; H, 4.6; N, 1.9%; M^+, 650. $C_{30}H_{29}MoNO_2Sn$ requires C, 55.4; H, 4.5; N, 2.2%; M^+, 650).

Crystal Data for $[\{Mo(CNBu^t)(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (**9**).—$C_{24}H_{28}Mo_2N_2O_4$, M = 600.29 (crystallises from dichloromethane–light petroleum as small, dark red prisms; crystal dimensions 0.08 × 0.17 × 0.06 mm), monoclinic, a = 10.354(7), b = 11.672(5), c = 10.793(5) Å, β = 103.68(4)°, U = 1 267.4(11) Å^3, Z = 2, D_c = 1.573 g cm^{-3}, space group $P2_1/c$ (C_{2h}^5, no. 14), graphite-monochromated Mo-K_α radiation ($\bar{\lambda}$ = 0.710 69 Å), μ(Mo-K_α) = 9.95 cm^{-1}, F(000) = 604.

Three-dimensional X-ray diffraction data were collected in the range 3.5 < 2θ < 50° on a Nicolet $R3m$ diffractometer by the ω-scan method. 1 102 Independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects and for absorption. The structure was solved by standard Patterson and Fourier techniques and refined by block-diagonal least-squares methods. Hydrogen atoms were placed in calculated positions [C–H(methyl) 0.96 Å, C–C–H(methyl) 111°]; their contributions were included in structure factor calculations (B = 7.0 Å^2) but no refinement of positional parameters was permitted. In view of the limited quantity and quality of the data, it was found necessary to apply geometric constraints to the cyclopentadienyl ring (D_{5h} symmetry, C–C 1.42, C–H 0.95 Å) and the carbonyl groups (Mo–C 1.987, C–O 1.147 Å, Mo–C–O 180°). Refinement converged at R 0.0519 with allowance for anisotropic thermal motion of all non-hydrogen atoms and for the anomalous scattering of molybdenum. Table 7 lists the atomic positional parameters with estimated standard deviations.

Crystal Data for $[Mo_2(\mu\text{-}\eta^2\text{-}CNBu^t)(CO)_4(\eta\text{-}C_5H_5)_2]$ (**2**).—$C_{19}H_{19}Mo_2NO_4$, M = 517.16 (crystallises from light petroleum as black, platey needles; crystal dimensions 0.66 × 0.26 × 0.065 mm), orthorhombic, a = 31.75(3), b = 8.171(11), c = 15.722(17) Å, U = 4 079(8) Å^3, Z = 8, D_m = 1.71, D_c = 1.684 g cm^{-3}, space group $Pbca$ (D_{2h}^{15}, no. 61), graphite-monochromated Mo-K_α radiation ($\bar{\lambda}$ = 0.710 69 Å), μ(Mo-K_α) = 12.23 cm^{-1}, F(000) = 2 048.

The data were collected (6.5 < 2θ < 50° on a Stoe Stadi-2 diffractometer) and processed (1 775 independent reflections) and the structure solved and refined (R 0.0357) as above. Hydrogen atoms were detected and positioned [C–H 0.98 Å, C–C–H(methyl) 114°]. No constraints were applied during refinement. Table 4 lists atomic positions and estimated standard deviations.

Scattering factors were taken from ref. 23; unit weights were used throughout the refinements. Computer programs formed part of the Sheffield X-Ray System.

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