Synthetic and Structural Studies on Organomolybdenum and Organotungsten Complexes containing Bismuth. *X*-Ray Crystal Structures of $[BiCl\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ and $[BiCl\{Mo(CO)_2(CNBu^t)(\eta\text{-}C_5H_5)\}_2]$ *

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The reaction between $BiCl_3$ and 3 equivalents of $Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$ affords the trimolybdenum–bismuth complex $[Bi\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_3]$, (**1**), which has been characterised by spectroscopic methods. The corresponding reaction involving 2 equivalents of $Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$ affords the disubstituted product $[BiCl\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$, (**3**), which has been characterised by *X*-ray diffraction. The molecular structure comprises a trigonal pyramidal bismuth atom bonded to one chlorine and two $Mo(CO)_3(\eta\text{-}C_5H_5)$ fragments and containing a stereochemically active lone pair at the apex of the pyramid. The two crystallographically independent molecules have similar conformations but a weak intermolecular Bi ••• Cl interaction, which is present for both molecules, is significantly different in each case. Treatment of a solution of compound (**1**) with 0.5 equivalent of $BiCl_3$ affords (**3**) and when pure samples of (**3**) are treated with 1 equivalent of $BiCl_3$ a redistribution reaction is also observed forming $[BiCl_2\{Mo(CO)_3(\eta\text{-}C_5H_5)\}]$. A similar range of compounds has been synthesised containing the methylcyclopentadienyl ligand. The analogous tungsten chemistry has also been investigated and similar tri-, di-, and mono-tungsten–bismuth compounds have been synthesised. Slight differences between the molybdenum and tungsten systems are observed, however, under the reaction conditions employed and these are discussed in terms of the possible mechanisms involved. Finally, the reactions between $BiCl_3$ and 2 equivalents of the carbonyl-substituted anions $[Mo(CO)_2L(\eta\text{-}C_5H_5)]^-$ ($L = Bu^tNC$, MeNC, or PPh_3) have been examined. These result in the dimolybdenum–bismuth complexes $[BiCl\{Mo(CO)_2L(\eta\text{-}C_5H_5)\}_2]$, $L = Bu^tNC$ (**15**), MeNC (**16**), or PPh_3 (**17**). The first two complexes exist as mixtures of isomers, *viz, cis,trans* and *trans,trans* with regard to the stereochemistry at the molybdenum centres, whilst the latter exists as the *trans,trans* form. The *cis,trans* form of (**15**) was characterised by *X*-ray diffraction. The structure is similar to that observed for compound (**3**) except that no short intermolecular Bi ••• Cl interactions are present. Spectroscopic and analytical data for the complexes are presented.

Organotransition metal complexes incorporating atoms of or fragments containing the heavier main group metals are currently attracting attention. Moreover, this interest is more than academic since a number of important industrial catalysts contain both a transition metal and a main group metal. An example of this class of compound is the bismuth molybdate system at the heart of the SOHIO alkene oxidation and ammoxidation processes,[1,2] and this is probably responsible, at least in part, for the growth and continuing interest in transition metal–bismuth complexes.

A few examples of this type of compound have been known for some years such as $[Bi\{Co(CO)_4\}_3]$[3] and $[Ir_3(CO)_9(\mu_3\text{-}Bi)]$.[4] More recently, however, Whitmire *et al.*[5] have synthesised a range of bismuth-containing iron carbonyl clusters and further examples of Group 8 metal–bismuth compounds have also been reported. This latter class of compounds includes $[Co_3(CO)_6(\mu\text{-}CO)_3(\mu_3\text{-}Bi)]$,[6] $[Bi_2Co_4(CO)_{11}]^-$,[6b] and a number of ruthenium– and osmium–bismuth clusters.[7] Compounds containing earlier transition metals are less common but include examples such as $[Bi\{Mn(CO)_5\}_3]$,[8] $[\{W(CO)_5\}_3(\mu_3\text{-}\eta^2\text{-}Bi_2)]$,[9] and $[W_2(CO)_8(\mu\text{-}\eta^2\text{-}Bi_2)\{\mu\text{-}Bi(Me)W(CO)_5\}]$.[10]

Of particular interest to the present work are complexes containing a transition metal-bound cyclopentadienyl ligand. Relatively few reports dealing with this type of compound have appeared and most of these have been concerned with molecules containing the cyclopentadienyliron dicarbonyl fragment. Cullen *et al.*[11] have reported the synthesis of $[(C_5H_5)(OC)_2FeBiCl_2]$ from the reaction between $BiCl_3$ and $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and more recently, Malisch and co-workers[12] and Wieber *et al.*[13] have described the synthesis of $[(C_5H_5)(OC)_2FeBiMe_2]$ and $[(C_5H_5)(OC)_2FeBi(S_2CR)_2]$ ($R = NEt_2$ or OMe) respectively. The reaction between $BiCl_3$ and 2 or 3 equivalents of $[Fe(CO)_2(\eta\text{-}C_5H_5)]^-$ has been the subject of studies by both Schmidbaur and co-workers[14] and ourselves.[15]

Examples of cyclopentadienyl transition metal–bismuth complexes containing metals other than iron are even more scarce. von Seyerl and Huttner[16] have described the synthesis and structure of $[\{[Mn(CO)_2(\eta\text{-}C_5H_5)]_2BiCl\}_2]$[16] whilst Panster and Malisch[17] have reported the reaction between

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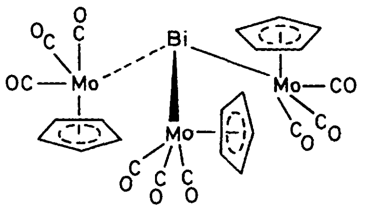
* Chlorobis[tricarbonyl(η-cyclopentadienyl)molybdenio]bismuth and chlorobis[dicarbonyl(η-cyclopentadienyl)(t-butyl isocyanide)molybdenio]bismuth.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.



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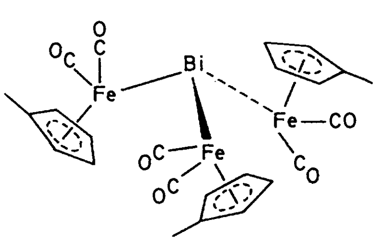

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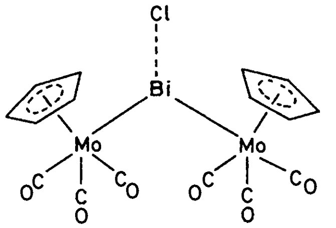

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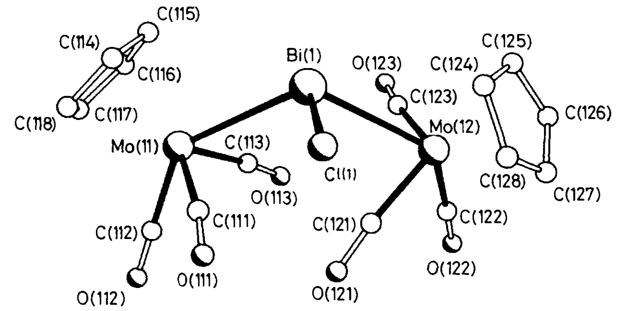


Figure 1. The molecular structure of molecule A of compound (**3**) showing the atom numbering scheme adopted

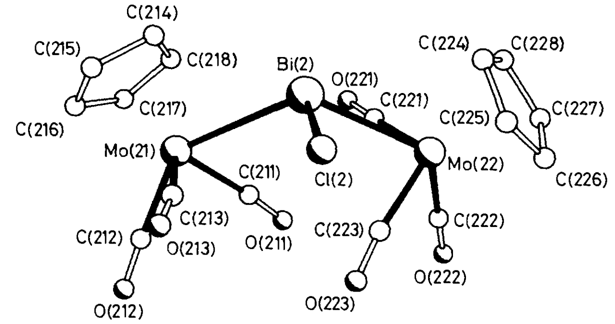


Figure 2. The molecular structure of molecule B of compound (**3**) showing the atom numbering scheme adopted

$[M(CO)_3(\eta\text{-}C_5H_5)]^-$ (M = Cr, Mo, or W) and $BiBrMe_2$ which affords both mono- and di-metal–bismuth complexes.

In view of the importance of bismuth–molybdenum materials in catalysis involving organic substrates, the scarcity of reports dealing with organomolybdenum–bismuth complexes is surprising and prior to the work reported herein, no such complexes had been structurally characterised. In this paper we report details of the reactions between $BiCl_3$ and $[M(CO)_3(\eta\text{-}C_5H_5)]^-$ (M = Mo or W), and simple derivatives of these species, some aspects of which have been the subject of a preliminary communication.[18]

Results and Discussion

Addition of a tetrahydrofuran (thf) solution of $BiCl_3$ to a thf solution containing 3 equivalents of $Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$ initially produced a dark green solution which became deep red after complete addition of the bismuth trichloride. Purification of the resulting reaction mixture by column chromatography afforded a deep red solution from which a dark red powder was obtained from thf–hexane mixtures at −20 °C. Analytical and spectroscopic data (Tables 1 and 2) were sufficient to identify this material as the trimolybdenum–bismuth complex, (**1**). Little structural information can be directly deduced from these data but it is presumed that the bismuth adopts a trigonal-pyramidal co-ordination geometry analogous to the related and structurally characterised tri-iron complex $[Bi\{Fe(CO)_2(\eta\text{-}C_5H_4Me)\}_3]$, (**2**).[15b] Unfortunately many attempted crystallisations of (**1**) failed to produce crystals of a quality suitable for *X*-ray diffraction.

The observation of an initial green colour in the above mentioned reaction was suggestive of an intermediate compound in the formation of (**1**). This was confirmed in a separate experiment in which 2 equivalents of $Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$ were added to a solution of $BiCl_3$. An immediate green colour developed which persisted throughout the addition of the molybdenum carbonylate anion. Filtration of the resulting reaction mixture followed by crystallisation from CH_2Cl_2–hexane mixtures afforded dark green crystals of the dimolybdenum complex (**3**). Characterisation by normal analytical and spectroscopic methods (Tables 1 and 2) indicated that (**3**) was a dimolybdenum–bismuth complex and this was confirmed by an *X*-ray crystallographic study. Crystals of (**3**) have two independent molecules in the asymmetric unit and views of each of these are shown in Figures 1 and 2. Selected bond distances and angles for both molecules are given in Table 3 and atomic positional parameters are presented in Table 4. Each molecule consists of a single bismuth atom bonded to one chlorine and two molybdenum atoms, such that the bismuth atoms have a trigonal-pyramidal co-ordination geometry [sum of angles: Bi(*1*), 311.5; Bi(2), 319.0°]. In addition to bismuth, each molybdenum atom is bonded to one cyclopentadienyl and three terminal carbonyl ligands, all of normal geometry, and the complete ligand set around each molybdenum is of the familiar $(C_5H_5)ML_4$ 'piano-stool' type. Moreover, the relative conformations of both molecules are similar, as is evident from a comparison of Figures 1 and 2; Figure 3 shows a best-fit superposition of line diagrams of both molecules. The molybdenum–bismuth bond lengths are all similar (Table 3, av. Bi–Mo 2.951 Å) and consistent with single bonding, as required by electron-counting procedures. However, this statement is based on a predicted reasonable single bond length derived from a sum of covalent radii ($\approx$ 2.8 Å) since (**3**) [and (**15**), see later] are the first molecules to be structurally characterised which contain unsupported Bi–Mo bonds.

Of further interest are the intermolecular interactions in this structure which are represented in Figure 4. Thus in molecule A, a substantial interaction exists between the chlorine atom, Cl(1), and the bismuth atom, Bi(1′), of an adjacent but symmetry-

Table 1. Analytical[a] and physical data for the complexes

Compound	Colour	Yield (%)	$\tilde{\nu}$(CO)[b]/cm^{-1}	Analysis (%) C	Analysis (%) H
(1) $[\mathrm{Bi}\{\mathrm{Mo(CO)_3}(\eta\text{-}\mathrm{C_5H_5})\}_3]$	Red	69	2 004m, 1 966s, 1 929w, 1 896m	30.8 (30.5)	1.7 (1.6)
(3) $[\mathrm{BiCl}\{\mathrm{Mo(CO)_3}(\eta\text{-}\mathrm{C_5H_5})\}_2]$	Dark green	53	2 051w, 2 010s, 1 978s, 1 912s	26.3 (26.2)	1.4 (1.4)[c]
(5) $[\mathrm{Bi}\{\mathrm{Mo(CO)_3}(\eta\text{-}\mathrm{C_5H_4Me})\}_3]$	Red	60	2 002m, 1 963s, 1 927w, 1 894m	32.4 (32.9)	1.9 (2.1)
(6) $[\mathrm{BiCl}\{\mathrm{Mo(CO)_3}(\eta\text{-}\mathrm{C_5H_4Me})\}_2]$	Dark green	62	2 047w, 2 007s, 1 974s, 1 917s	—	—
(7) $[\mathrm{BiCl_2}\{\mathrm{Mo(CO)_3}(\eta\text{-}\mathrm{C_5H_5})\}]$	Orange	90	2 007s, 1 927s[d]	—	—
(8) $[\mathrm{BiCl_2}\{\mathrm{Mo(CO)_3}(\eta\text{-}\mathrm{C_5H_4Me})\}]$	Orange	85	2 008s, 1 945s	—	—
(9) $[\mathrm{Bi}\{\mathrm{W(CO)_3}(\eta\text{-}\mathrm{C_5H_5})\}_3]$	Red	51	2 000m, 1 960s, 1 922w, 1 885m	23.1 (23.8)	1.3 (1.3)
(10) $[\mathrm{BiCl}\{\mathrm{W(CO)_3}(\eta\text{-}\mathrm{C_5H_5})\}_2]$	Purple	38	2 038w, 2 006s, 1 973s, 1 899s	20.9 (21.1)	1.1 (1.1)
(12) $[\mathrm{BiCl}\{\mathrm{W(CO)_3}(\eta\text{-}\mathrm{C_5H_4Me})\}_2]$	Purple	40	2 040w, 2 004s, 1 971s, 1 901s	22.3 (23.0)	1.2 (1.5)
(13) $[\mathrm{WCl(CO)_3}(\eta\text{-}\mathrm{C_5H_4Me})]$	Orange	—	2 040m, 1 951s 2 048m, 1 968s, 1 949m[e]	27.6 (28.2)	1.6 (1.8)
(14) $[\mathrm{BiCl_2}\{\mathrm{W(CO)_3}(\eta\text{-}\mathrm{C_5H_5})\}]$	Orange	90	2 005s, 1 913s	15.5 (15.7)	0.6 (0.8)
(15) $[\mathrm{BiCl}\{\mathrm{Mo(CO)_2(CNBu^t)}(\eta\text{-}\mathrm{C_5H_5})\}_2]$	Dark green	75	1 983w, 1 942s, 1 921m, 1 877s[f]	33.6 (34.1)	3.2 (3.3)[g]
(16) $[\mathrm{BiCl}\{\mathrm{Mo(CO)_2(CNMe)}(\eta\text{-}\mathrm{C_5H_5})\}_2]$	Dark green	—	1 975w, 1 946s, 1 923m, 1 880s[h]	—	—
(17) $[\mathrm{BiCl}\{\mathrm{Mo(CO)_2(PPh_3)}(\eta\text{-}\mathrm{C_5H_5})\}_2]$	Dark green	—	1 899m, 1 855s, 1 826m, 1 797m	—	—

[a] Calculated values are given in parentheses. [b] Measured in thf unless otherwise stated. [c] Chlorine analysis 5.0 (4.8)%. [d] Recorded in acetone solution. [e] Recorded in hexane solution. [f] ν(CN) for CNBu^t ligands: 2 114 cm^{-1} (broad shoulder at *ca.* 2 060 cm^{-1}). [g] Nitrogen analysis 3.2 (3.3)%. [h] ν(CN) for CNMe ligands: 2 152 cm^{-1}.

Table 2. Proton and ^{13}C-{^{1}H} n.m.r. data for the complexes[a]

Compound	^{1}H(δ)[b]	^{13}C(δ)[b,c]
(1)	5.52 ($\mathrm{C_5H_5}$)	93.0 ($\mathrm{C_5H_5}$)
(3)	5.57 ($\mathrm{C_5H_5}$)	94.0 ($\mathrm{C_5H_5}$)
(5)	2.13 (s, 3 H, $\mathrm{C_5H_4}\mathit{Me}$), 5.41 (br s, 4 H, $\mathrm{C_5}\mathit{H}_4\mathrm{Me}$)	14.4 (s, $\mathrm{C_5H_4}\mathit{Me}$), 92.9 (s, $\mathit{C}_5\mathrm{H_4Me}$)
(6)	2.18 (s, 3 H, $\mathrm{C_5H_4}\mathit{Me}$), 5.41 (m, 2 H, $\mathrm{C_5}\mathit{H}_4\mathrm{Me}$), 5.54 (m, 2 H, $\mathrm{C_5}\mathit{H}_4\mathrm{Me}$)	14.1 (s, $\mathrm{C_5H_4}\mathit{Me}$), 92.6 (s, $\mathit{C}_5\mathrm{H_4Me}$, ring C–H), 95.2 (s, $\mathit{C}_5\mathrm{H_4Me}$, ring C–H), 113.4 (s, $\mathit{C}_5\mathrm{H_4Me}$, ring *C*–Me)
(7)	5.69 ($\mathrm{C_5H_5}$) 5.78 ($\mathrm{C_5H_5}$)[d]	94.7 ($\mathrm{C_5H_5}$) 94.5 ($\mathrm{C_5H_5}$)[d]
(8)	2.20 (s, 3 H, $\mathrm{C_5H_4}\mathit{Me}$), 5.58 (m, 2 H, $\mathrm{C_5}\mathit{H}_4\mathrm{Me}$), 5.66 (m, 2 H, $\mathrm{C_5}\mathit{H}_4\mathrm{Me}$) 2.37 (s, 3 H, $\mathrm{C_5H_4}\mathit{Me}$), 5.78 (m, 2 H, $\mathrm{C_5}\mathit{H}_4\mathrm{Me}$), 5.89 (m, 2 H, $\mathrm{C_5}\mathit{H}_4\mathrm{Me}$)[d]	14.0 (s, $\mathrm{C_5H_4}\mathit{Me}$), 93.5 (s, $\mathit{C}_5\mathrm{H_4Me}$, ring C–H), 95.8 (s, $\mathit{C}_5\mathrm{H_4Me}$, ring C–H), 112.9 (s, $\mathit{C}_5\mathrm{H_4Me}$, ring *C*–Me) 14.4 (s, $\mathrm{C_5H_4}\mathit{Me}$), 92.9 (s, $\mathit{C}_5\mathrm{H_4Me}$, ring C–H), 95.6 (s, $\mathit{C}_5\mathrm{H_4Me}$, ring C–H), 113.3 (s, $\mathit{C}_5\mathrm{H_4Me}$, ring *C*–Me)[d]
(9)	5.61 ($\mathrm{C_5H_5}$)	91.8 ($\mathrm{C_5H_5}$)
(10)	4.86 ($\mathrm{C_5H_5}$)[e]	92.1 ($\mathrm{C_5H_5}$)[e]
(12)	1.83 (s, 3 H, $\mathrm{C_5H_4}\mathit{Me}$), 4.93 (m, 4 H, $\mathrm{C_5}\mathit{H}_4\mathrm{Me}$)[e]	14.3 (s, $\mathrm{C_5H_4}\mathit{Me}$), 90.7 (s, $\mathit{C}_5\mathrm{H_4Me}$, ring C–H), 93.5 (s, $\mathit{C}_5\mathrm{H_4Me}$, ring C–H), 110.2 (s, $\mathit{C}_5\mathrm{H_4Me}$, ring *C*–Me), 217.0 (s, CO)[e]
(13)	1.58 (s, 3 H, $\mathrm{C_5H_4}\mathit{Me}$), 4.12 (m, 2 H, $\mathrm{C_5}\mathit{H}_4\mathrm{Me}$), 4.79 (m, 2 H, $\mathrm{C_5}\mathit{H}_4\mathrm{Me}$)[e]	14.7 (s, $\mathrm{C_5H_4}\mathit{Me}$), 86.4 (s, $\mathit{C}_5\mathrm{H_4Me}$, ring C–H), 93.1 (s, $\mathit{C}_5\mathrm{H_4Me}$, ring C–H), 94.3 (s, $\mathit{C}_5\mathrm{H_4Me}$, ring *C*–Me)[e]
(14)	5.87 ($\mathrm{C_5H_5}$) 5.96 ($\mathrm{C_5H_5}$)[d]	93.8 ($\mathrm{C_5H_5}$) 93.6 ($\mathrm{C_5H_5}$)[d]
(15)	1.40 (s, 9 H, $\mathrm{CMe_3}$), 1.50 (s, 9 H, $\mathrm{CMe_3}$), 5.24 (s, 5 H, $\mathrm{C_5H_5}$), 5.39 (s, 5 H, $\mathrm{C_5H_5}$)[f]	
(15a)	1.52 (s, 9 H, $\mathrm{CMe_3}$), 5.30 (s, $\mathrm{C_5H_5}$)[f]	
(16)	3.81 (s, 3 H, CNMe), 3.83 (s, 3 H, CNMe), 5.25 (s, 5 H, $\mathrm{C_5H_5}$), 5.37 (s, 5 H, $\mathrm{C_5H_5}$)[f]	
(16a)	3.82 (s, 3 H, CNMe), 5.28 (s, 5 H, $\mathrm{C_5H_5}$)[f]	
(17)[g]	4.96 (d, 5 H, $\mathrm{C_5H_5}$, J_{PH} = 1.2 Hz), 7.40—7.65 (m, 15 H, $\mathrm{PPh_3}$)	

[a] Chemical shifts in p.p.m., coupling constants in Hz; measurements at room temperature. [b] Measured in [^{2}H$_8$]tetrahydrofuran unless otherwise stated. [c] ^{1}H decoupled, chemical shifts are positive to high frequency of SiMe$_4$. [d] Recorded in [^{2}H$_6$]acetone. [e] Recorded in C$_6$D$_6$. [f] Recorded in CD$_2$Cl$_2$. [g] Phosphorus-31 n.m.r. spectrum: δ = 65.0 p.p.m., recorded in C$_6$D$_6$, reference 85% H$_3$PO$_4$ (external).

related molecule, *i.e.* another molecule A rather than molecule B. A similar interaction exists between Cl(2) in molecule B and an adjacent bismuth atom, Bi(2′), also in a molecule B. The overall situation is therefore one in which molecule A forms a linear, chlorine-bridged polymer *via* Bi••• Cl interactions with other symmetry-related A molecules. A similar arrangement is adopted by molecule B and its symmetry-related neighbours, there being no cross-interactions between the adjacent, but symmetry-unrelated chains of molecules, A and B. Some form of intermolecular interaction of this type is not surprising in view of the known Lewis acidity of three-co-ordinate bismuth(III), and, in the related iron–bismuth compound $[\mathrm{BiCl}\{\mathrm{Fe(CO)_2}(\eta\text{-}\mathrm{C_5H_4Me})\}_2]$, **(4)**,[14,15] a cyclotrimeric structure is observed in the solid state as a result of Bi–Cl bridging.

In **(3)**, therefore, the intermolecular association takes the form of an infinite one-dimensional chain rather than of a cyclic oligomer. However, closer inspection of the bond distances involved reveals substantial differences between the molecule A

Table 3. Selected bond lengths (Å) and angles (°) for compound (**3**)

Bi(1)–Mo(11)	2.960(1)	Bi(1)–Mo(12)	2.939(1)	Bi(2)–Mo(21)	2.983(1)	Bi(2)–Mo(22)	2.921(1)
Bi(1)–Cl(1)	2.746(2)	Bi(1)–Cl(1b)	3.039(3)	Bi(2)–Cl(2)	2.612(3)	Bi(2)–Cl(2d)	3.596(4)
Mo(11)–C(111)	1.992(9)	Mo(11)–C(112)	1.979(10)	Mo(21)–C(211)	1.986(10)	Mo(21)–C(212)	1.994(10)
Mo(11)–C(113)	1.999(8)	Mo(11)–C(114)	2.338(10)	Mo(21)–C(213)	1.991(10)	Mo(21)–C(214)	2.336(14)
Mo(11)–C(115)	2.356(11)	Mo(11)–C(116)	2.356(10)	Mo(21)–C(215)	2.325(11)	Mo(21)–C(216)	2.330(10)
Mo(11)–C(117)	2.312(8)	Mo(11)–C(118)	2.328(9)	Mo(21)–C(217)	2.320(11)	Mo(21)–C(218)	2.336(16)
Mo(12)–C(121)	1.968(10)	Mo(12)–C(122)	1.978(9)	Mo(22)–C(221)	1.990(9)	Mo(22)–C(222)	1.963(10)
Mo(12)–C(123)	1.988(9)	Mo(12)–C(124)	2.345(11)	Mo(22)–C(223)	2.005(9)	Mo(22)–C(224)	2.376(9)
Mo(12)–C(125)	2.333(12)	Mo(12)–C(126)	2.325(9)	Mo(22)–C(225)	2.334(9)	Mo(22)–C(226)	2.331(9)
Mo(12)–C(127)	2.322(10)	Mo(12)–C(128)	2.340(11)	Mo(22)–C(227)	2.328(9)	Mo(22)–C(228)	2.335(9)

Mo(11)–Bi(1)–Mo(12)	118.3(1)	Mo(11)–Bi(1)–Cl(1)	101.6(1)	Mo(21)–Bi(2)–Cl(2)	106.7(1)	Mo(22)–Bi(2)–Cl(2)	95.9(1)
Mo(12)–Bi(1)–Cl(1)	91.6(1)	Mo(11)–Bi(1)–Cl(1b)	96.3(1)	Mo(21)–Bi(2)–Cl(2d)	106.1(1)	Mo(22)–Bi(2)–Cl(2d)	86.9(1)
Mo(12)–Bi(1)–Cl(1b)	99.2(1)	Cl(1)–Bi(1)–Cl(1b)	151.6(1)	Cl(2)–Bi(2)–Cl(2d)	141.6(1)	Bi(2)–Mo(21)–C(211)	76.9(2)
Bi(1)–Mo(11)–C(111)	77.8(2)	Bi(1)–Mo(11)–C(112)	136.5(2)	Bi(2)–Mo(21)–C(212)	135.9(3)	C(211)–Mo(21)–C(212)	74.7(3)
C(111)–Mo(11)–C(112)	77.4(4)	Bi(1)–Mo(11)–C(113)	75.1(2)	Bi(2)–Mo(21)–C(213)	76.7(2)	C(211)–Mo(21)–C(213)	105.2(4)
C(111)–Mo(11)–C(113)	105.9(3)	C(112)–Mo(11)–C(113)	78.1(4)	C(212)–Mo(21)–C(213)	79.0(4)	Bi(2)–Mo(22)–C(221)	74.1(3)
Bi(1)–Mo(12)–C(121)	73.0(2)	Bi(1)–Mo(12)–C(122)	132.8(2)	Bi(2)–Mo(22)–C(222)	131.1(2)	C(221)–Mo(22)–C(222)	78.6(4)
C(121)–Mo(12)–C(122)	76.2(3)	Bi(1)–Mo(12)–C(123)	78.0(2)	Bi(2)–Mo(22)–C(223)	73.3(3)	C(221)–Mo(22)–C(223)	107.2(3)
C(121)–Mo(12)–C(123)	107.2(4)	C(122)–Mo(12)–C(123)	77.9(3)	C(222)–Mo(22)–C(223)	77.2(4)	Bi(2)–Cl(2)–Bi(2c)	138.0(1)
Bi(1)–Cl(1)–Bi(1a)	148.2(1)	Mo(21)–Bi(2)–Mo(22)	116.4(1)				

Symmetry operators (a) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{3}{2} - z$; (b) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$; (c) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (d) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

Table 4. Atomic co-ordinates ($\times 10^4$) for compound (**3**)

Atom	x	y	z	Atom	x	y	z
Bi(1)	2 792(1)	6 759(1)	7 321(1)	Bi(2)	2 495(1)	6 769(1)	1 942(1)
Mo(11)	2 645(1)	6 738(1)	5 796(1)	Mo(21)	1 499(1)	6 864(1)	505(1)
Mo(12)	4 248(1)	7 309(1)	8 251(1)	Mo(22)	3 964(1)	7 840(1)	2 120(1)
Cl(1)	2 943(1)	4 268(2)	7 634(1)	Cl(2)	2 940(1)	4 465(2)	2 162(1)
C(111)	3 068(5)	5 062(8)	6 083(4)	C(211)	2 396(5)	7 751(8)	402(4)
O(111)	3 306(4)	4 073(6)	6 167(3)	O(211)	2 861(4)	8 279(6)	280(3)
C(112)	3 308(5)	6 475(8)	5 172(5)	C(212)	1 585(5)	6 447(8)	−453(5)
O(112)	3 695(4)	6 326(8)	4 820(4)	O(212)	1 665(4)	6 198(7)	−984(3)
C(113)	3 455(5)	7 953(7)	6 178(4)	C(213)	1 788(6)	5 078(9)	623(4)
O(113)	3 936(4)	8 633(6)	6 345(3)	O(213)	1 872(6)	4 024(6)	614(4)
C(114)	1 382(5)	6 359(11)	5 621(5)	C(214)	707(7)	7 482(19)	1 185(6)
C(115)	1 490(6)	7 596(12)	5 808(4)	C(215)	315(5)	6 691(12)	664(7)
C(116)	1 732(6)	8 195(9)	5 274(6)	C(216)	241(6)	7 204(12)	44(6)
C(117)	1 783(5)	7 331(12)	4 792(4)	C(217)	581(7)	8 346(10)	146(7)
C(118)	1 550(5)	6 189(10)	4 997(5)	C(218)	873(7)	8 547(14)	835(8)
C(121)	4 416(4)	6 266(8)	7 489(5)	C(221)	3 256(5)	9 187(8)	1 715(4)
O(121)	4 594(4)	5 700(7)	7 052(4)	O(221)	2 872(4)	10 010(6)	1 497(3)
C(122)	5 171(5)	7 981(8)	8 082(4)	C(222)	4 443(5)	8 584(10)	1 441(4)
O(122)	5 686(4)	8 367(7)	7 968(4)	O(222)	4 733(4)	9 047(7)	1 045(3)
C(123)	3 930(4)	8 975(8)	7 849(4)	C(223)	3 859(5)	6 507(9)	1 392(4)
O(123)	3 814(4)	9 973(6)	7 682(3)	O(223)	3 877(5)	5 761(7)	995(4)
C(124)	3 647(5)	6 358(11)	9 022(5)	C(224)	3 964(5)	7 443(11)	3 301(4)
C(125)	3 858(8)	7 610(10)	9 270(5)	C(225)	4 455(6)	6 649(10)	3 115(4)
C(126)	4 625(7)	7 705(14)	9 444(5)	C(226)	5 032(5)	7 340(12)	2 972(4)
C(127)	4 896(6)	6 546(12)	9 329(5)	C(227)	4 873(5)	8 653(10)	3 041(4)
C(128)	4 316(6)	5 714(11)	9 070(5)	C(228)	4 203(6)	8 685(10)	3 242(4)

chains and those of molecule B. Thus, in the former, the secondary Bi–Cl interaction is much shorter than that found in the latter, and this in turn influences the primary Bi–Cl bond distances. For A the relevant parameters are Bi(1)–Cl(1) 2.746(2), Bi(1)–Cl(1b) 3.039(3) Å, Bi(1)–Cl(1)–Bi(1a) 148.2(1)°, whilst for B the corresponding values are Bi(2)–Cl(2) 2.612(3), Bi(2)–Cl(2d) 3.596(4) Å, Bi(2)–Cl(2)–Bi(2c) 138.0(1)°, which reveal that, as the secondary Bi–Cl distance shortens, that of the primary distance lengthens. Such an effect is not surprising, but the substantial and significant difference between the associative interactions in the two different chains, each made up of identical molecules, and in a single crystal structure, is more unexpected. There is no obvious explanation for these observations other than to invoke the all-embracing statement of crystal packing forces. Such an explanation is trite, but the observation itself is a good example of how careful any interpretation of bond distances for weak secondary interactions between molecules must be.

Complexes analogous to (**1**) and (**3**) but containing the methylcyclopentadienyl ligand were also prepared, namely (**5**) and (**6**). Both syntheses proceeded in an identical manner to those described for (**1**) and (**3**) respectively and both compounds were characterised by usual methods (Tables 1 and 2). The primary objective in preparing these derivatives, particularly in

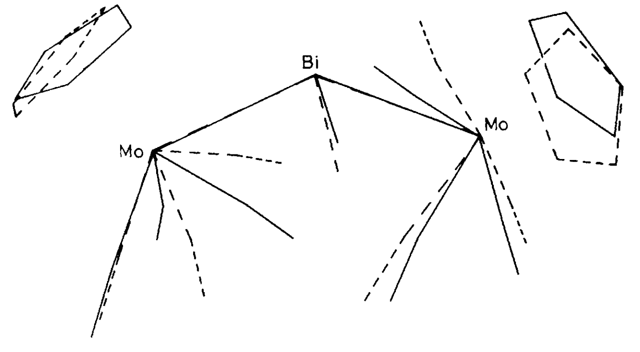


Figure 3. A superposition of line drawings of molecules A and B generated from a least-squares fit of the Bi and Mo atoms

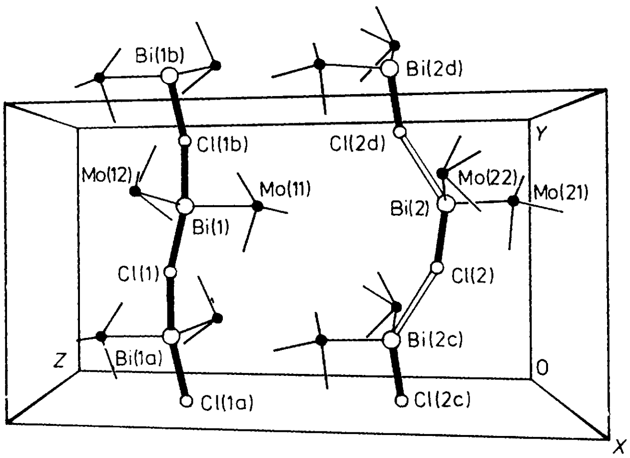
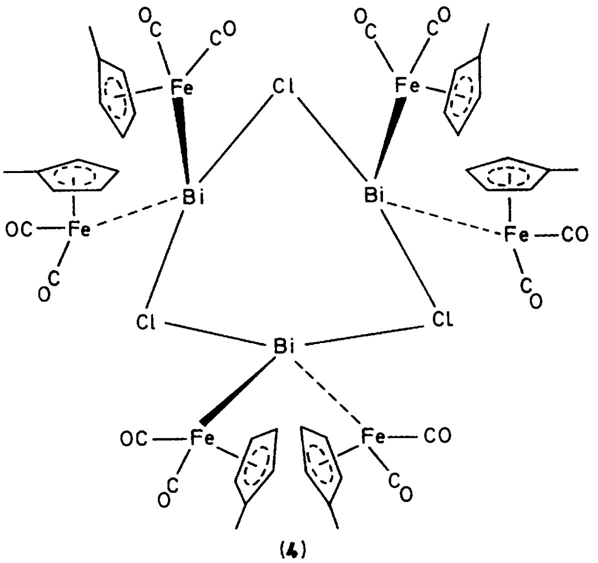


Figure 4. A view of part of the crystal structure of compound (**3**) showing the intermolecular Bi ••• Cl contacts. Each $\mathrm{Mo(CO)_3(C_5H_5)}$ fragment is represented as a filled circle and three lines to the carbonyl carbons. The cyclopentadienyl ligands are omitted for clarity

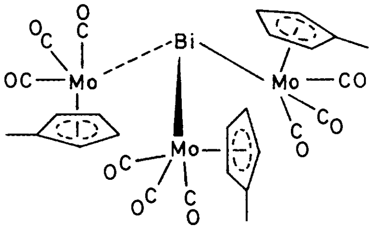
the case of (**5**), was to obtain crystals suitable for *X*-ray diffraction. Unfortunately, whilst (**5**) is more visibly crystalline than (**1**), *X*-ray quality crystals could not be obtained.

One point of interest concerning the syntheses of (**1**) and (**3**) [and (**5**) and (**6**)] arises from details of how the reactions are carried out. In order to maximise the yields of the trimolybdenum compounds, (**1**) and (**5**), it is important that the $\mathrm{BiCl_3}$ is added to the molybdenum carbonylate anion, thereby keeping the latter reactant in excess in the initial stages of the reaction. If the reaction is carried out in the reverse manner, appreciable quantities of the dimolybdenum compounds (**3**) and (**6**) are formed, which persist throughout the reaction, resulting in mixtures of products and corresponding difficulties during work-up. In order to maximise yields and purity in the synthesis of the dimolybdenum compounds, (**3**) and (**6**), it is preferable that the molybdenum anion is added to the $\mathrm{BiCl_3}$, thereby avoiding the production of any of the respective trisubstituted compounds.

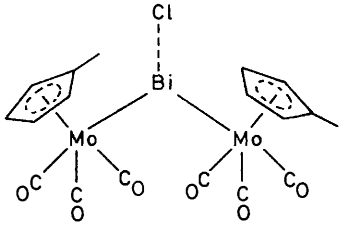
A further point of importance in all the above reactions concerns stoicheiometry, it being necessary to control this precisely if high yields of the desired products are to be obtained. This is important because undesirable equilibria in solution are avoided. This is particularly the case in the synthesis of (**1**) and (**5**), where an excess of $\mathrm{BiCl_3}$ leads to appreciable amounts of the dimolybdenum compounds (**3**) and (**6**) respectively. That such solution equilibria occur was demonstrated in a separate experiment, in which a thf solution of $\mathrm{BiCl_3}$ was added to a red thf solution of (**1**), resulting in an immediate colour change to green as a result of the formation of (**3**). Presumably an equilibrium as shown in equation (1) exists in solution.



(**4**)



(**5**)



(**6**)

$$\underset{(\mathbf{1})}{2[\mathrm{Bi}\{\mathrm{Mo(CO)_3(\eta\text{-}C_5H_5)}\}_3]} + \mathrm{BiCl_3} \rightleftharpoons \underset{(\mathbf{3})}{3[\mathrm{BiCl}\{\mathrm{Mo(CO)_3(\eta\text{-}C_5H_5)}\}_2]} \quad (1)$$

Further redistribution and exchange reactions in solution were also evident when a solution of $\mathrm{BiCl_3}$ was added to solutions of the molybdenum compounds, (**3**) and (**6**). Thus if an $\mathrm{Et_2O}$ solution of (**3**) is added to an $\mathrm{Et_2O}$ solution of $\mathrm{BiCl_3}$ an orange solid is precipitated over a period of a few hours. Spectroscopic data (Tables 1 and 2) are consistent with a monomolybdenum complex $[\mathrm{BiCl_2}\{\mathrm{Mo(CO)_3(\eta\text{-}C_5H_5)}\}]$, (**7**), which formulation is in accordance with an equilibrium (2). In

$$\underset{(\mathbf{3})}{[\mathrm{BiCl}\{\mathrm{Mo(CO)_3(\eta\text{-}C_5H_5)}\}_2]} + \mathrm{BiCl_3} \rightleftharpoons \underset{(\mathbf{7})}{2[\mathrm{BiCl_2}\{\mathrm{Mo(CO)_3(\eta\text{-}C_5H_5)}\}]} \quad (2)$$

particular, i.r. spectra recorded in the carbonyl region for (**7**) reveal two sharp absorptions (Table 1) indicative of a complex containing a single $Mo(CO)_3(C_5H_5)$ fragment.

Compound (**7**) may be isolated in a relatively pure solid form as described above by carrying out the reactions in Et_2O, since both $BiCl_3$ and (**3**) are soluble in this solvent whereas (**7**) is not. The equilibrium (2) may thus be displaced entirely to the right-hand side by exploiting the fortuitous differing solubilities of the various compounds. However, in solvents in which all the components of (2) are soluble, appreciable concentrations of all species are found to be present. In the solvents studied (thf and acetone) the equilibrium constants were calculated from the relative concentrations of (**3**) and (**7**), as judged by integration of the respective C_5H_5 resonances in the ^1H n.m.r. spectra, according to equation (3). Thus it is found that $K_{thf} \approx 1$ whilst

$$K = \frac{[BiCl_2\{Mo(CO)_3(C_5H_5)\}]^2}{[BiCl\{Mo(CO)_3(C_5H_5)\}_2][BiCl_3]} \qquad (3)$$

$K_{acetone} \approx 10$, indicating that in acetone the equilibrium is shifted further towards (**7**) than is the case in thf. There is no obvious explanation for this difference other than that donor solvents such as thf and acetone are almost certainly not innocent and might thus be expected subtly to influence the equilibrium concentrations.

Analogous chemistry with the methylcyclopentadienyl systems, *viz.* (**6**) and (**8**), proceeds similarly, and values for the equilibrium constants in both thf and acetone are essentially the same as those found for the cyclopentadienyl analogues, although this is more difficult to judge due to overlapping signals in the ^1H n.m.r. spectra. Data for (**8**) are presented in Tables 1 and 2. Satisfactory microanalytical data could not be obtained for either (**7**) or (**8**) due to contamination of the samples with $[MoCl(CO)_3(\eta\text{-}C_5H_5)]$ and $[MoCl(CO)_3(\eta\text{-}C_5H_4Me)]$ respectively. That such compounds were present was evident from both i.r. and n.m.r. spectra and each is presumably formed as a by-product in the synthesis of (**7**) and (**8**).

Having established that a range of bismuth–molybdenum complexes could be synthesised, it was of interest to examine the corresponding chemistry involving tungsten. Accordingly the reaction between $BiCl_3$ and 3 equivalents of $Na[W(CO)_3(\eta\text{-}C_5H_5)]$ was carried out with the aim of producing a tritungsten–bismuth complex, (**9**), analogous to the molybdenum complex, (**1**). In contrast to the molybdenum system, however, this reaction afforded a mixture of products consisting of (**9**), the ditungsten complex (**10**), and $[WCl(CO)_3(\eta\text{-}C_5H_5)]$, (**11**). The last compound, (**11**), was obtained in relatively pure form by column chromatography of the reaction mixture and further purified by crystallisation from thf–hexane which afforded yellow-orange crystals. Identification was effected by i.r. spectroscopy [$\nu(C{\equiv}O)$(thf) 2 043m and 1 953s cm^{-1}] and elemental analysis. The first two complexes, (**9**) and (**10**), could not easily be separated or purified by either column chromatography or fractional crystallisation. Both may, however, be obtained in pure form by other routes.

The ditungsten complex (**10**) was obtained in good yield from the reaction between $BiCl_3$ and 2 equivalents of $Na[W(CO)_3(\eta\text{-}C_5H_5)]$. Although traces of (**11**) were formed in this reaction, the two compounds are readily separated by column chromatography and, on further work up, purple crystals of (**10**) were obtained. Analytical and spectroscopic data (Tables 1 and 2), particularly i.r. (Figure 5), were in complete accord with a structure for (**10**) analogous to that of the molybdenum complex (**3**).

The method by which the tritungsten complex, (**9**), was obtained in pure form resulted from an observation which had been made while studying the reaction chemistry of (**3**). Thus it was observed that reduction of (**3**) with 1 equivalent of sodium dihydronaphthylide afforded (**1**) as the only molybdenum-containing compound in high yield rather than an anticipated coupling product. Accordingly, the reaction between (**10**) and sodium dihydronaphthylide was carried out, which resulted in good yields of (**9**), readily purified by column chromatography and crystallisation from thf–hexane. Full analytical and spectroscopic data are presented in Tables 1 and 2, the

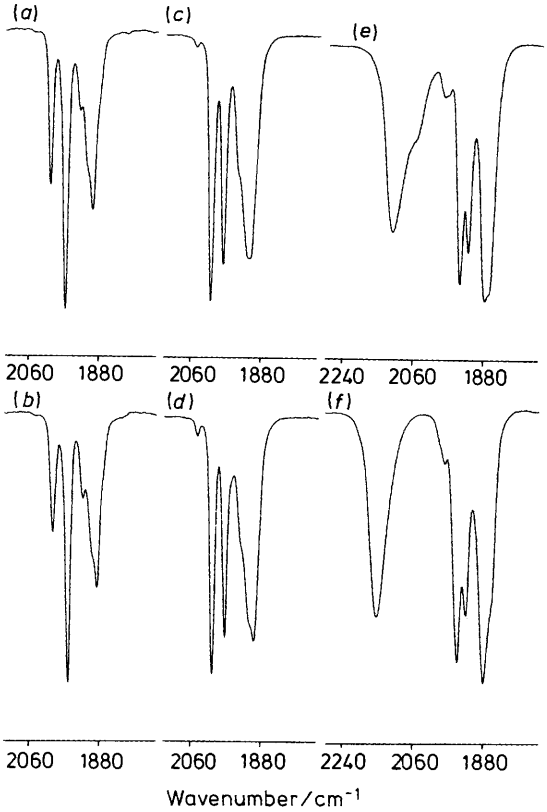
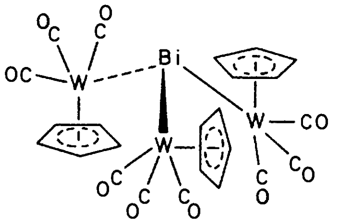
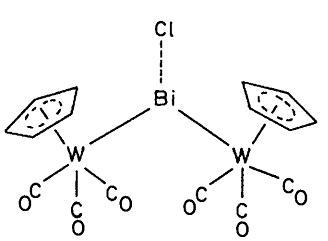


Figure 5. Infrared spectra of representative compounds recorded in the carbonyl stretching region in thf solution: (*a*) (**1**); (*b*) (**9**); (*c*) (**3**); (*d*) (**10**); (*e*) (**15**); and (*f*) (**16**); see Table 1 for numerical data



(**9**)



(**10**)

isostructural relationship between (**1**) and (**9**) being particularly apparent from a comparison of the i.r. spectra (Figure 5). The mechanism by which these reactions occur [reaction (4)] and the fate of the excess of bismuth remain obscure and must await further, more detailed studies on the reactivity of (**3**) and (**10**).

$$\begin{aligned}&3[\mathrm{BiCl}\{\mathrm{M(CO)_3(\eta\text{-}C_5H_5)}\}_2] + 3\mathrm{Na[C_{10}H_8]} \longrightarrow \\ &(\mathbf{3})\ \mathrm{M} = \mathrm{Mo}, (\mathbf{10})\ \mathrm{M} = \mathrm{W} \\ &2[\mathrm{Bi}\{\mathrm{M(CO)_3(\eta\text{-}C_5H_5)}\}_3] + 3\mathrm{NaCl} + 3\mathrm{C_{10}H_8} + \mathrm{Bi} \qquad (4) \\ &(\mathbf{1})\ \mathrm{M} = \mathrm{Mo}, (\mathbf{9})\ \mathrm{M} = \mathrm{W}\end{aligned}$$

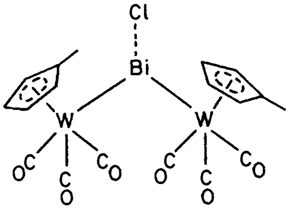
A somewhat more rational route to compound (**9**) involved treatment of a thf solution of (**10**) with 1 equivalent of $\mathrm{Na[W(CO)_3(\eta\text{-}C_5H_5)]}$ which, after chromatographic work-up, afforded reasonable yields of (**9**). Appreciable amounts of (**11**) were also produced, but since (**9**) and (**11**) are readily separable by chromatography this synthetic method is viable as a route to pure samples of (**9**).

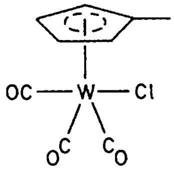
The differences between the corresponding molybdenum and tungsten reactions are interesting and deserve some comment. In the 2:1 reactions the same dimetal–bismuth structures are formed, but in the case of tungsten this is accompanied by the formation of the tungsten chloro complex (**11**), the molybdenum analogue of which is never observed. This suggests that the mechanism of the tungsten reaction is more complex. The desired process in all of these reactions is nucleophilic substitution at bismuth of chloride by the metal (Mo or W). In the molybdenum systems the products formed are consistent with this process. For tungsten, however, it would appear that competing electron-transfer processes are also operating. Any such process in which the bismuth centre was reduced would readily generate chlorine atoms, whereupon the formation of the chloro complex (**11**) might be expected. These observations are at odds with any predictions which might have been made regarding nucleophilicity alone, since it has been reported that $[\mathrm{W(CO)_3(\eta\text{-}C_5H_5)}]^-$ is approximately ten times more nucleophilic than $[\mathrm{Mo(CO)_3(\eta\text{-}C_5H_5)}]^-$.[19]

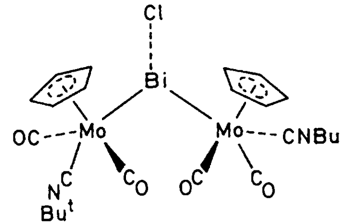
In the case of the 3:1 reactions a similar situation is observed. Thus, for molybdenum simple substitution occurs, resulting exclusively in the formation of compound (**1**). For tungsten, however, a mixture of (**9**)—(**11**) is formed, indicative of the same competing mechanisms previously described for the 2:1 reactions.

Analogous chemistry occurs when 2 equivalents of the methylcyclopentadienyl tungsten complex $\mathrm{Na[W(CO)_3(\eta\text{-}C_5H_4Me)]}$ are allowed to react with $\mathrm{BiCl_3}$. The resulting ditungsten–bismuth complex, (**12**), and the tungsten chloro species, (**13**), were characterised by normal methods (Tables 1 and 2).

Finally we note that the ditungsten–bismuth complex, (**10**), reacts in $\mathrm{Et_2O}$ with 1 equivalent of $\mathrm{BiCl_3}$, affording the monotungsten species $[\mathrm{BiCl_2\{W(CO)_3(\eta\text{-}C_5H_5)\}}]$, (**14**), which was characterised spectroscopically (Tables 1 and 2). In contrast to the molybdenum analogues, satisfactory micro-analytical data were obtained for (**14**), since only small amounts of (**11**) were present (determined by i.r. and ^{1}H n.m.r. spectroscopy) as a by-product. Moreover, ^{1}H n.m.r. spectra obtained in both $[^2\mathrm{H}_6]$acetone and $[^2\mathrm{H}_8]$tetrahydrofuran reveal that mixtures of (**14**) and smaller amounts of (**10**) were present in these solutions, with equilibrium constants very similar to those observed in the analogous molybdenum system. No crystalline samples of any of the compounds (**7**), (**8**), or (**14**) could be obtained and so it is not possible to comment on the precise structures of these compounds.


(**12**)


(**13**)


(**15**)

It should also be noted at this point that the bromo analogues of (**3**) and (**10**) have been reported by Panster and Malisch[17] from a reaction between $[\mathrm{M(CO)_3(\eta\text{-}C_5H_5)}]^-$ (M = Mo or W) and $\mathrm{BiBrMe_2}$, their formation being explained by a mechanism involving an intermolecular elimination of $\mathrm{BiBrMe_2}$ from a proposed intermediate, $[\mathrm{Bi(Br)Me\{M(CO)_3(\eta\text{-}C_5H_5)\}}]$. The i.r. spectra reported for these two complexes are essentially identical to those described for the chloro analogues herein. Also reported were spectroscopic details for the complexes $[\mathrm{BiMe\{M(CO)_3(\eta\text{-}C_5H_5)\}_2}]$ and $[\mathrm{BiMe_2\{M(CO)_3(\eta\text{-}C_5H_5)\}}]$ (M = Cr, Mo, or W), although no structural information was presented.

In addition to the complexes described above, which all contain cyclopentadienylmetal tricarbonyl fragments, a range of carbonyl substituted complexes was also examined. Thus treatment of a solution of $\mathrm{BiCl_3}$ with 2 equivalents of the isonitrile substituted anion $[\mathrm{Mo(CO)_2(CNBu^t)(\eta\text{-}C_5H_5)}]^-$ resulted in a dark green solution from which green crystals of (**15**) were isolated after work-up. Analytical and spectroscopic data indicated that (**15**) was a dimolybdenum–bismuth complex analogous to (**3**) and this was confirmed by an *X*-ray diffraction study, the results of which are shown in Figure 6. Selected bond distance and angle data are shown in Table 5, whilst atomic positional parameters are presented in Table 6. The crystal structure reveals a monomeric system with no short intermolecular contacts involving bismuth and chlorine in contrast to those observed in (**3**) (the shortest intermolecular Bi $\cdots$ Cl contact is 7.15 Å). The bismuth is bonded to a single chlorine [Bi–Cl 2.610(2) Å] and two molybdenum atoms (av. Bi–Mo 2.955 Å), these values being consistent with single bonding and similar to those observed in (**3**). The co-ordination geometry around the bismuth atom is trigonal pyramidal (slightly distorted, sum of angles 315.9°), in accordance with the presence of a stereochemically active lone pair. In addition to bismuth, each molybdenum is bonded to one cyclopentadienyl, one t-butyl isocyanide, and two carbonyl ligands, the overall ligand geometry about each molybdenum centre being of the familiar $\mathrm{(C_5H_5)ML_4}$ 'piano-stool' type. Of interest, however, is the relative stereochemistry at each molybdenum centre, which is arranged such that on one molybdenum atom [Mo(1)] the isonitrile ligand is *trans* to the bismuth, whilst on the other

Table 5. Selected bond lengths (Å) and angles (°) for compound (**15**)

Bi–Mo(1)	2.978(1)	Bi–Mo(2)	2.931(1)
Bi–Cl	2.610(2)	Mo(1)–C(11)	1.975(4)
Mo(1)–C(12)	1.956(5)	Mo(1)–C(13)	2.064(5)
Mo(1)–C(14)	2.328(8)	Mo(1)–C(15)	2.352(7)
Mo(1)–C(16)	2.337(5)	Mo(1)–C(17)	2.318(6)
Mo(1)–C(18)	2.314(6)	Mo(2)–C(21)	1.961(6)
Mo(2)–C(22)	1.967(7)	Mo(2)–C(23)	2.065(5)
Mo(2)–C(24)	2.370(8)	Mo(2)–C(25)	2.325(6)
Mo(2)–C(26)	2.297(7)	Mo(2)–C(27)	2.319(9)
Mo(2)–C(28)	2.354(14)		
Mo(1)–Bi–Mo(2)	114.8(1)	Mo(1)–Bi–Cl	102.3(1)
Mo(2)–Bi–Cl	98.8(1)	Bi–Mo(1)–C(11)	75.9(2)
Bi–Mo(1)–C(12)	70.8(2)	C(11)–Mo(1)–C(12)	105.3(2)
Bi–Mo(1)–C(13)	132.4(2)	C(11)–Mo(1)–C(13)	77.7(2)
C(12)–Mo(1)–C(13)	79.1(2)	Bi–Mo(2)–C(21)	123.5(2)
Bi–Mo(2)–C(22)	74.8(1)	C(21)–Mo(2)–C(22)	78.6(3)
Bi–Mo(2)–C(23)	67.4(1)	C(21)–Mo(2)–C(23)	78.4(3)
C(22)–Mo(2)–C(23)	112.0(2)		

Table 6. Atomic co-ordinates ($\times 10^4$) for compound (**15**)

Atom	x	y	z
Bi	5 000	5 265(1)	5 000
Mo(1)	5 921(1)	4 006(1)	4 245(1)
Mo(2)	3 693(1)	6 233(1)	3 204(1)
Cl	5 701(1)	7 192(1)	5 779(1)
C(11)	4 952(2)	3 831(4)	2 997(3)
O(11)	4 424(2)	3 687(4)	2 215(3)
C(12)	5 911(3)	3 165(4)	5 487(4)
O(12)	5 936(3)	2 638(3)	6 229(3)
C(13)	5 926(3)	2 314(4)	3 757(4)
N(13)	5 899(3)	1 367(4)	3 475(4)
C(131)	5 779(4)	187(4)	3 077(6)
C(132)	5 066(8)	131(10)	2 124(12)
C(133)	5 889(11)	−555(9)	4 045(12)
C(134)	6 344(8)	−83(11)	2 760(17)
C(14)	6 746(3)	4 347(5)	3 602(5)
C(15)	6 316(3)	5 331(5)	3 336(5)
C(16)	6 409(3)	5 841(4)	4 330(5)
C(17)	6 908(3)	5 173(5)	5 216(5)
C(18)	7 114(3)	4 256(5)	4 753(6)
C(21)	3 221(3)	5 596(6)	1 692(5)
O(21)	2 937(4)	5 242(6)	808(4)
C(22)	4 427(3)	6 468(4)	2 726(4)
O(22)	4 814(2)	6 709(4)	2 388(4)
C(23)	3 588(2)	4 510(4)	3 508(4)
N(23)	3 524(2)	3 548(4)	3 700(4)
C(231)	3 389(3)	2 330(4)	3 775(5)
C(232)	3 085(11)	2 188(10)	4 551(15)
C(233)	4 081(7)	1 766(9)	4 303(18)
C(234)	2 892(13)	1 943(13)	2 727(12)
C(24)	3 692(4)	7 425(6)	4 624(6)
C(25)	3 798(4)	8 110(5)	3 888(6)
C(26)	3 207(4)	8 059(6)	2 886(6)
C(27)	2 714(4)	7 340(8)	2 929(8)
C(28)	3 025(6)	6 914(6)	4 063(10)

[Mo(2)] it is *cis*. Such an unusual arrangement is most probably steric rather than electronic in origin, but any such influences are probably small and subtle. Apart from the obvious difference between (**15**) and the all-carbonyl derivative, (**3**), with regard to secondary Bi · · · Cl interactions, it is worth noting that the relative conformations about the Bi–Mo bonds are also different in these two structures, as can easily be seen if Figures 1 or 2 and 6 are compared.

Proton n.m.r. spectra obtained for (**15**) (Table 2) indicate the presence of two isomers in solution. The cyclopentadienyl resonances at 5.39 and 5.24 p.p.m. and the t-butyl signals at 1.50 and 1.40 p.p.m. are assigned to the *cis,trans* isomer, observed in the solid state, whilst the singlets observed at 5.30 and 1.52 p.p.m. are assigned to a symmetric isomer which, on the basis of steric arguments, probably has the *trans,trans* configuration (**15a**). The overall relative intensities indicate that the ratio of

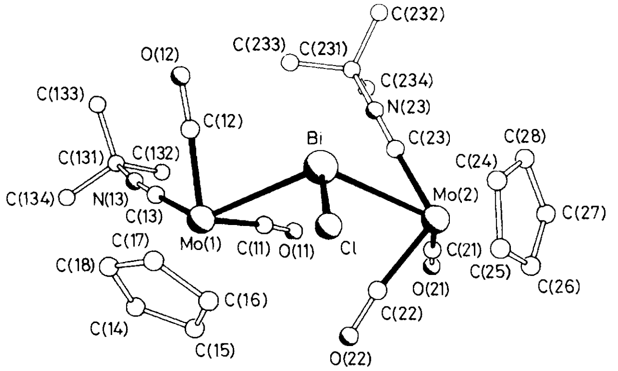
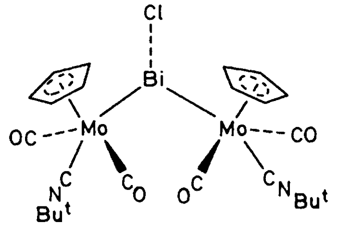
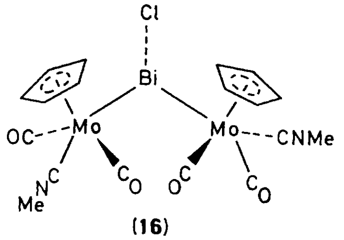


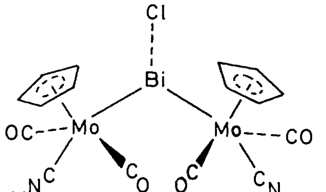
Figure 6. The molecular structure of compound (**15**) showing the atom numbering scheme adopted



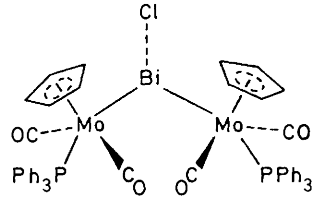
(**15a**)



(**16**)



(**16a**)



(**17**)

(**15**):(**15a**) in CD_2Cl_2 (the n.m.r. solvent) is approximately 1.5:1 and variable-temperature studies revealed that this remains constant over the temperature range 213—300 K.

The i.r. spectrum obtained in thf is shown in Figure 5 (numerical data in Table 1) and shows absorptions attributable to both carbonyl, ν(C≡O), and isonitrile, ν(C≡N), stretching vibrations.

The analogous reaction between $BiCl_3$ and 2 equivalents of $[Mo(CO)_2(CNMe)(\eta\text{-}C_5H_5)]^-$ proceeds in a similar manner and affords, after work-up, a dark green complex, (**16**). The i.r. spectrum of this material in thf (Figure 5 and Table 1) is very similar to that obtained for (**15**) indicating that the complexes are structurally similar. Moreover, examination of the ^1H n.m.r. spectrum (Table 2) indicates the presence of two isomers, the cyclopentadienyl region being very similar to that observed for (**15**), (**15a**). The methyl isocyanide derivative therefore appears to be analogous to the t-butyl complex in that solutions of the former compound also comprise a mixture of two isomers, *viz. cis,trans* (**16**) and *trans,trans* (**16a**) in a ratio of 1.5:1 respectively.

The reaction between $BiCl_3$ and 2 equivalents of $[Mo(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]^-$ also affords a dark green complex, (**17**), which n.m.r. data indicate is present as a single isomer for which the probable configuration is *trans,trans*. This is based on steric arguments, since any isomer involving a *cis* interaction between phosphorus and bismuth is likely to be subject to intramolecular steric crowding.

The reactions between $BiCl_3$ and the carbene-containing anions $[M(CO)_2(\eta\text{-}\overline{C[CH_2]_3O})(\eta\text{-}C_5H_5)]^-$, M = Mo or W, were also investigated. Reactions do occur, resulting in green solutions, but the products proved to be rather unstable and pure compounds could not be obtained.

Experimental

General Considerations.—All experiments were performed using standard Schlenk techniques under an atmosphere of dry oxygen-free dinitrogen. All solvents were freshly distilled over appropriate drying agents immediately prior to use. Proton and ^{13}C n.m.r. spectra were recorded on a Bruker WP200 spectrometer operating at 200.13 and 50.324 MHz respectively and ^{31}P n.m.r. spectra at 121.49 MHz on a Bruker WM300 instrument. Infrared spectra were recorded on a Nicolet 20 SXB FTIR spectrophotometer and mass spectra were obtained on Kratos MS9 and MS80 spectrometers. Microanalytical data were obtained either at the University of Newcastle or from Malissa and Reuter Analytische Laboratorien, West Germany. Bismuth trichloride (99%+) was procured commercially and used without further purification, and the cyclopentadienyl-metal carbonyl dimers $[\{M(CO)_3(\eta\text{-}C_5H_5)\}_2]$ (M = Mo or W) and $[\{M(CO)_3(\eta\text{-}C_5H_4Me)\}_2]$ (M = Mo or W) were prepared by the method of Manning and co-workers.[20] The dimers $[\{Mo(CO)_2L(\eta\text{-}C_5H_5)\}_2]$ (L = CNBu^t or CNMe)[21] and $[\{Mo(CO)_2(PPh_3)(\eta\text{-}C_5H_5)\}_2]$[22] were also prepared according to literature methods. The carbene anions mentioned briefly in the text were prepared by the method of Osborn and Winter.[23] Analytical, spectroscopic, and other relevant data for all new compounds are presented in Tables 1 and 2.

Synthetic Methods.—$[Bi\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_3]$, (**1**). A sample of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (0.838 g, 1.71 mmol) was dissolved in thf (25 cm^3) and stirred over a sodium amalgam for 2 h. The resulting solution of $Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$ (3.42 mmol) was transferred to a separate nitrogen-filled flask, stirred, and cooled to 0 °C. Dropwise addition of a solution of $BiCl_3$ (0.359 g, 1.14 mmol) in thf (15 cm^3) led to an initial green colouration, which rapidly became deep red. The solution was stirred for a further hour, after which time it was filtered through Celite. The solvent volume was reduced to approximately 20 cm^3, over which hexane (60 cm^3) was layered. Solvent diffusion at −30 °C over 72 h afforded a dark red powder (0.742 g, 69% yield). Further recrystallisations failed to result in suitable *X*-ray quality crystals. Compound (**1**) was found to be insoluble in all common solvents except thf.

The methylcyclopentadienyl derivative (**5**) was prepared in an exactly analogous manner although, as with (**1**), crystals of *X*-ray quality were not obtained.

$[BiCl\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$, (**3**). A sample of $BiCl_3$ (0.554 g, 1.76 mmol) was dissolved in thf (15 cm^3) and stirred at 0 °C. To this, a solution of 2 equivalents of $Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$, prepared by sodium amalgam reduction of the dimer $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (0.862 g, 1.76 mmol) in thf (30 cm^3), was added with constant stirring over 10 min. This caused an immediate colour change to deep green, which remained throughout the addition. After complete addition the mixture was allowed to warm to room temperature and stirred for a further 30 min. The resulting mixture was filtered through Celite, to remove dispersed NaCl, and after removal of all volatiles *in vacuo* a dark green solid remained. The crude solid was redissolved in CH_2Cl_2 (15 cm^3), over which was layered hexane (60 cm^3). Solvent diffusion over 72 h at −20 °C afforded green needle-like crystals of (**3**) suitable for *X*-ray diffraction studies.

The methylcyclopentadienyl derivative, (**6**), was prepared in an analogous manner.

$[BiCl_2\{Mo(CO)_3(\eta\text{-}C_5H_5)\}]$, (**7**). A solution of $BiCl_3$ (0.056 g, 0.177 mmol) in Et_2O (10 cm^3) was added to a stirred solution of compound (**3**) (0.130 g, 0.177 mmol) in Et_2O (10 cm^3). Stirring was continued for 3 h, during which time the solution changed from dark green to almost colourless, with concomitant formation of a red-brown precipitate. Removal of the Et_2O followed by washing with fresh Et_2O (3 × 10 cm^3) afforded (**7**) as a dark orange solid which was dried *in vacuo* (0.17 g, *ca.* 90% yield). The precise yield was difficult to determine, since samples of (**7**) produced as described above are always contaminated with small amounts of $[MoCl(CO)_3(\eta\text{-}C_5H_5)]$. The methylcyclopentadienyl derivative, (**8**), was prepared in an analogous manner.

$[Bi\{W(CO)_3(\eta\text{-}C_5H_5)\}_3]$, (**9**). *Method A*. A purple solution of compound (**10**) (0.12 g, 0.132 mmol) in thf (20 cm^3) was prepared and cooled to −78 °C. To this, a sodium dihydronaphthylide solution (0.132 mmol) in thf (10 cm^3) was added over 5 min with constant stirring, resulting in a red-brown solution. This was allowed to warm to room temperature and was stirred for a further hour. Purification by column chromatography (Florisil) yielded a major red-brown fraction (thf) which on removal of all volatiles afforded a red-brown solid. This was redissolved in thf (5 cm^3), over which hexane (20 cm^3) was layered. Solvent diffusion at −20 °C over 72 h resulted in a red-brown solid (0.054 g, 51%).

Method B. To a purple solution of compound (**10**) (0.252 g, 0.277 mmol) in thf (20 cm^3), 1 equivalent of $Na[W(CO)_3(\eta\text{-}C_5H_5)]$, prepared by sodium amalgam reduction of the dimer $[W_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (0.092 g, 0.138 mmol) in thf (20 cm^3), was added with constant stirring. The colour changed immediately to deep red and the mixture was allowed to stir for a further hour. Purification by column chromatography (Florisil) yielded a major red-brown fraction (thf). Solvent diffusion at −20 °C of a thf–hexane mixture led to a red-brown solid (0.15 g, 45%).

$[BiCl\{W(CO)_3(\eta\text{-}C_5H_5)\}_2]$, (**10**). A sample of $[W_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (0.50 g, 0.751 mmol) was dissolved in thf (20 cm^3) and stirred over a sodium amalgam for 2 h. The resulting solution of $Na[W(CO)_3(\eta\text{-}C_5H_5)]$ was transferred to a separate nitrogen-filled flask, stirred and cooled to 0 °C. Dropwise addition of a solution of $BiCl_3$ (0.157 g, 0.508 mmol, W:Bi = 3:1) in thf (10 cm^3) over 10 min resulted in an intense purple solution. The mixture was allowed to warm to room temperature and stirred for a further 30 min. Purification by column chromatography (Florisil) afforded two fractions, an initial yellow fraction (hexane–diethyl ether, 3:1) followed by a second purple fraction (thf). Yellow crystals of [$WCl(CO)_3(\eta$-$C_5H_5)$], (**11**), were obtained by solvent diffusion at −20 °C from diethyl ether (3 cm^3)–hexane (15 cm^3). Purple crystals of (**10**) (0.18 g, 38%) were obtained from thf (5 cm^3)–hexane (20 cm^3) by solvent diffusion at −20 °C over 72 h. The methylcyclopentadienyl derivatives, (**12**) and (**13**), were prepared in an analogous manner.

[$BiCl_2\{W(CO)_3(\eta$-$C_5H_5)\}$], (**14**). To a stirred solution of compound (**10**) (0.270 g, 0.295 mmol) in Et_2O (10 cm^3), a solution of $BiCl_3$ (0.093 g, 0.295 mmol) in Et_2O (10 cm^3) was added. After stirring for 4 h the solution had changed from purple to colourless and an orange-brown precipitate had formed. Removal of the Et_2O followed by washing in Et_2O (3 × 10 cm^3) afforded a dark orange solid, which was dried *in vacuo*. Recrystallisation was effected from thf–hexane mixtures at −20 °C.

[$BiCl\{Mo(CO)_2(CNBu^t)(\eta$-$C_5H_5)\}_2$], (**15**). A sample of $BiCl_3$ (0.149 g, 0.473 mmol) was dissolved in thf (10 cm^3) and stirred at 0 °C. To this, a solution of 2 equivalents of Na[$Mo(CO)_2(CNBu^t)(C_5H_5)$], prepared by sodium amalgam reduction of the dimer [$Mo_2(CO)_4(CNBu^t)_2(C_5H_5)_2$] (0.284 g, 0.473 mmol) in thf (20 cm^3), was added. The solution immediately turned dark green and remained so throughout the addition. The mixture was allowed to warm to room temperature and stirred for a further hour. Two successive filtrations through Celite and removal of all volatiles *in vacuo* afforded a dark green solid. The crude solid was redissolved in fresh CH_2Cl_2 (5 cm^3), over which was layered hexane (20 cm^3). Solvent diffusion over 72 h at −30 °C afforded dark green crystals of compound (**15**) (0.30 g, 75%).

The methyl isocyanide complex, [$BiCl\{Mo(CO)_2(CNMe)$-$(\eta$-$C_5H_5)\}_2$], (**16**), and the phosphine complex, (**17**), were prepared in an analogous manner.

X-Ray Crystallography.—Crystal data for compound (**3**). $C_{16}H_{10}BiClMo_2O_6$, M_r = 734.6, monoclinic, a = 18.724(3), b = 10.744(2), c = 19.791(3) Å, β = 104.60(1)°, U = 3 852.8 Å^3 (from 2θ values of 32 reflections in the range 20—25°), Z = 8, D_c = 2.532 g cm^{-3}, F(000) = 2 704, μ(Mo-K_α) = 10.51 mm^{-1}, λ = 0.710 73 Å, space group $P2_1/n$.

Data collection and reduction. Siemens AED2 diffractometer with graphite monochromator, crystal size 0.15 × 0.27 × 0.38 mm, T = 295 K, $2\theta_{max.}$ = 50°. Index ranges: h −7 to 7, k 0 to 9, l 0 to 7, with some equivalent reflections (l < 0) ω—θ scan mode, on-line profile fitting,[24] no significant variation for three standard reflections. Semiempirical absorption correction (transmission 0.036—0.098), no extinction correction. Of 7 195 measured data, 6 804 were unique, and 5 119 with $F > 4\sigma_c(F)$ were used for structure determination ($R_{int.}$ = 0.011, σ_c from counting statistics only).

Structure solution and refinement.[25] Atom positions were determined from Patterson and difference syntheses, and refined together with anisotropic thermal parameters to minimise $\Sigma w\Delta^2$; $\Delta = |F_o| - |F_c|$, $w^{-1} = \sigma^2(F) = \sigma^2_c(F) - 77 + 1\,600G + 1\,188G^2 + 16S + 169S^2 - 2\,769GS$ ($G = F_o/F_{max.}$, $S = \sin\theta/\sin\theta_{max.}$).[26] Hydrogen atoms were constrained on ring angle external bisectors with C–H 0.96 Å, U(H) = 1.2$U_{eq.}$(C). For 469 refined parameters, R = 0.0422, R' = 0.040, goodness of fit = 1.42. The largest features in a final difference synthesis were close to Bi atoms. Scattering factors were taken from ref. 27.

Crystal data for compound (**15**). $C_{24}H_{28}BiClMo_2N_2O_4$, M_r = 844.8, monoclinic, a = 21.256(2), b = 11.539(1), c = 13.589(1) Å, β = 117.810(6)°, U = 2 948.1 Å^3 (from 32 reflections), Z = 4, D_c = 1.903 g cm^{-3}, F(000) = 1 608, μ(Mo-K_α) = 6.88 mm^{-1}, space group Cc.

Data collection and reduction. As for compound (**3**), except: crystal size 0.2 × 0.4 × 0.4 mm, whole sphere of data, index ranges h ± 25, k ± 13, l ± 16; transmission 0.228—0.314. Of 10 428 data, 5 204 were unique (Friedel opposites not merged), and 5 083 had $F > 4\sigma_c(F)$.

Structure solution and refinement. As for (**3**); $w^{-1} = \sigma^2_c(F) + 4 + 20G + 60G^2 - 9S + 9S^2 - 56GS$. Angle H–C–H 109.5° in constrained methyl groups. For 306 refined parameters, R = 0.0171, R' = 0.0201, goodness of fit = 1.06. The absolute structure was determined by refinement of η = +1.048(8).[28]

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

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References

1 R. K. Grasselli and J. D. Burrington, *Adv. Catal.*, 1981, **30**, 133.
2 R. K. Grasselli, *J. Chem. Educ.*, 1986, **63**, 216.
3 G. Etzrodt, R. Boese, and G. Schmid, *Chem. Ber.*, 1979, **112**, 2574; P. Klüfers, *Z. Kristallogr.*, 1981, **156**, 74.
4 W. Kruppa, D. Bläser, R. Boese, and G. Schmid, *Z. Naturforsch., Teil B*, 1982, **37**, 209.
5 K. H. Whitmire, C. B. Lagrone, M. R. Churchill, J. C. Fettinger, and L. V. Biondi, *Inorg. Chem.*, 1984, **23**, 4227; M. R. Churchill, J. C. Fettinger, and K. H. Whitmire, *J. Organomet. Chem.*, 1985, **284**, 13; K. H. Whitmire, M. R. Churchill, and J. C. Fettinger, *J. Am. Chem. Soc.*, 1985, **107**, 1056; K. H. Whitmire, K. S. Raghuveer, M. R. Churchill, J. C. Fettinger, and R. F. See, *ibid.*, 1986, **108**, 2778; K. H. Whitmire, T. A. Albright, S-K. Kang, M. R. Churchill, and J. C. Fettinger, *Inorg. Chem.*, 1986, **25**, 2799; M. R. Churchill, J. C. Fettinger, K. H. Whitmire, and C. B. Lagrone, *J. Organomet. Chem.*, 1986, **303**, 99; K. H. Whitmire, C. B. Lagrone, and A. L. Rheingold, *Inorg. Chem.*, 1986, **25**, 2472; K. H. Whitmire, M. Shieh, C. B. Lagrone, B. H. Robinson, M. R. Churchill, J. C. Fettinger, and R. F. See, *ibid.*, 1987, **26**, 2798.
6 (*a*) K. H. Whitmire, J. S. Leigh, and M. E. Cross, *J. Chem. Soc., Chem. Commun.*, 1987, 926; (*b*) S. Martinengo and G. Ciani, *ibid.*, p. 1589.
7 H. G. Ang, C. M. Hay, B. F. G. Johnson, J. Lewis, P. R. Raithby, and A. J. Whitton, *J. Organomet. Chem.*, 1987, **330**, C5.
8 J. M. Wallis, G. Müller, and H. Schmidbaur, *Inorg. Chem.*, 1987, **26**, 458.
9 G. Huttner, U. Weber, and L. Zsolnai, *Z. Naturforsch., Teil B*, 1982, **37**, 707.
10 A. M. Arif, A. H. Cowley, N. C. Norman, and M. Pakulski, *J. Am. Chem. Soc.*, 1985, **107**, 1062; *Inorg. Chem.*, 1986, **25**, 4836.
11 W. R. Cullen, D. J. Patmore, J. R. Sams, M. J. Newlands, and L. K. Thompson, *Chem. Commun.*, 1971, 952; W. R. Cullen, D. J. Patmore, and J. R. Sams, *Inorg. Chem.*, 1973, **12**, 867.
12 H-A. Kaul, D. Greissinger, M. Luksza, and W. Malisch, *J. Organomet. Chem.*, 1982, **228**, C29.
13 M. Wieber, D. Wirth, and C. Burschka, *Z. Naturforsch., Teil B*, 1985, **40**, 258.
14 J. M. Wallis, G. Müller, and H. Schmidbaur, *J. Organomet. Chem.*, 1987, **325**, 159.
15 W. Clegg, N. A. Compton, R. J. Errington, and N. C. Norman, (*a*) *Polyhedron*, 1987, **6**, 2031; (*b*) *J. Chem. Soc., Dalton Trans.*, 1988, 1671.
16 J. von Seyerl and G. Huttner, *J. Organomet. Chem.*, 1980, **195**, 207.
17 P. Panster and W. Malisch, *J. Organomet. Chem.*, 1977, **134**, C32.
18 W. Clegg, N. A. Compton, R. J. Errington, and N. C. Norman, *J. Organomet. Chem.*, 1987, **335**, C1.
19 R. E. Dessy, R. L. Pohl, and R. B. King, *J. Am. Chem. Soc.*, 1966, **88**, 5121.

20 R. Birdwhistell, P. Hackett, and A. R. Manning, *J. Organomet. Chem.*, 1978, **157**, 239.

21 H. Adams, N. A. Bailey, C. Bannister, M. A. Faers, P. Fedorko, V. A. Osborn, and M. J. Winter, *J. Chem. Soc., Dalton Trans.*, 1987, 341.

22 R. J. Klingler, W. Butler, and M. D. Curtis, *J. Am. Chem. Soc.*, 1975, **97**, 3535.

23 V. A. Osborn and M. J. Winter, *J. Chem. Soc., Chem. Commun.*, 1985, 1744.

24 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.

25 G. M. Sheldrick, SHELXTL: an integrated system for solving, refining, and displaying crystal structures from diffraction data, Revision 5, University of Göttingen, 1985.

26 W. Hong and B. E. Robertson, 'Structure and Statistics in Crystallography,' ed. A. J. C. Wilson, Adenine Press, New York, 1985, pp. 125—136.

27 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 99, 149.

28 D. Rogers, *Acta Crystallogr., Sect. A*, 1981, **37**, 734.

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