Dibismuth as a Four-electron Donor Ligand. Synthesis and Molecular and Electronic Structure of $[M_2(CO)_4(\eta\text{-}C_5H_4Me)_2(\mu\text{-}\eta^2\text{-}Bi_2)]$ (M = Mo or W)†

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The compounds $[M_2(CO)_4(\eta\text{-}C_5H_4R)_2(\mu\text{-}\eta^2\text{-}Bi_2)]$ (M = Mo or W, R = H or Me) have been prepared by the solid-state thermolysis or solution-state photolysis of $[Bi\{M(CO)_3(\eta\text{-}C_5H_4R)\}_3]$. The structures of the methylcyclopentadienyl derivatives were determined by X-ray crystallography and show a $M_2(CO)_4(\eta\text{-}C_5H_4Me)_2$ unit in which the M–M vector is transversely bridged by a Bi_2 ligand so as to give a tetrahedral M_2Bi_2 core. The Bi_2 ligand acts as a four-electron donor. The electronic structure of $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2(\mu\text{-}\eta^2\text{-}Bi_2)]$ has been examined by extended-Huckel molecular orbital calculations and compared with the related diphosphorus complex $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2(\mu\text{-}\eta^2\text{-}P_2)]$. Substantial differences are found in the nature of those frontier orbitals which are localised primarily on the P_2 and Bi_2 units. These are consistent with the observed differences in the chemistry of P_2 *vs.* Bi_2 ligands in general. The chromium complexes $[BiCl\{Cr(CO)_3(\eta\text{-}C_5H_5)\}_2]$ and $[Bi\{Cr(CO)_3(\eta\text{-}C_5H_5)\}_3]$ are also described.

In this paper we describe our results on the synthesis and structure of the dibismuth complexes $[M_2(CO)_4(\eta\text{-}C_5H_4R)_2(\mu\text{-}\eta^2\text{-}Bi_2)]$ (R = H or Me, M = Mo or W) in which the dibismuth ligand acts as a four-electron donor. Some aspects of this work were the subject of a preliminary communication [1] but as a general introduction to this paper we shall briefly review other known complexes which contain the Bi_2 ligand. The Bi–Bi bond distance determined by X-ray crystallography is given in parentheses.

Huttner *et al.*[2] have synthesised the tritungsten complex $[Bi_2\{\mu\text{-}W(CO)_5\}_3]$ **1** [2.818(3) Å] from the reaction between $BiCl_3$ and $[W_2(CO)_{10}]^{2-}$ and a report of the molybdenum analogue has also appeared.[3] The metal core in **1** has approximate D_{3h} symmetry, with each $W(CO)_5$ fragment bridging the Bi–Bi bond, and the Bi_2 ligand acts as a formal six-electron donor, two to each tungsten. Cowley and co-workers[4] also isolated **1** from the reaction between $BiCl_2[CH(SiMe_3)_2]$ and $[W_2(CO)_{10}]^{2-}$ together with the tritungstentribismuth complex $[W_2(CO)_8(\mu\text{-}\eta^2\text{-}Bi_2)\{\mu\text{-}Bi(Me)W(CO)_5\}]$ **2** [2.796(1) Å] in which the Bi_2 ligand transversely bridges the W–W bond and acts as a four-electron donor.

A manganese complex analogous to **1** has recently been described by Huttner and co-workers,[5] $[Bi_2\{Mn(CO)_2(\eta\text{-}C_5H_4Me)\}_3]$ [2.813 Å] resulting from the reaction between $BiCl_3$ and $Na[Mn_2(CO)_4(\eta\text{-}C_5H_4Me)_2(\mu\text{-}H)]$.

In Group 8, $[Bi_2Fe_2Co(CO)_{10}]^-$ **4** [3.092(2) Å] has been isolated by Whitmire *et al.*[6] from the reaction between $[Bi_2Fe_3(CO)_9]$ and $[Co(CO)_4]^-$, whilst Lewis and co-workers[7] have characterised the tetraosmium cluster $[Bi_2Os_4(CO)_{12}]$ **5** [3.017(2) Å] as one product of the reaction between $[Os_3(CO)_{12}]$ and $NaBiO_3$. In **5** the Bi_2Os_4 core geometry is octahedral with the bismuth atoms occupying *cis* or 1,2 sites but in the isomeric ruthenium complex $[Bi_2Ru_4(CO)_{12}]$ the bismuth atoms are 1,6 or *trans* and are therefore not directly bonded.[7,8] In both **4** and **5** the dibismuth unit can be considered as a six-electron donor.

Finally we mention the paramagnetic, anionic, tetracobalt cluster $[Bi_2Co_4(CO)_{11}]^-$ **6** which also contains a six-electron donor dibismuth. This complex was obtained either from refluxing $[NMe_4][Bi\{Co(CO)_4\}_4]$ in tetrahydrofuran (thf) by Martinengo and Ciani[9a] as the $[NMe_4]^+$ salt [3.088(1) Å] or by reduction of $[Bi\{Co(CO)_4\}_3]$ with $[Co(\eta\text{-}C_5H_5)_2]$ in CH_2Cl_2, as the $[Co(\eta\text{-}C_5H_5)_2]^+$ salt [3.078(3) Å], by Whitmire and co-workers.[9b] We have reported the dicobalt complex $[Bi_2Co_2(CO)_4(PPh_3)_2]$ **7** although we were not able to obtain X-ray-quality crystals and therefore any structural data.[10] A recent review article[11] describes in more detail the above-mentioned dibismuth complexes together with related diantimony complexes.

The complexes $[M_2(CO)_4(\eta\text{-}C_5H_4R)_2(\mu\text{-}\eta^2\text{-}Bi_2)]$ (R = H, M = Mo, **8**; R = Me, M = Mo, **9**; R = H, M = W, **10**; R = Me, M = W, **11**) all contain a transverse bridging, four-electron donor dibismuth ligand. The only previous complexes which contain Bi_2 as a four-electron donor are **2** and **7**; in all other complexes Bi_2 acts as a six-electron donor but we will have more to say on this matter later.

Results and Discussion

(*i*) *Synthesis.*—We were first alerted to the existence of **8** while studying the trimetallobismuthine complex $[Bi\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_3]$ **12**.[12] Specifically we observed that electron-impact mass spectra of **12** showed no signals attributable to this complex, *i.e.* a molecular ion or fragments containing the $BiMo_3$ unit, but rather always produced spectra consistent with the formula given for **8**. That this species was in fact a dimolybdenumdibismuth complex was confirmed by a subsequent high-resolution mass measurement study, details of which are given in the Experimental section. It therefore seemed clear that **12** (at least partially) underwent thermal rearrangement to **8** in the probe of the mass spectrometer and that this latter

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† Tetracarbonyl-1κ²*C*,2κ²*C*-bis[1,2(η⁵)-methylcyclopentadienyl]-*tetrahedro*-dibismuth-dimolybdenum and -ditungsten.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Non-SI unit employed: eV ≈ 1.60×10^{-19} J.

Table 1 Analytical[a] and spectroscopic data for the complexes

Compound	ν(CO)[b]/cm^{-1}	Analysis (%) C	Analysis (%) H
8 $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2(\mu\text{-}\eta^2\text{-}Bi_2)]$	1917s, 1866m	20.20 (19.75)	1.20 (1.20)
9 $[Mo_2(CO)_4(\eta\text{-}C_5H_4Me)_2(\mu\text{-}\eta^2\text{-}Bi_2)]$	1913s, 1863m	22.05 (21.85)	1.60 (1.60)
10 $[W_2(CO)_4(\eta\text{-}C_5H_5)_2(\mu\text{-}\eta^2\text{-}Bi_2)]$	1912s, 1858m	16.55 (16.35)	0.95 (1.00)
11 $[W_2(CO)_4(\eta\text{-}C_5H_4Me)_2(\mu\text{-}\eta^2\text{-}Bi_2)]$	1910s, 1856m	18.40 (18.20)	1.25 (1.35)
15 $[Bi\{W(CO)_3(\eta\text{-}C_5H_4Me)\}_3]$	1998m, 1957s, 1921w, 1883m	25.55 (25.95)	1.60 (1.70)
16 $[Bi\{Cr(CO)_3(\eta\text{-}C_5H_5)\}_3]$	1994m, 1955s, 1925w, 1894m	34.40 (35.50)	2.15 (1.85)
17 $[BiCl\{Cr(CO)_3(\eta\text{-}C_5H_5)\}_2]$	1998s, 1967s, 1901s	31.85 (29.70)	1.75 (1.55)

[a] Calculated values in parentheses. [b] Measured in thf solution.

Table 2 Proton and $^{13}C\text{-}\{^1H\}$ NMR data for the complexes[a]

Compound	^1H (δ)[b]	^{13}C (δ)[b,c]
8	5.21 (C_5H_5)	83.1 (C_5H_5)[d]
9[e]	5.12 (m, 4 H, C_5H_4Me)	82.8 (C_5H_4Me)
	4.94 (m, 4 H, C_5H_4Me)	81.7 (C_5H_4Me)
	2.12 (s, 6 H, C_5H_4Me)	15.2 (C_5H_4Me)
11[e]	5.16 (m, 4 H, C_5H_4Me)	
	5.05 (m, 4 H, C_5H_4Me)	
	2.31 (s, 6 H, C_5H_4Me)	
15[f]	5.51 (m, 8 H, C_5H_4Me)	108.4 (C_5H_4Me, CMe)
	2.24 (s, 6 H, C_5H_4Me)	92.2 (C_5H_4Me)
		91.7 (C_5H_4Me)
		14.1 (C_5H_4Me)
16[e]	5.33 (C_5H_5)	
17[e]	5.24 (C_5H_5)	89.7 (C_5H_5)

[a] Chemical shifts in ppm, measurements at room temperature. [b] Measured in $[^2H_6]$acetone unless otherwise stated. [c] ^1H-Decoupled; chemical shifts are positive to high frequency of $SiMe_4$. [d] Measured in $[^2H_6]$acetone–thf (1:1). [e] Measured in CD_2Cl_2. [f] Measured in $[^2H_8]$thf.

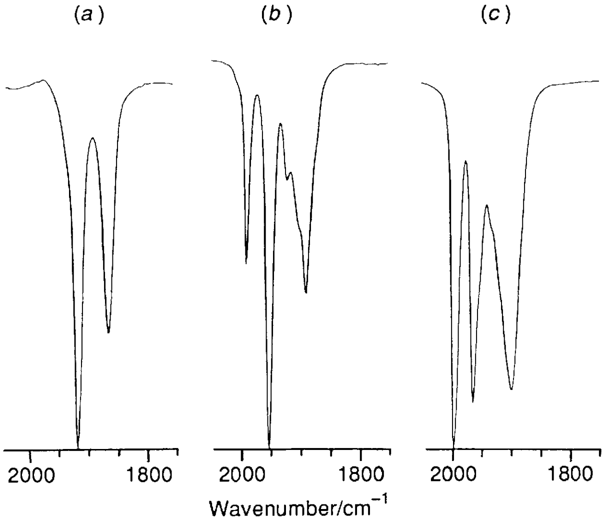

Fig. 1 Solution infrared data in the carbonyl stretching region for the complexes in thf: (*a*) **8**, (*b*) **16** and (*c*) **17**

complex was sufficiently volatile for a mass spectrum to be obtained. Of further interest was the fact that these observations indicated that **8** might be sufficiently stable to present a reasonable synthetic target. This expectation was subsequently realised and we were able to synthesise **8** from **12** either by UV photolysis in thf solution or by solid-state thermolysis followed by extraction with thf. Details of both methods are given in the Experimental section and, although isolated yields of crystalline **8** were rarely high (typically 20–40%), sufficient material could be obtained for further study. An infrared spectrum of **8** is shown in Fig. 1(*a*) while numerical and analytical data are given in Table 1 and NMR details in Table 2.

Compounds **9** and **10** were prepared similarly from $[Bi\{M(CO)_3(\eta\text{-}C_5H_4R)\}_3]$ (R = Me, M = Mo, **13**; R = H, M = W, **14**)[12]; **11** was prepared from $[Bi\{W(CO)_3(\eta\text{-}C_5H_4Me)\}_3]$ **15**, a compound which we have not previously reported and data for which are given in Tables 1 and 2. Compound **15** is similar to **12–14**, full details for which are given in ref. 12.

Spectroscopic and analytical data for complexes **8–11** (Table 1) were consistent with the expected formulae and the structures of **9** and **11** were confirmed by X-ray crystallography. We shall discuss these results together with related structures in the next section and this will also be an appropriate place to look at the infrared spectra in more detail. At this point, however, we turn to some related chromium chemistry.

We were interested in synthesising the chromium analogues of **8** and **10** and so as a prelude investigated the reactions between $BiCl_3$ and $Na/K[Cr(CO)_3(\eta\text{-}C_5H_5)]$. Addition of a thf solution of $BiCl_3$ to 3 equivalents of $Na/K[Cr(CO)_3(\eta\text{-}C_5H_5)]$ in thf afforded, after work-up, the trichromiumbismuth complex $[Bi\{Cr(CO)_3(\eta\text{-}C_5H_5)\}_3]$ **16** as a green solid. An infrared spectrum of **16** is shown in Fig. 1(*b*) and spectroscopic and analytical data are given in Table 1. The complex is similar in most respects to the molybdenum and tungsten analogues **12** and **14**,[12] although it is markedly less stable in solution, decomposing with formation of some $[Cr_2(CO)_6(\eta\text{-}C_5H_5)_2]$ if left standing for long periods. This is probably due to the much weaker Bi–Cr bonds which readily undergo homolysis to generate $[Cr(CO)_3(\eta\text{-}C_5H_5)]^{\bullet}$ radicals, an important facet of the chemistry of $[Cr_2(CO)_6(\eta\text{-}C_5H_5)_2]$ itself. We were also able to synthesise **16** directly from $[Cr_2(CO)_6(\eta\text{-}C_5H_5)_2]$ and bismuth metal in thf although prolonged stirring was required to obtain reasonable yields. This is in fact the reverse of the decomposition we have just mentioned so perhaps there is an equilibrium of sorts in thf. There is only one other example of a reaction between elemental bismuth and a metal carbonyl complex under such mild conditions, namely the formation of $[Bi\{Co(CO)_4\}_3]$ from Bi and $[Co_2(CO)_8]$ in Et_2O reported by Schmid and co-workers[13] although, as we have shown, this reaction is a little more complicated in thf.[10] It is likely that the formation of **16** involves $[Cr(CO)_3(\eta\text{-}C_5H_5)]^{\bullet}$ radicals reacting with the bismuth since, as we have mentioned, such radicals readily form in solutions containing the dimer $[Cr_2(CO)_6(\eta\text{-}C_5H_5)_2]$. This is in contrast to the molybdenum and tungsten analogues for which no reaction with elemental bismuth is observed.*

All attempts to synthesise a dichromiumdibismuth complex

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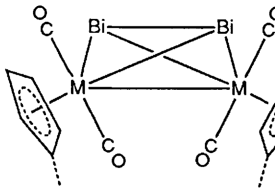
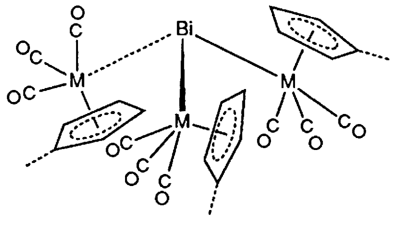
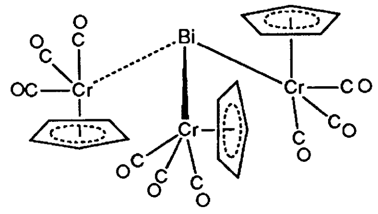
* We note the similarity here between the reactions of metal carbonyls with either elemental bismuth or with Bi_2Ph_4. The latter species reacts with $[Co_2(CO)_8]$ and $[Cr_2(CO)_6(\eta\text{-}C_5H_5)_2]$ to give $[Co(CO)_4(BiPh_2)]$ and $[Cr(CO)_3(BiPh_2)(\eta\text{-}C_5H_5)]$ respectively but not with other metal carbonyl dimers. For a detailed account of this work see ref. 14.



8–11



12–15



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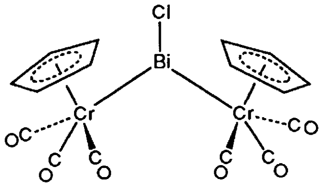

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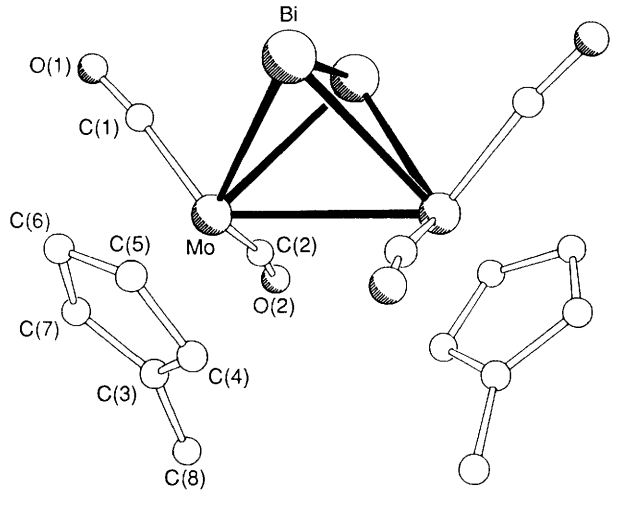


Fig. 2 A view of the molecular structure of complex **9** showing the atom numbering scheme

Table 3 Selected bond lengths (Å) and angles (°) for complexes **9** and **11**

9		**11**	
Bi–Mo	2.848(1)	Bi–W	2.985(2)
Bi–Mo′	2.985(1)	Bi–W′	2.852(2)
Bi–Bi′	2.838(1)	Bi–Bi′	2.845(3)
Mo–Mo′	3.167(2)	W–W′	3.131(3)
Mo–Bi–Bi′	63.3(1)	W–Bi–Bi′	58.5(1)
Mo–Bi–Mo′	65.7(1)	W–Bi–W′	64.8(1)
Bi–Mo–Bi′	58.2(1)	Bi–W–Bi′	58.3(1)
Bi–Mo–Mo′	59.2(1)	Bi–W–W′	55.5(1)
Bi′–Mo–Mo′	55.1(1)	Bi′–W–W′	59.6(1)
Bi′–Bi–Mo′	58.5(1)	Bi′–Bi–W′	63.2(1)

Table 4 Atomic coordinates (× 10^4) for complex **9**

Atom	*x*	*y*	*z*
Bi	8 859(1)	5 313(1)	2 225(1)
Mo	8 281(1)	2 780(1)	1 232(1)
C(1)	7 327(13)	3 897(12)	655(5)
O(1)	6 637(11)	4 412(11)	302(4)
C(2)	9 805(13)	2 962(12)	483(4)
O(2)	10 522(11)	2 864(12)	15(4)
C(3)	7 247(13)	− 189(13)	1 195(5)
C(4)	7 446(15)	256(14)	1 889(5)
C(5)	6 305(15)	865(13)	2 032(5)
C(6)	5 410(14)	817(16)	1 447(6)
C(7)	5 990(13)	136(12)	939(5)
C(8)	8 095(21)	− 1 075(17)	838(8)

from **16** were unsuccessful nor have we seen any evidence for such a species in mass spectra of **16**. We suspect that $[Cr_2Bi_2(CO)_4(\eta\text{-}C_5H_5)_2]$ is likely to be a stable complex if synthesised (the P_2 analogues have recently been reported, see later), but that **16** is not a suitable precursor owing to alternative decomposition routes.

While studying the chromium system we synthesised and characterised the chloro complex $[BiCl\{Cr(CO)_3(\eta\text{-}C_5H_5)\}_2]$ **17** [Fig. 1(*c*), Table 1] and demonstrated that the reactions shown in equations (1) and (2) proceed readily. This exactly parallels the chemistry observed for the related molybdenum and tungsten systems which we have described in detail in ref. 12 and we will not comment further on these matters here.

$$\underset{\mathbf{17}}{[BiCl\{Cr(CO)_3(\eta\text{-}C_5H_5)\}_2]} + Na/K[Cr(CO)_3(\eta\text{-}C_5H_5)] \longrightarrow \underset{\mathbf{16}}{[Bi\{Cr(CO)_3(\eta\text{-}C_5H_5)\}_3]} + Na/KCl \quad (1)$$

$$2\underset{\mathbf{16}}{[Bi\{Cr(CO)_3(\eta\text{-}C_5H_5)\}_3]} + BiCl_3 \longrightarrow 3\underset{\mathbf{17}}{[BiCl\{Cr(CO)_3(\eta\text{-}C_5H_5)\}_2]} \quad (2)$$

(*ii*) *Structures*.—The structure of complex **9** is shown in Fig. 2; selected bond lengths and angles are given in Table 3 and atomic positional parameters in Table 4. The molecule resides on a crystallographic C_2 axis, and comprises a dimolybdenum unit transversely bridged by a dibismuth ligand giving a tetrahedral Mo_2Bi_2 core, although the Bi–Bi and Mo–Mo vectors are not quite perpendicular (84.9°). Each molybdenum atom is also bonded to a methylcyclopentadienyl and two terminal carbonyl ligands. The structure of the ditungsten complex **11** is enantiomorphous with **9** (the crystal chosen for **9** crystallised in the chiral space group $P3_121$, that for **11** in $P3_221$) and a view of the structure is shown in Fig. 3. Selected bond distances and angles are given in Table 3, atomic positional parameters in Table 5.

The Mo–Mo and W–W bond lengths are 3.167(2) and 3.131(3) Å respectively and are in the range usually observed for complexes of this type (see below). The Bi–Bi distances are 2.838(1) Å for **9** and 2.845(3) Å for **11** both of which are within the range observed for other Bi_2 complexes[2,4–9,11] but we will discuss this matter in more detail in the next section.

The C_2 symmetry of complexes **9** and **11** (crystallographically

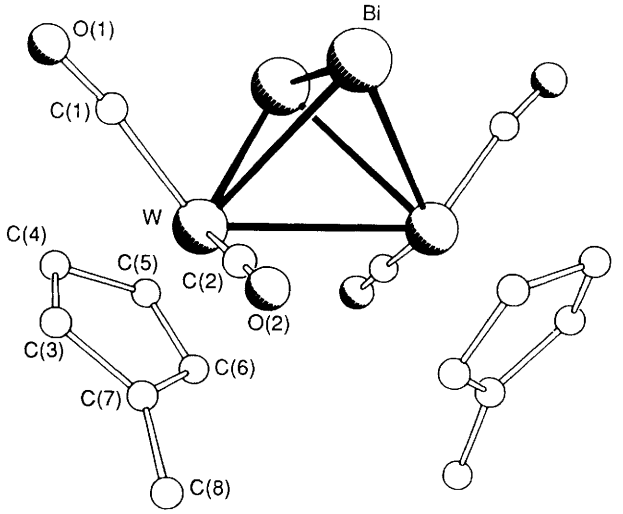
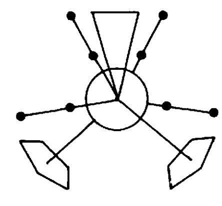


Fig. 3 A view of the molecular structure of complex **11** showing the atom numbering scheme

Table 5 Atomic coordinates ($\times 10^4$) for complex **11**

Atom	*x*	*y*	*z*
Bi	6 440(1)	11 142(1)	1 099(1)
W	2 744(1)	8 290(1)	1 234(1)
C(1)	3 852(40)	7 270(41)	720(12)
O(1)	4 348(36)	6 643(35)	309(12)
C(2)	2 897(35)	9 700(36)	443(11)
O(2)	2 934(31)	10 539(30)	1(11)
C(3)	211(40)	6 011(41)	937(12)
C(4)	762(65)	5 384(63)	1 443(21)
C(5)	880(45)	6 462(49)	2 037(17)
C(6)	214(51)	7 520(50)	1 887(17)
C(7)	−236(53)	7 299(49)	1 182(17)
C(8)	−1 183(46)	8 080(50)	840(16)



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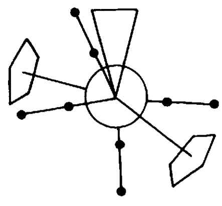

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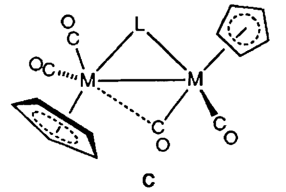

C

imposed) is illustrated schematically as a Newman projection in **A**. This is similar to the analogous complexes containing $\mathrm{Sb_2}$, $\mathrm{As_2}$ and $\mathrm{P_2}$ ligands, *viz.* $[\mathrm{Mo_2(CO)_4(\eta\text{-}C_5H_5)_2(\mu\text{-}\eta^2\text{-}Sb_2)}]$ **18**,[15] $[\mathrm{M_2(CO)_4(\eta\text{-}C_5H_5)_2(\mu\text{-}\eta^2\text{-}As_2)}]$ (M = Mo, **19**; or W, **20**),[16] $[\mathrm{Mo_2(CO)_4(\eta\text{-}C_5H_4Pr^i)_2(\mu\text{-}\eta^2\text{-}As_2)}]$ **21**,[17] $[\mathrm{Mo_2(CO)_4(\eta\text{-}C_5H_5)_2(\mu\text{-}\eta^2\text{-}P_2)}]$ **22**[18] and $[\mathrm{Cr_2(CO)_4(\eta\text{-}C_5H_5)_2(\mu\text{-}\eta^2\text{-}P_2)}]$ **23**,[19] all of which have been crystallographically characterised. A convenient way of comparing these structures is to examine the torsion angle defined as ($\mathrm{C_5H_5}$ ring centroid)–M–M–($\mathrm{C_5H_5}$ ring centroid). This information is collected in Table 6 together with the angle between the E–E (E = P, As, Sb or Bi) and M–M vectors which provides a measure of the twisting of the $\mathrm{E_2M_2}$ tetrahedron about the C_2 axis. From these data it is apparent that all of the above compounds are essentially isostructural (in molecular, not crystallographic, terms).

Table 6 Relevant torsion angle data (°) for the complexes $[\mathrm{M_2(CO)_4(\eta\text{-}C_5H_4R)_2(\mu\text{-}\eta^2\text{-}E_2)}]$ (E = P, As, Sb or Bi) described in the text

Compound	$\mathrm{C_5H_5\text{-}M\text{-}M\text{-}C_5H_5}$[a]	E-E/M-M[b]	Ref.
9	84.2	84.9	This work
11	−82.7	85.0	This work
18	−78.2	86.5	15
19[c]	−78.0	85.5	16
	−75.9	85.9	
20[c]	−80.3	85.4	16
	−76.7	86.0	
21	83.1	86.2	17
22	84.3	85.9	18
23	−80.4	84.5	19

[a] Defined in the text. [b] This is defined as the angle between the E–E and M–M vectors when looking down the C_2 axis. [c] Values for two crystallographically independent molecules.

It is also worth commenting at this point on the solution spectra of the complexes. Data for compounds **8**–**11** are given in Table 1 and, for **8**, in Fig. 1(*a*) and all show two strong absorptions at ≈1915 ± 5 and 1860 ± 6 $\mathrm{cm^{-1}}$ (see above). We suggest that this is consistent with the symmetric structure observed in the solid state being maintained in solution (thf), but we also draw attention to the spectra for compounds **18**–**23**. Data for these complexes are collected in Table 7 together with data for the $\mathrm{C_5Me_5}$ derivatives $[\mathrm{Mo_2(CO)_4(\eta\text{-}C_5Me_5)_2(\mu\text{-}\eta^2\text{-}As_2)}]$ **24**,[21] $[\mathrm{Mo_2(CO)_4(\eta\text{-}C_5Me_5)_2(\mu\text{-}\eta^2\text{-}P_2)}]$ **25**[22a] and $[\mathrm{W_2(CO)_4(\eta\text{-}C_5Me_5)_2(\mu\text{-}\eta^2\text{-}P_2)}]$ **26**,[22b] none of which has been characterised by X-ray crystallography (further mention of **23** is made in refs. 24–26 and of **25** in ref. 27; review articles covering $\mathrm{P_2}$ and $\mathrm{As_2}$ complexes are also available[28]). The spectra for **18**–**20**, **22** and **23** also exhibit two strong absorptions in the carbonyl region (although in the case of **19**, **20** and **23** additional weaker signals are seen as well) and thus are also consistent with the solid-state structures being maintained in solution. It seems likely, however, that the $\mathrm{C_5Me_5}$ derivatives, **24**–**26**, have different solution-state structures. Further insight can be gained by examining complexes containing the $\mathrm{M_2(CO)_4(\eta\text{-}C_5H_5)_2}$ fragment in which the M–M bond is bridged by other four-electron donor ligands. Specifically, we refer to the alkyne complexes $[\mathrm{M_2(CO)_4(\eta\text{-}C_5H_5)_2(\mu\text{-}RC{\equiv}CR)}]$ and the phosphinidene species $[\mathrm{M_2(CO)_4(\eta\text{-}C_5H_5)_2(\mu\text{-}PR)}]$.[29] Two structural types are observed. Some complexes adopt structures which contain a C_2 axis and are therefore analogous to **9**, **11** and **18**–**23** (diagram **A**); others adopt a lower symmetry C_1 structure which is shown in **B** (Newman projection) and **C**.

Factors which influence the structure are discussed, for phosphinidene complexes, in ref. 29; relevant data on the alkyne complexes can be found in ref. 30, but an indication of which structure is present in solution can be inferred from the carbonyl infrared spectra. For the C_2 isomer two absorptions are observed whereas for the C_1 structure four absorptions are seen, one of which is at low frequency consistent with the semi-bridging mode found for one CO ligand (diagram **C**).* This signal is usually at *ca.* 1850 $\mathrm{cm^{-1}}$ (refs. 29 and 30) and thus, since **24**, **25** and **26** have CO absorptions at 1823, 1829 and 1820 $\mathrm{cm^{-1}}$ respectively (Table 7), we suggest that these complexes adopt the C_1 structure (*i.e.* **B**/**C**).

(*iii*) *Electronic Structures*.—We were interested in studying the electronic structure of the dibismuth complex **8** and also in comparing this compound with the diphosphorus congener, **22**. Accordingly, we have carried out extended-Hückel molecular

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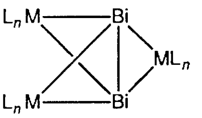
* The spectrum of any particular complex may be more complicated due to the presence of both isomers in solution.

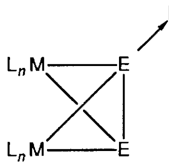
Table 7 Infrared data in the carbonyl stretching region for the complexes **18**–**20** and **22**–**25**

Compound	ν(CO)/cm^{-1}	Ref.
18	1936, 1885[a]	15
19/**20**	1985 (sh), 1960m, 1910s[b]	16
19	1985w, 1960s, 1910vs[b]	20
	1953s, 1900s[a]	23
20	1983w, 1960s, 1915vs[b]	20
	1946s, 1891s[a]	23
22	1965s, 1913s[a]	18
23	1970s (sh), 1950vs, 1925s (sh), 1890vs[c]	19
24	1976, 1913, 1897, 1823[c]	21
25	1980s, 1920s, 1905s, 1829s[d]	22*a*
26	1978s, 1915s, 1905s, 1820m[d]	22*b*

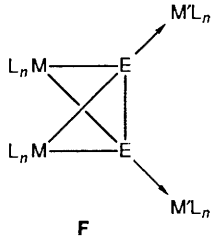
[a] Measured in CH_2Cl_2. [b] KBr disc. [c] Measured in toluene. [d] Measured in heptane solution.



D



E



F

orbital (EHMO) calculations on both **8** and **22**, the results of which we describe in this section. Before doing this, however, we will highlight some of the observations which led us to tackle this problem in the first place.

It is evident from the Introduction that in most of the dibismuth complexes this unit acts as a six-electron donor, *i.e.* **1** and **3**–**6**. With the exception of **2**, the only examples of Bi_2 as a four-electron donor which have been crystallographically characterised are reported herein. Moreover, in *all* cases of six-electron donation the metal fragments bridge the Bi–Bi vector as shown in **D**. Much less is known for diantimony complexes[11] although examples which contain a six-electron donor Sb_2 ligand are isostructural with bismuth analogues. For P_2 and As_2 complexes the situation is rather different. The arsenic analogue of **1** has been reported[31] but in general six-electron donor P_2 and As_2 complexes adopt a structure represented in **E** (M′L$_n$ = 16-electron fragment) and eight-electron donation as shown in **F** is also known. Examples of type **E** structures are $[Cr_2(CO)_4(\eta\text{-}C_5H_5)_2\{\mu\text{-}\eta^2\text{-}PP[Cr(CO)_5]\}]$[25] and $[Co_2(CO)_6\{\mu\text{-}\eta^2\text{-}AsAs[M(CO)_5]\}]$ (M = Cr, Mo or W);[32] examples of type **F** structures are $[Co_2(CO)_4\{P(OMe)_3\}_2\{\mu\text{-}\eta^2\text{-}As_2[W(CO)_5]_2\}]$,[32] $[Cr_2(CO)_4(\eta\text{-}C_5H_5)_2\{\mu\text{-}\eta^2\text{-}P_2[Cr(CO)_5]_2\}]$,[24] $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2\{\mu\text{-}\eta^2\text{-}As_2[Mn(CO)_2(\eta\text{-}C_5H_5)]_2\}]$[20] and $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2\{\mu\text{-}\eta^2\text{-}As_2[Cr(CO)_5]_2\}]$[23] (data on the parent dicobalt, P_2 and As_2 compounds can be found in ref. 33; see also ref. 10 and refs. therein and ref. 34).

In order to understand why six-electron donor Bi_2 and P_2 complexes should have such different structures, a series of EHMO calculations were performed on the complexes **8** and **22** and on the respective neutral $Mo_2(CO)_4(\eta\text{-}C_5H_5)_2$, Bi_2 and P_2 fragments. We were expecting to find, based on the aforementioned structural results, that for **8** the highest-energy bismuth-based orbital would be associated with the Bi–Bi bond whereas for the P_2 complex **22** we anticipated a build up of electron density on each phosphorus atom, *i.e.* in the form of lone pairs. This prediction was borne out by the results of the calculations.

Computational and geometric details are given in the Experimental section. As the geometries of the $Mo_2(CO)_4(\eta\text{-}C_5H_5)_2$ fragments in **8** and **22** are virtually identical (Table 6), the orbital energies are essentially the same and these are presented in the centre of Fig. 4. The major differences between the two compounds will lie in the differences in energies and the shapes of the Bi_2 and P_2 fragment orbitals and their interactions with the Mo_2 fragment. The Bi_2 energy levels are shown on the extreme left of Fig. 4, those for P_2 on the extreme right.

The Bi_2 and P_2 fragments each contain eight molecular orbitals which can be described as follows. The lowest-energy orbital is the σ bond of largely s character lying at -17.62 eV for Bi_2 and -22.53 eV for P_2. Next is a σ^* level which is largely E–E non-bonding corresponding to the out-of-phase combination of the lone pairs (-15.16 eV for Bi_2, -18.42 eV for P_2). At -11.65 eV for Bi_2 (-16.58 eV for P_2) are the π-bonding levels which are degenerate in $D_{\infty h}$ symmetry but are of different irreducible representations in C_2 symmetry. The fragment highest occupied molecular orbital (HOMO) is essentially the in-phase combination of the lone pair lying at -11.41 eV for Bi_2 and -12.92 eV for P_2. For P_2 there is some P–P σ-bonding character in this orbital whereas for Bi_2 this orbital is largely localised between the two Bi nuclei and is a strong Bi–Bi σ bond of mainly p character (see Figs. 5 and 6). The fragment lowest unoccupied molecular orbitals (LUMOs) are the π^* orbitals at -8.93 eV for Bi_2 and -8.91 eV for P_2. Finally we have the p σ^* orbitals which are too high in energy to interact with any filled levels on the Mo_2 fragment.

For the Mo_2 fragment there should be six filled levels of largely d character corresponding to the d^6 configuration on Mo. The five highest-lying filled fragment orbitals are clearly the Mo–d block, and are well separated from the remaining levels. The Mo atoms each have a charge of *ca.* $+1.07$ in the fragments, with the negative charge being localised on the CO ligands. Thus the configuration is perhaps best viewed as d^5-Mo^I. The next four levels all contain some molybdenum character but are largely C_5H_5 ring based.

For complex **22** the three highest-lying molecular orbitals (53–55) are Mo based with essentially no phosphorus character. Three of the next four levels (56, 58, 59) are stabilised by the interaction with P–P π^* levels. One orbital, 57, is an antibonding combination of C_5H_5Mo levels with P–P σ with the bonding level lying much lower in energy, closer to that of the P–P lone pair level. The remaining four filled P–P levels are much too low in energy to interact with any Mo-based orbitals.

Overall there is relatively little mixing of the P–P and Mo–Mo orbitals in the frontier molecular levels which is largely due to the electronegativity of the phosphorus.

The bonding in complex **8** is considerably different from that in **22**. Both of the Bi_2 π levels and highest-lying σ level are close in energy to the Mo_2 frontier orbitals; Bi_2 π^* lies at almost the same energy as for the P_2 π^* and mixes in slightly with the high-lying molybdenum orbitals in a stabilising fashion. The HOMO and second HOMO of **8** are essentially Mo-based orbitals. The third HOMO however is almost entirely the Bi_2 p σ bond with relatively little molybdenum character. There is only a minor interaction of the Bi–Bi bonding orbital with the second LUMO of the Mo_2 fragment. Apparently the stability of the Bi–Bi level combined with the slight twisting of the Bi_2 unit with respect to the Mo–Mo unit (see above) leads to minimal overlap between the Bi_2 σ bond and any Mo-based levels. This is reflected in a short Bi–Bi bond length. Moreover, the fact that this Mo_2Bi_2 level is localised between the two Bi atoms suggests that an additional unsaturated metal fragment, M′L$_n$, might complex to the Bi–Bi bond rather than to a single Bi atom thus consistent with the known six-electron donor properties of Bi_2. This is a major difference between **8** and **22** in that, in the latter, the lone-pair orbitals on the phosphorus atoms are both available for conventional σ bonding to additional unsaturated metal fragments (see Fig. 7). In summary, therefore, the bismuth- and phosphorus-based frontier orbitals in **8** and **22** respectively are of a form which enables us to rationalise the difference in six-electron donor structures, *i.e.* **D** *vs.* **E**.

The Mo–Mo reduced overlap populations (r.o.p.s) are similar in the two compounds, 0.14 in **22** and 0.16 in **8**, however the

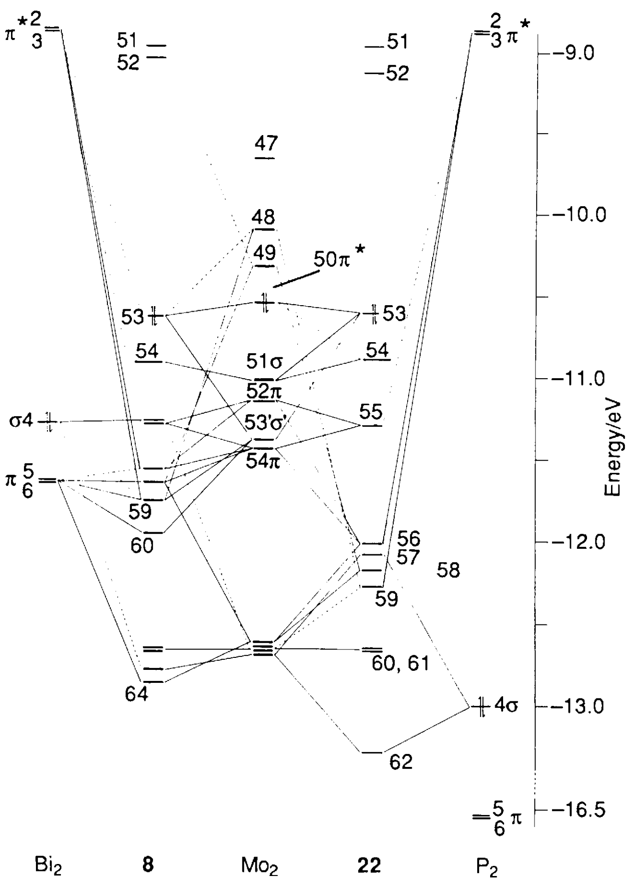


Fig. 4 An orbital interaction diagram for complexes **8** and **22**

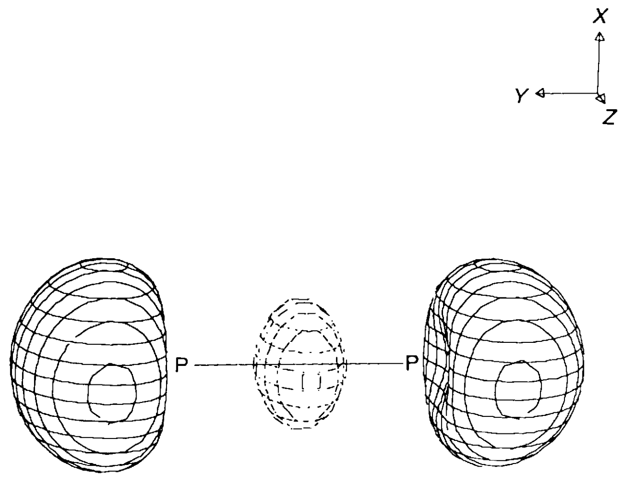


Fig. 5 An orbital plot for the P_2 fragment HOMO in complex **22**

Bi–Bi r.o.p. is 0.81 whereas the P–P r.o.p. is 1.13. The Mo–P r.o.p.s are 0.19 and 0.24 whereas the Mo–Bi r.o.p.s are 0.25 and 0.29. The Mo_2–P_2 fragment r.o.p. is 1.14 whereas that for the Mo_2–Bi_2 fragment is 1.64. Although it is difficult to compare the r.o.p.s between dissimilar elements, these figures are consistent with there being stronger M–E interactions in the bismuth compound. The substantial P–P and Bi–Bi r.o.p.s are consistent with the short E–E contacts and thus some degree of multiple bonding. Finally, consistent with the greater electronegativity of P compared with Bi, the final fragment charges in **22** are +0.60 on Mo_2 and −0.60 on P_2, and in **8** are −0.64 on Mo_2 and +0.64 on Bi_2.

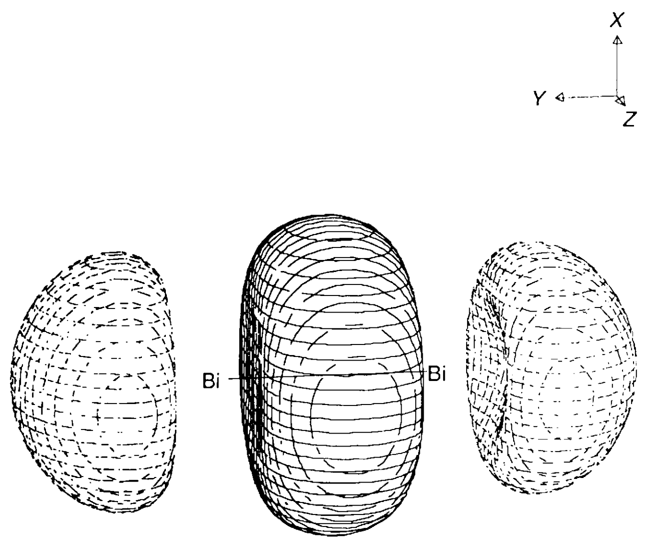


Fig. 6 An orbital plot for the Bi_2 fragment HOMO in complex **8**

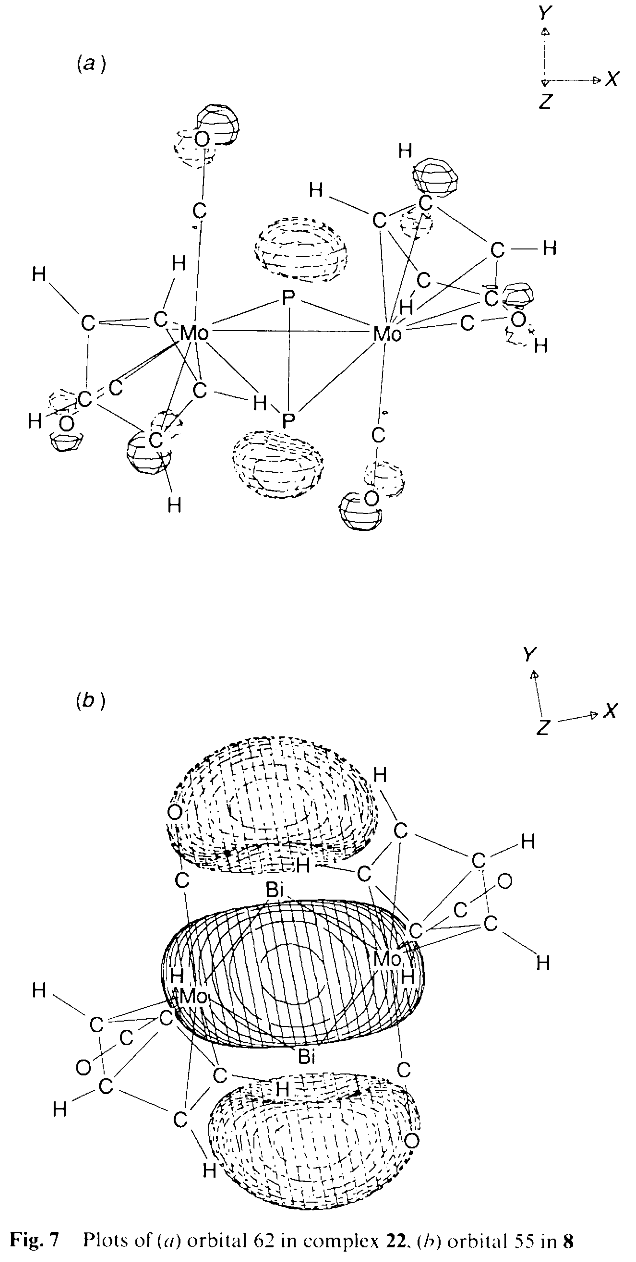


Fig. 7 Plots of (*a*) orbital 62 in complex **22**, (*b*) orbital 55 in **8**

Experimental

General Considerations.—All experiments were performed under an atmosphere of dry, oxygen-free dinitrogen using standard Schlenk techniques. All solvents were dried and distilled over appropriate drying agents immediately prior to use (sodium-benzophenone for all solvents except CH_2Cl_2 for which CaH_2 was used). Proton and ^{13}C NMR spectra were recorded in dried and degassed deuteriated solvents on a Bruker WP200 spectrometer operating at 200.13 and 50.324 MHz, respectively. Chemical shifts are referenced to solvent peaks in all cases with values taken from ref. 35. Infrared spectra were recorded on a Nicolet 20 SXB FTIR spectrophotometer. Microanalytical data were obtained either at the University of Newcastle or from Malissa and Reuter Analytische Laboratorien, Germany.

Bismuth trichloride was procured commercially and used without further purification and the cyclopentadienylmetal carbonyl dimers $[M_2(CO)_6(\eta\text{-}C_5H_4R)_2]$ (M = Cr, Mo or W; R = H or Me) were prepared by the method of Manning and co-workers.[36]

Analytical and infrared data for all new compounds are presented in Table 1, NMR data in Table 2.

Preparations.—$[Bi\{W(CO)_3(\eta\text{-}C_5H_4Me)\}_3]$ **15**. To a purple solution of $[BiCl\{W(CO)_3(\eta\text{-}C_5H_4Me)\}_2]$ (0.545 g, 0.582 mmol) in thf (20 cm^3) was added 1 equivalent of $Na[W(CO)_3(\eta\text{-}C_5H_4Me)]$ {prepared by a Na/Hg reduction of the dimer $[W_2(CO)_6(\eta\text{-}C_5H_4Me)_2]$ (0.201 g, 0.291 mmol)} in thf (30 cm^3) with constant stirring. The colour changed immediately to deep red and the mixture was allowed to stir for 1 h. Purification by column chromatography (Florisil) yielded a major red-brown fraction (thf). Solvent diffusion at −30 °C of a thf–hexane mixture gave complex **15** as a dark red solid (yield 0.39 g, 60%).

$[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2(\mu\text{-}\eta^2\text{-}Bi_2)]$ **8**, *by solution photolysis.* A sample of $[Bi\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_3]$ (0.357 g, 0.378 mmol) was dissolved in thf (80 cm^3) and photolysed with a N_2 purge for 35 min using a 100 W medium-pressure UV lamp. The solution rapidly changed colour from dark red to brown. Purification by column chromatography (Florisil) afforded two fractions, an initial red-purple fraction [hexane–diethyl ether (4:1)] followed by a second yellow-brown fraction (thf). Purple crystals of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ were obtained from the first fraction by solvent diffusion at −20 °C from thf (1 cm^3)–hexane (6 cm^3). Black crystals of complex **8** (0.138 g, 86% based on Bi) were obtained from the second fraction from thf (3 cm^3)–hexane (20 cm^3) by solvent diffusion at −30 °C.

The methylcyclopentadienyl derivative **9** was prepared in an exactly analogous manner. X-Ray-quality crystals were obtained from thf–hexane mixtures by solvent diffusion at −30 °C (yield 32% based on Bi).

$[W_2(CO)_4(\eta\text{-}C_5H_5)_2(\mu\text{-}\eta^2\text{-}Bi_2)]$ **10**, *by solution photolysis.* A sample of $[Bi\{W(CO)_3(\eta\text{-}C_5H_5)\}_3]$ (0.214 g, 0.177 mmol) was dissolved in thf (80 cm^3) and photolysed for 45 min as described for **8**. The solution rapidly changed colour from red to dark yellow-brown. Purification by column chromatography (Florisil) afforded two fractions, an initial red fraction [hexane–diethylether (1:1)], characterised as a mixture of $[W_2(CO)_6(\eta\text{-}C_5H_5)_2]$ and $[W_2(CO)_4(\eta\text{-}C_5H_5)_2]$ by infrared spectroscopy, followed by a second dark brown fraction (thf). Black crystals of **10** were obtained from thf (3 cm^3)–hexane (20 cm^3) by solvent diffusion over a period of days at −22 °C (yield 0.01 g, ≈10%).

The methylcyclopentadienyl derivative **11** was prepared in an exactly analogous manner. Black crystals suitable for X-ray diffraction studies were obtained from thf–hexane mixtures by solvent diffusion at −30 °C (yield 40% based on Bi).

The yields for all of the preparations described above are very dependent on the photolysis time and also to a lesser extent on the concentration of the trimetallobismuthine in solution.

$[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2(\mu\text{-}\eta^2\text{-}Bi_2)]$ **8**, *by solid-state thermolysis.* A sample of $[Bi\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_3]$ was heated under vacuum to 150 °C for 1 h. During this time the solid darkened from dark red to black and a red solid sublimed onto the walls of the flask; this was identified as $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ by infrared spectroscopy. The remaining black solid was washed with hexane, to remove traces of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$, and then with thf which afforded a dark yellow-brown solution identified, after filtration through Florisil, as complex **8** by infrared spectroscopy.

$[Bi\{Cr(CO)_3(\eta\text{-}C_5H_5)\}_3]$ **16**. *Method A.* Dropwise addition of a solution of $BiCl_3$ (0.231 g, 0.732 mmol) in thf (10 cm^3) to a solution of $Na/K[Cr(CO)_3(\eta\text{-}C_5H_5)]$ {prepared by Na/K reduction of $[Cr_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (0.441 g, 1.098 mmol)} in thf (20 cm^3) at 0 °C resulted in an initial orange colouration which rapidly turned green. After complete addition of the $BiCl_3$ solution, stirring was continued for 2 h and the reaction mixture allowed to warm to room temperature. Filtration through Celite followed by removal of all the volatiles under vacuum gave a dark green solid which was redissolved in thf (10 cm^3). Crystallisation by solvent diffusion with hexane (40 cm^3) at −25 °C over a period of days afforded complex **16** as a green powder (0.274 g, 47%).

Method B. Bismuth powder (1.46 g, 6.97 mmol) was added to a solution of $[Cr_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (0.280 g, 0.697 mmol) in thf (30 cm^3) and the mixture stirred for 24 h. Filtration through Celite followed by removal of all volatiles gave a dark green powder which was recrystallised by solvent diffusion from thf–hexane mixtures (10 cm^3 thf, 40 cm^3 hexane) at −25 °C. After a few days a green solid had precipitated and this was shown by infrared spectroscopy to be $[Cr_2(CO)_6(\eta\text{-}C_5H_5)_2]$. The mother-liquor from this crystallisation was taken to dryness by vacuum and redissolved in thf (5 cm^3). Further crystallisation using hexane (30 cm^3) at −25 °C over a period of days afforded complex **16** (0.196 g, 52%) as a dark green solid.

$[BiCl\{Cr(CO)_3(\eta\text{-}C_5H_5)\}_2]$ **17**. A solution of $Na/K[Cr(CO)_3(\eta\text{-}C_5H_5)]$ {prepared by Na/K reduction of $[Cr_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (0.422 g, 1.050 mmol)} in thf (20 cm^3) was added to a solution of $BiCl_3$ (0.331 g, 1.050 mmol) in thf (10 cm^3) at 0 °C. The solution initially developed an orange colouration which rapidly became dark green after further addition. The reaction mixture was stirred for 2 h and allowed to warm to room temperature. Filtration through Celite followed by removal of all volatiles gave a dark green solid. Crystallisation from thf (5 cm^3)–hexane (30 cm^3) by solvent diffusion over a period of days afforded complex **17** as a dark green powder (0.285 g, 42%).

Satisfactory analytical data could not be obtained for **16** and **17** due to the low stability of these complexes and difficulties in rigorous purification. However, there is little doubt as to their nature on the basis of the similarity of the infrared spectra to those of the molybdenum and tungsten analogues.[12]

Mass Spectrometric Studies.—Mass spectra were obtained on AEI MS9 and Kratos MS80 instruments using the electron impact (EI) mode at 70 eV. As stated in the Results and Discussion and in ref. 12, the trimetalbismuth complexes $[Bi\{M(CO)_3(\eta\text{-}C_5H_5)\}_3]$ gave mass spectra consistent with the formula $[M_2Bi_2(CO)_4(\eta\text{-}C_5H_5)_2]$. We also obtained similar spectra using the complexes $[BiCl\{M(CO)_3(\eta\text{-}C_5H_5)\}_2]$; for the molybdenum complexes the probe temperature was 150 °C whereas for tungsten 200 °C was used. The spectra reported below, however, were obtained using samples of the isolated complex $[M_2Bi_2(CO)_4(\eta\text{-}C_5H_4R)_2]$.

Compound **8** (probe temperature 140 °C); *m/z* 852, P $[= Mo_2Bi_2(CO)_4(\eta\text{-}C_5H_5)_2$ for $^{96}Mo]$; 796, P − 2CO; 768, P − 3CO; and 740, P − 4CO. Other fragment ions observed were: *m/z* 610, Mo_2Bi_2; 836, Bi_4; 627 Bi_3; 418, Bi_2; 209, Bi. We also observed signals corresponding to the complex $[MoBi_3(CO)_2(\eta\text{-}C_5H_5)]$, *m/z* 844, together with the carbonyl-loss fragments at *m/z* 816 and 788. These latter signals are interesting since this tribismuth complex, which has not been isolated, is a heavier congener of the known phosphorus and arsenic species $[MoE_3(CO)_2(\eta\text{-}C_5H_5)]$ (E = P or As).[21,28a,b,37] High-resolution mass spectrum calculated for the Mo_2Bi_2 fragment ion; 601.7758; found 601.7719.

Compound **9** (probe temperature 150 °C); *m/z* 880, P [= $Mo_2Bi_2(CO)_4(\eta\text{-}C_5H_4Me)_2$ for ^{96}Mo]; 824, P − 2CO; 796, P − 3CO; and 768, P − 4CO. Also observed was a signal at *m/z* 858 corresponding to [$MoBi_3(CO)_2(C_5H_4Me)$].

Compound **11** (probe temperature 200 °C); *m/z* 1056, P [= $W_2Bi_2(CO)_4(C_5H_4Me)_2$ for ^{184}W]; 1000, P − 2CO; 972, P − 3CO; and 944, P − 4CO.

We note that the complex [$BiCl\{Mo(CO)_2(CNBu^t)(\eta\text{-}C_5H_5)\}_2$][12] gave mass spectra consistent with the presence of **8** and [$Mo_2Bi_2(CO)_2(CNBu^t)_2(\eta\text{-}C_5H_5)_2$] but that none of the chromiumbismuth complexes gave spectra indicating the presence of [$Cr_2Bi_2(CO)_4(\eta\text{-}C_5H_5)_2$].

EHMO Calculations.—Molecular orbital calculations were of the extended-Hückel type[38] using the program ICON8 with fragment MO analysis.[39] The Hückel constant was set to 1.75 and weighted H_{ij} values (modified Helmholz–Wolfsberg formula)[40] were used throughout. Parameters for the calculations were taken from ref. 41 except for those for bismuth which were taken from ref. 42. Calculations were performed on [$Mo_2(CO)_4(\eta\text{-}C_5H_5)_2(\mu\text{-}\eta^2\text{-}E_2)$] (E = P or Bi) in C_2 symmetry as found in the solid-state structures of **22** and **8** respectively, with the Mo–Mo and E–E midpoints lying along z and defining the C_2 axis. Geometric parameters were taken from the crystal structures with the C_5H_5 rings constrained to local D_{5h} symmetry.

X-Ray Crystallography.—Crystal data for complex **9**. $C_{16}H_{14}Bi_2Mo_2O_4$, $M = 880.1$, trigonal, space group $P3_121$, $a = 8.8996(5)$, $c = 19.944(2)$ Å, $U = 1368.0$ Å^3 (from 2θ values of 32 reflections in the range 20–25°, measured at ±ω), $Z = 3$, $D_c = 3.205$ g cm^{-3}, $F(000) = 1176$, λ(Mo-Kα) = 0.710 73 Å, μ(Mo-Kα) = 20.5 mm^{-1}, $T = 295$ K.

Data collection and processing. Stoe-Siemens diffractometer, ω–θ scans with on-line profile fitting[43] from a crystal of size 0.2 × 0.2 × 0.4 mm, $2\theta_{max} = 50°$, maximum indices h 10, k 10, l 23, with two or three equivalents measured for each reflection and a complete set of Friedel opposites. Corrections were made for absorption (semiempirically: transmission factors 0.069–0.094) and for a decay of about 7% in the intensities of three periodically measured standard reflections. From 4830 measured reflections, the unique set comprised 1604 data, of which 1511 with $F > 4\sigma_c(F)$ were used in structure determination (σ_c from counting statistics only); $R_{int} = 0.031$.

Structure solution and refinement.[44] All non-hydrogen atoms were located from Patterson and difference syntheses and were refined with anisotropic thermal parameters to minimise $\Sigma w\Delta^2$; $\Delta = |F_o| - |F_c|$. Hydrogen atoms were not included. Atomic scattering factors were taken from ref. 45. The weighting scheme[46] was $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + 48 + 68G - 46G^2 - 138H + 102H^2 - 131GH$ ($G = F_o/F_{max}$, $H = \sin\theta/\sin\theta_{max}$). Extinction effects appeared to be negligible. The space group was established (choice between $P3_121$ and $P3_221$) by refinement[47] of $\eta = +1.05(2)$. At convergence, $R = 0.0273$, $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}} = 0.0281$, goodness of fit = 1.19, for 109 parameters. All shift/e.s.d. values were <0.01; a final difference synthesis contained maximum and minimum features of +1.70 and −1.60 e Å^{-3}, close to Bi atoms.

Crystal data for complex **11**. $C_{16}H_{14}Bi_2O_4W_2$, $M = 1055.9$, trigonal, space group $P3_221$, $a = 8.863(4)$, $c = 19.748(14)$ Å, $U = 1343$ Å^3 (from 2θ values of 34 reflections in the range 16–24°), $Z = 3$, $D_c = 3.915$ g cm^{-3}, $F(000) = 1368$, μ(Mo-Kα) = 32.6 mm^{-1}, $T = 295$ K.

Data collection and processing. As for **9**, except crystal size 0.24 × 0.24 × 0.28 mm, transmission factors 0.009–0.042, intensity decay approximately 5%; 3522 measured reflections, 1585 unique data, 1411 with $F > 4\sigma_c(F)$, $R_{int} = 0.078$.

Structure solution and refinement. As for **9**, except anisotropic thermal parameters for W and Bi, isotropic for C and O atoms; weighting scheme, $w^{-1} = \sigma_c^2(F) + 137 + 214G + 2739G^2 - 215H + 287H^2 - 2318GH$; extinction parameter $x = 5(2) \times 10^{-7}$, whereby $F_c' = F_c/(1 + xF_c^2/\sin2\theta)^{\frac{1}{4}}$; $\eta = +0.93(8)$ for preference of $P3_221$ over $P3_121$; $R = 0.061$, $R' = 0.060$, goodness of fit = 1.29, for 60 parameters; maximum shift/e.s.d. = 0.003, largest features in final difference synthesis +4.43 and −3.99 e Å^{-3} close to heavy atoms.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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