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MELDOLA MEDAL LECTURE*

Organotransition Metal Complexes Incorporating Bismuth

By Nicholas C. Norman
DEPARTMENT OF INORGANIC CHEMISTRY,
THE UNIVERSITY, NEWCASTLE UPON TYNE, NE1 7RU

1 Introduction

The synthesis of organotransition metal complexes incorporating atoms or fragments containing the heavier main group elements is an area that is currently attracting significant attention.[1] Specifically, this review is concerned with bismuth–transition metal complexes in which the two types of atom are mutually bonded.

Prior to 1980 there were relatively few reports in the literature dealing with well characterized transition metal–bismuth compounds but recent years have seen the number of publications in this area increase substantially. One of the major reasons for this increased interest is probably associated with the use of mixed bismuth–transition metal oxide catalysts, particularly the bismuth–molybdate materials used in the SOHIO process for acrylonitrile synthesis,[2] and more generally to catalyse amination and oxidation reactions. This review is not intended to be comprehensive, but rather to illustrate the types of complexes which are known and to outline the recent work of ourselves and other workers in this field.

2 Bismuthine and Bismuthido Complexes

Bismuth(III) is the most commonly observed oxidation state in the chemistry of this element, such being illustrated by the archetypal compounds $BiCl_3$ and $BiPh_3$. The latter is a heavier congener of the ubiquitous triphenylphosphine (PPh_3) ligand, but whilst examples of phosphine coordination to a transition metal centre are legion, relatively few examples of transition metal coordinated bismuthines are known. Examples include $[Mn(CO)_2(BiPh_3)(\eta\text{-}C_5H_5)]$,[3] $[Fe(CO)_3(BiPh_3)_2]$,[4] and more recently, a range of molybdenum and tungsten complexes reported by Baker *et al.* $[MX_2(CO)_3L(BiPh_3)]$ (X = halide; L = NCMe, PR_3, AsR_3, $P(OR)_3$).[5] The only such complex to have been characterized crystallographically,

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* The present text is based upon the lecture delivered on 22 February 1988 at a meeting of the Dalton Division of the Royal Society of Chemistry at the Scientific Societies' Lecture Theatre, Savile Row, London W1

[1] For recent reviews see: (*a*) W. A. Herrmann, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 56; (*b*) M. Di Vaira, P. Stoppioni, and M. Peruzzini, *Polyhedron*, 1987, **6**, 351; (*c*) O. J. Scherer, *Comments Inorg. Chem.*, 1987, **6**, 1; (*d*) O. J. Scherer, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 924.

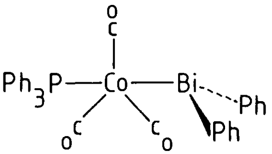
[2] (*a*) R. K. Grasselli and J. D. Burrington, *Adv. Catal.*, 1981, **30**, 133; (*b*) R. K. Grasselli, *J. Chem. Educ.*, 1986, **63**, 216.

[3] C. Barbeau, *Can. J. Chem.*, 1967, **45**, 161.

[4] (*a*) F. Hein and H. Pobloth, *Z. Anorg. Allg. Chem.*, 1941, **248**, 84; (*b*) J. Desnoyers and R. Rivest, *Can. J. Chem.*, 1965, **43**, 1879.

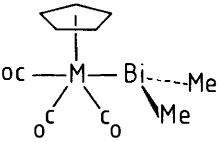
[5] P. K. Baker and S. G. Fraser, *J. Coord. Chem.*, 1987, **16**, 97.

however, is the chromium complex $[Cr(CO)_5(BiPh_3)]$.[6] The reason for the scarcity of these complexes is probably a result of the poor Lewis basicity of three-coordinate bismuth(III) resulting primarily from the residence of the bismuth lone pair in an orbital of mostly *s* character.



(1)

This lack of basicity is also apparent in the properties of transition metal–bismuthido complexes, L_nMBiR_2. Calderazzo *et al.*[7] have reported the synthesis and *X*-ray crystal structure of (1), containing the $BiPh_2$ fragment, but unlike lighter congeneric analogues containing PPh_2, $AsPh_2$, and $SbPh_2$ moieties, (1) shows no tendency to dimerize or oligomerize through an interaction involving the bismuth lone pair and a second cobalt centre. Such behaviour probably also results from a high degree of *s* character associated with the lone pair, this factor being reflected in the interbond angles at bismuth which are all significantly less than the tetrahedral angle.[7,8]



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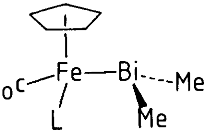

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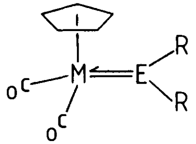

E = P, As

(4)

Additional examples of bismuthido complexes have been prepared by Malisch and co-workers, *viz.* $[(C_5H_5)(CO)_3M\text{–}BiMe_2]$ (M = Cr, Mo, W)[9] and $[(C_5H_5)(CO)(L)Fe\text{–}BiMe_2]$ (L = CO, PMe_3)[10] and by Cullen *et al.*[11] No structural data have been obtained for these complexes, but they most probably contain an η^1-bonded, trigonal pyramidal bismuth atom, *viz.* (2) and (3). Many structurally similar examples exist for phosphorus and arsenic but, for these elements, an analogue of (2) exists in which a carbonyl ligand has been lost and the resulting vacant coordination site at the metal centre is filled by donation from the

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[6] A. J. Carty, N. J. Taylor, A. W. Coleman, and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1979, 639.

[7] F. Calderazzo, R. Poli, and G. Pelizzi, *J. Chem. Soc., Dalton Trans.*, 1984, 2535.

[8] Interbond angles in three-coordinate bismuth(III) compounds are usually in the range 92—102°. This reflects a predominance of *p* character in the bonding orbitals and a correspondingly large degree of *s* character in the lone pair. Three-coordinate bismuth is therefore less Lewis basic than its lighter congeners.

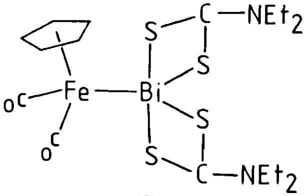
[9] P. Panster and W. Malisch, *J. Organomet. Chem.*, 1977, **134**, C32.

[10] H.-A. Kaul, D. Greissinger, M. Luksza, and W. Malisch, *J. Organomet. Chem.*, 1982, **228**, C29.

[11] (*a*) W. R. Cullen, D. J. Patmore, J. R. Sams, M. J. Newlands, and L. K. Thompson, *Chem. Comm.*, 1971, 952; (*b*) W. R. Cullen, D. J. Patmore, and J. R. Sams, *Inorg. Chem.*, 1973, **12**, 867.

phosphorus or arsenic lone pair, *i.e.* (4).[12] There appear to be no examples in the literature of analogous bismuth-containing compounds although this is perhaps unsurprising due to the aforementioned poorly basic bismuth centre and the anticipated reluctance of bismuth to partake in any degree of multiple bonding.

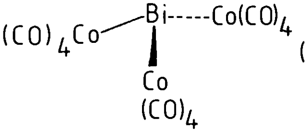
A final example of a formal bismuthido complex is $[(C_5H_5)(CO)_2Fe\text{–}Bi\{S_2CR\}_2]$ ($R = NEt_2, OMe$) reported by Wieber *et al.*[13] for which a structure determination was carried out on the dithiocarbamate derivative, (5). This complex is similar



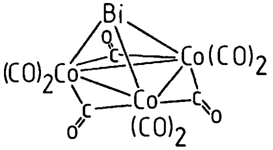
(5)

to (3) in containing a formal Fe–Bi single bond but differs in having additional bonding interactions with its attendant groups as shown in the diagram. Such interactions are commonly observed in structural bismuth chemistry and reflect the appreciable Lewis acidity (rather than basicity) associated with bismuth(III).[14]

3 Transition Metal Carbonyl Complexes Incorporating Bismuth Atoms



(6)



(7)

A. Mono–bismuth Clusters.—One of the earliest complexes to be fully characterized, in which the bismuth is bonded solely to transition metal centres,[15] was the tricobalt complex $[Bi\{Co(CO)_4\}_3]$, (6), prepared by Schmid and co-workers.[16] This compound contains three unsupported Bi–Co bonds spatially disposed such that the bismuth has a trigonal pyramidal coordination geometry resulting from

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[12] For examples of these types of complex, see: (*a*) L. D. Hutchins, H.-U. Reisacher, G. L. Wood, E. N. Duesler, and R. T. Paine, *J. Organomet. Chem.*, 1987, **335**, 229; (*b*) E. Gross, K. Jorg, K. Fiederling, A. Gottlein, W. Malisch, and R. Boese, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 738; (*c*) A. H. Cowley, D. M. Giolando, C. M. Nunn, M. Pakulski, D. Westmoreland, and N. C. Norman, *J. Chem. Soc., Dalton Trans.*, 1988, 2127.

[13] M. Wieber, D. Wirth, and C. Burschka, *Z. Naturforsch., Teil B*, 1985, **40**, 258.

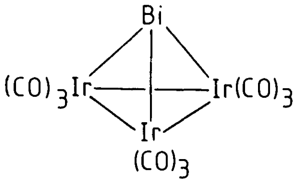
[14] An interesting comparison can be made between (5) and the tris dithiocarbamate complex, $Bi\{S_2CNEt_2\}_3$. The structure of the latter complex has been determined by *X*-ray methods and involves six-coordinate bismuth(III), the dithiocarbamate ligands being bidentate as observed in (5); see C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1976, 791.

[15] Such compounds have been described as containing 'bare' main group elements, see reference 1*a*.

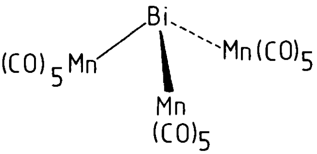
[16] G. Etzrodt, R. Boese, and G. Schmid, *Chem. Ber.*, 1979, **112**, 2574; see also P. Klüfers, *Z. Kristallogr.*, 1981, **156**, 74.

the presence of a stereochemically active lone pair. The compound may therefore be described as a trimetalla-bismuthine. More recently, a related tetrahedral $BiCo_3$ cluster has been reported by Whitmire[17] and Martinengo and Ciani[18] derived from (6) by thermal loss of three CO ligands. The cluster contains both terminal and bridging carbonyls as shown in the diagram, but of more interest is the *closo* $BiCo_3$ core geometry. This factor was discussed by both sets of authors,[17,18] in view of an argument originally promulgated by Schmid[19] that such clusters containing a large main group element and three lighter transition metals might be sterically untenable as a result of the large size of the main group atom, in this case bismuth. The synthesis of cluster (7) (and a related tri-iron cluster, see later) obviates the need for such an argument; moreover, the relevant bond lengths within (7) are in the usual ranges and not indicative of any large degree of steric strain.

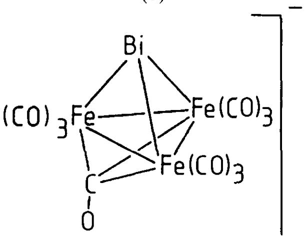
Other examples of M_3Bi clusters have also been reported. Schmid and coworkers[20] have described the synthesis and structural characterization of



(8)



(9)



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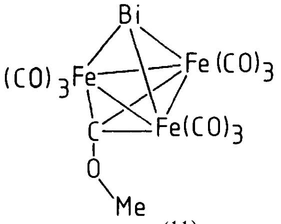

(11)

$[BiIr_3(CO)_9]$, (8), a complex closely related to the tricobalt cluster, (7), differing only in that all carbonyls are terminally bonded. Complexes (7) and (8) may thus be structurally compared with the tetranuclear carbonyl clusters $M_4(CO)_{12}$ (M = Co, Ir) from which they are formally derived by isolobal[21] replacement of a $M(CO)_3$ fragment with bismuth. More recently a trimanganese bismuth species, $[Bi\{Mn(CO)_5\}_3]$, (9), has been prepared by Schmidbaur[22a] and shown to possess a trigonal pyramidal, trimetalla-bismuthine structure akin to (6). The analogous

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[17] K. H. Whitmire, J. S. Leigh, and M. E. Gross, *J. Chem. Soc., Chem. Commun.*, 1987, 926.

[18] S. Martinengo and G. Ciani, *J. Chem. Soc., Chem. Commun.*, 1987, 1589.

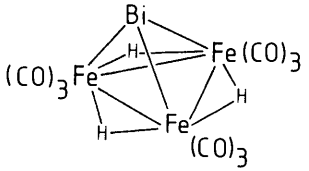
[19] G. Schmid, *Angew. Chem., Int. Ed. Engl.*, 1978, 17, 392.

[20] W. Kruppa, D. Bläser, R. Boese, and G. Schmid, *Z. Naturforsch., Teil B*, 1982, **37**, 209.

[21] (*a*) M. Elian, M. M. L. Chen, D. M. P. Mingos, and R. Hoffmann, *Inorg. Chem.*, 1976, **15**, 1148; (*b*) R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 711; (*c*) F. G. A. Stone, *ibid.*, 1984, **23**, 89.

[22] (*a*) J. M. Wallis, G. Müller, and H. Schmidbaur, *Inorg. Chem.*, 1987, **26**, 458; (*b*) N. A. Compton, R. J. Errington, and N. C. Norman, unpublished observations.

trirhenium complex [Bi{Re(CO)$_5$}$_3$] is assumed to have the same structure.[22b]

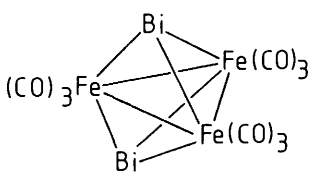


(12)

Also of interest in this section are a range of bismuth–metal carbonyl clusters incorporating metals of the iron subgroup. Whitmire[23] has reported the synthesis and structural characterization of the anionic cluster [BiFe$_3$(CO)$_{10}$]$^-$ (10), which, upon alkylation, affords the neutral cluster [BiFe$_3$(CO)$_9$(μ_3-COMe)] (11).[24] In addition, the novel trihydrido-bismuth cluster [H$_3$BiFe$_3$(CO)$_9$] (12),[24] has also been described, together with a more recent report from Johnson and Lewis and co-workers[25] on the ruthenium and osmium analogues [H$_3$BiM$_3$(CO)$_9$] (M = Ru, Os).

Examples of M$_4$Bi compounds include the anionic complexes [Bi{Co(CO)$_4$}$_4$]$^-$ [18] and [Bi{Fe(CO)$_4$}$_4$]$^{3-}$.[26] At least one example of a M$_5$Bi cluster has been reported, *viz.* [HBiRu$_5$(CO)$_{18}$],[25] although no structural details are as yet available for this complex.

B. Dibismuth Clusters.—(i) *Clusters containing Mutually Non-bonded Bismuth Centres.* Several examples of carbonyl clusters containing two mutually non-bonded bismuth centres have been reported in recent years. Whitmire *et al.* have described the synthesis of the tri-iron complex [Bi$_2$Fe$_3$(CO)$_9$], (13),[27] and more recently, the triruthenium and triosmium analogues have also been prepared.[25]



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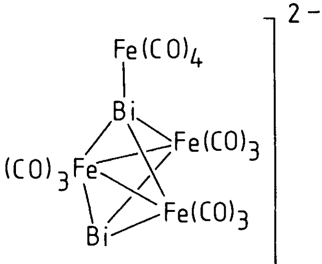

(14)

Other examples of dibismuth complexes in this category include [Bi$_2$Fe$_4$-

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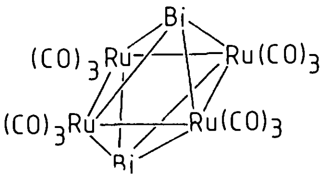
[23] K. H. Whitmire, C. B. Lagrone, M. R. Churchill, J. C. Fettinger, and L. V. Biondi, *Inorg. Chem.*, 1984, **23**, 4227.

[24] K. H. Whitmire, C. B. Lagrone, and A. L. Rheingold, *Inorg. Chem.*, 1986, **25**, 2472.

[25] 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.

[26] M. R. Churchill, J. C. Fettinger, K. H. Whitmire, and C. B. Lagrone, *J. Organomet. Chem.*, 1986, **303**, 99.

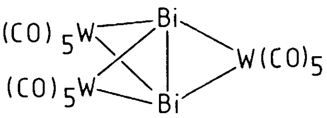
[27] M. R. Churchill, J. C. Fettinger, and K. H. Whitmire, *J. Organomet. Chem.*, 1985, **284**, 13.



(15)

$(CO)_{13}]^{2-}$, (14),[28] and the *closo* octahedral tetraruthenium complex $[Bi_2Ru_4(CO)_{12}]$, (15).[25]

(ii) *Clusters containing Mutually Bonded Bismuth Centres.* Dibismuth, Bi_2, is formally isoelectronic with dinitrogen, N_2, and although not stable in condensed phases, it is a major species in bismuth vapour. In concert with its lighter congeners, Bi_2 is anticipated to have an extensive coordination chemistry involving metal carbonyl fragments. Recent years have witnessed a steady growth in the number of P_2, As_2, and Sb_2 complexes that are known,[1] and, in accordance with expectations, several Bi_2 complexes have been prepared and fully characterized. One of the first such compounds to be reported was the unusual tritungsten complex $[Bi_2W_3(CO)_{15}]$, (16), prepared by Huttner *et al.*[29] in which Bi_2 functions as a six-electron donor. The trimolybdenum analogue has also been described[30] and the unusual bonding in these 'star-shaped' clusters has been discussed with reference to a related arsenic compound, $[As_2W_3(CO)_{15}]$.[31] The short Bi–Bi bond length in (16) [2.818(3) Å] has been taken to imply a residual degree of multiple bonding between the two bismuth atoms (a formal triple bond is present in Bi_2). Another example of Bi_2 acting as a six-electron donor in a trimetal cluster (and the only reported mixed transition metal, *i.e.* Co and Fe, bismuth cluster of which we are aware) is in



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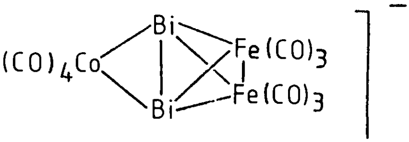

(17)

the anionic Fe_2Co complex $[Bi_2Fe_2Co(CO)_{10}]^-$, (17),[28] which also exhibits a relatively short Bi–Bi bond [3.092(2) Å].

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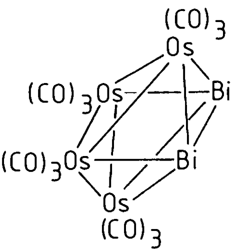
[28] (*a*) K. H. Whitmire, K. S. Raghuveer, M. R. Churchill, J. C. Fettinger, and R. F. See, *J. Am. Chem. Soc.*, 1986, **108**, 2778; (*b*) K. H. Whitmire, M. Shieh, C. B. Lagrone, B. H. Robinson, M. R. Churchill, J. C. Fettinger, and R. F. See, *Inorg. Chem.*, 1987, **26**, 2798.

[29] G. Huttner, U. Weber, and L. Zsolnai, *Z. Naturforsch., Teil B*, 1982, **37**, 707.

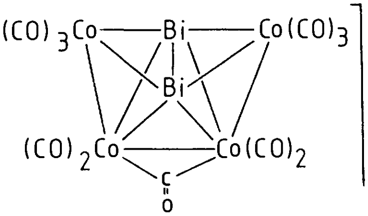
[30] G. Huttner, B. Sigwarth, O. Scheidsteger, L. Zsolnai, and O. Orama, *Organometallics*, 1985, **4**, 326.

[31] B. Sigwarth, L. Zsolnai, H. Berke, and G. Huttner, *J. Organomet. Chem.*, 1982, **226**, C5.



(18)

Additional examples of Bi_2 units coordinated within clusters have been reported recently. Johnson and Lewis and co-workers have described the tetra-osmium cluster $[Bi_2Os_4(CO)_{12}]$, (18),[25] [Bi–Bi = 3.017(2) Å] in which the Bi_2 group may be considered as a η^2-μ^4-bridging ligand within a Os_4 butterfly cluster. Alternatively, however, (18) may be compared with the tetraruthenium complex (15). Each structure represents a different valence isomer of a general *closo*-octahedral $Bi_2M_4(CO)_{12}$ cluster, the osmium system having a *cis* or 1,2-geometry, *vis à vis* the bismuth atoms, whilst the ruthenium complex adopts a *trans* or 1,6-geometry. It will be interesting to see whether both geometries can be obtained for a given metal system and thereby, perhaps, to establish whether the energies of the two isomers are comparable and what factors affect which structure is adopted.



(19)

Martinengo and Ciani[18] have also reported a Bi_2-containing cluster, namely the paramagnetic, anionic cobalt complex $[Bi_2Co_4(CO)_{11}]^-$, (19), [Bi–Bi = 3.088(1) Å].

A final example of a dibismuth complex is (20) in which the Bi_2 unit acts as a formal four-electron donor, transversely bridging a W–W bond.[32]

The Bi–Bi bond length [2.796(1) Å] is the shortest so far observed in a Bi_2 complex and may be taken to represent a considerable degree of multiple bond character still remaining in this bond. In addition to the W_2Bi_2 core, (20) also contains a μ_2-methylbismuthinidene (BiMe) bridging group, on the opposite side of the W–W vector to the Bi_2 ligand, which is further bonded to a $W(CO)_5$ fragment

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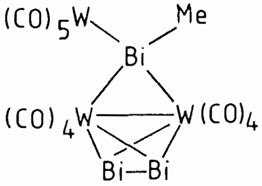
[32] (*a*) A. M. Arif, A. H. Cowley, N. C. Norman, and M. Pakulski, *J. Am. Chem. Soc.*, 1985, **107**, 1062; (*b*) A. M. Arif, A. H. Cowley, N. C. Norman, and M. Pakulski, *Inorg. Chem.*, 1986, **25**, 4836.

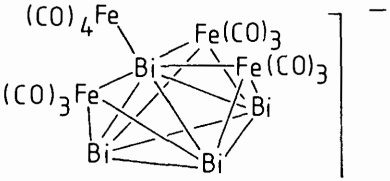


(20)

via the formal bismuthinidene lone pair. Compound (20) is derived from a reaction between $[W(CO)_5]^{2-}$ and $(Me_3Si)_2CHBiCl_2$ [which also affords the W_3Bi_2 complex, (16)], the latter reagent acting as a source of both BiMe and Bi_2 by what must remain a mechanistically obscure route.

C. Polybismuth Clusters

One such complex is worthy of mention under this heading, namely the tetra-iron–tetrabismuth cluster $[Bi_4Fe_4(CO)_{13}]^{2-}$, (21), synthesized by Whitmire *et al.*[33] This molecule consists of a central tetrahedral core of bismuth atoms, three faces of which are capped by $Fe(CO)_3$ fragments. The remaining iron atom, which carries four carbonyls, is bonded to the unique bismuth which lies on the approximate three-fold axis present in the compound. This cluster has been described as a Zintl ion–metal carbonyl hybrid.[33]



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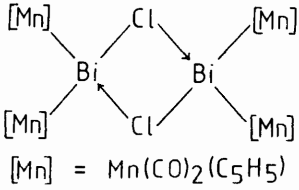
4 Cyclopentadienyl Transition Metal Carbonyl Complexes Incorporating Bismuth

Prior to our own work in the area of cyclopentadienyl transition metal–bismuth complexes, few examples of such species had been reported in the literature and most of those that had were either bismuthine or bismuthido complexes as described in Section 2. One such complex that had been described, however, was



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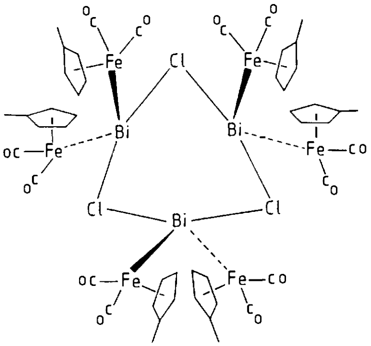
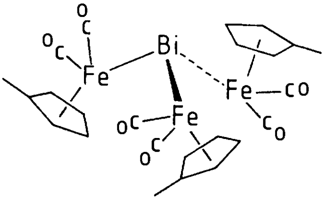
[33] (*a*) K. H. Whitmire, M. R. Churchill, and J. C. Fettinger, *J. Am. Chem. Soc.*, 1985, **107**, 1056; (*b*) K. H. Whitmire, T. A. Albright, S.-K. Kang, M. R. Churchill, and J. C. Fettinger, *Inorg. Chem.*, 1986, **25**, 2799.

the unusual chlorobismuthinidene dimer (22),[34] synthesized from $(C_5H_5)Mn(CO)_2(THF)$ and $BiCl_3$ and characterized by *X*-ray diffraction. The electronic structure of this molecule is interesting and probably involves some degree of multiple bonding between the manganese and bismuth centres, as is found in the lighter congeneric phosphinidene, arsinidene, and stibinidene compounds.[35] Moreover, such compounds are Lewis acidic at the main group element centre, and this general property coupled with the known propensity of bismuth to behave as a Lewis acid probably accounts for the chloro-bridged structure observed in the solid state.

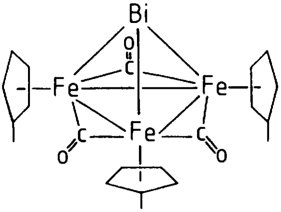


(23)

More recent work reported by ourselves[36] and Schmidbaur *et al.*[37] has described a series of cyclopentadienyl iron–bismuth complexes. The di-iron–bismuth chloro complexes $BiCl\{Fe(CO)_2(C_5H_4R)\}_2$ (R = H, Me), (23), exist in the solid state as a cyclotrimer as illustrated in the diagram and in Figure 1. This intermolecular association is further evidence of the Lewis acidity of bismuth(III),



(24)



(25)

such interaction occurring *via* bridging chlorines. In addition, the bismuth lone pairs remain stereochemically active leading to the observed geometry at each

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[34] J. von Seyerl and G. Huttner, *J. Organomet. Chem.*, 1980, **195**, 207.

[35] The type of compounds implied here are of the general formula $\{ML_n\}_2ER$, (E = P, As, Sb; ML_n is a 16-electron fragment such as $Cr(CO)_5$ or $Mn(CO)_2(C_5H_5)$. For reviews on this area of chemistry see: (*a*) G. Huttner, *Pure Appl. Chem.*, 1986, **58**, 585; (*b*) G. Huttner and K. Evertz, *Acc. Chem. Res.*, 1986, **19**, 406.

[36] (*a*) W. Clegg, N. A. Compton, R. J. Errington, and N. C. Norman, *Polyhedron*, 1987, **6**, 2031; (*b*) W. Clegg, N. A. Compton, R. J. Errington, and N. C. Norman, *J. Chem. Soc., Dalton Trans.*, 1988, 1671.

[37] J. M. Wallis, G. Müller, and H. Schmidbaur, *J. Organomet. Chem.*, 1987, **325**, 159.

bismuth, *i.e.* a distorted, equatorially vacant, trigonal bipyramid. This, in turn, results in fairly acute angles at the bridging chlorine atoms (av. = 85.1°) but it is the presence of the aforementioned lone pairs rather than any degree of Bi–Bi bonding that is considered responsible for this situation. The inter-bismuth separations (av. = 3.943 Å) are considered too long to imply any appreciable degree of Bi–Bi bonding.[36]

The related tri-iron complexes $[\mathrm{Bi}\{\mathrm{Fe(CO)_2(C_5H_4R)}\}_3]$ (R = H, Me), (24), have also been prepared [36,37] and structurally characterized by *X*-ray crystallography [36b] (Figure 2). They are further examples of trimetalla-bismuthine complexes, analogous to the tricobalt and trimanganese compounds (6) and (9) respectively, the coordination geometry around the bismuth being trigonal pyramidal as anticipated.

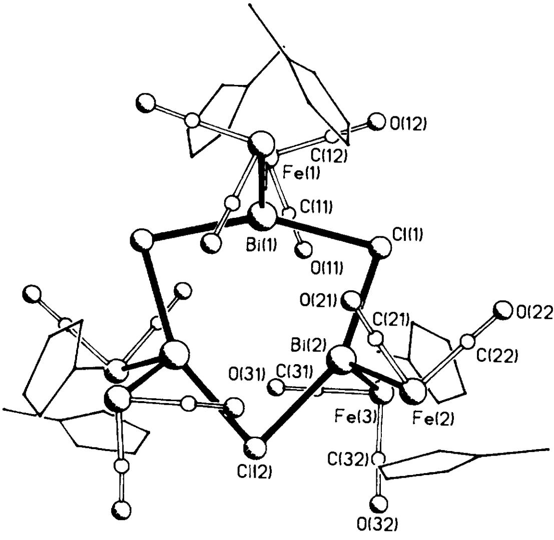


Figure 1 *A view of the molecular structure of* $[(\mathrm{BiCl}\{\mathrm{Fe(CO)_2(C_5H_4Me)}\}_2)_3]$, (23)

Moreover they can be induced to lose three carbonyl ligands by photolysis affording a *closo* tetrahedral tri-iron bismuth cluster (25) (Figure 3). This is analogous to the observed transformation of (6) into (7) observed by Whitmire *et al.*,[17] the two clusters being formally isoelectronic. Both also contain three bridging carbonyls and (25) is of further interest since it is another example of a tetrahedral cluster involving three first-row transition metals and a heavy main group element. This aspect has been discussed more fully with regard to (7) (see earlier) but it should also be noted that a number of the iron carbonyl clusters reported by Whitmire also contain $\mathrm{Fe_3Bi}$ tetrahedra.

Some related complexes have also been prepared by ourselves involving the

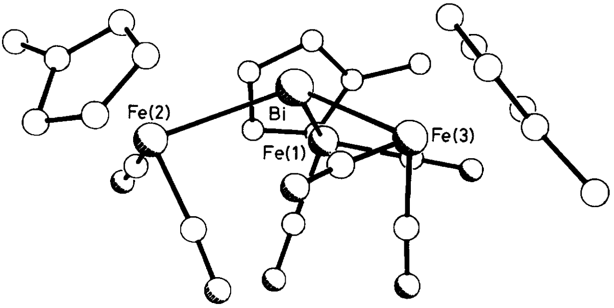


Figure 2 *A view of the molecular structure of* [Bi{Fe(CO)$_2$(C$_5$H$_4$Me)}$_3$], (24)

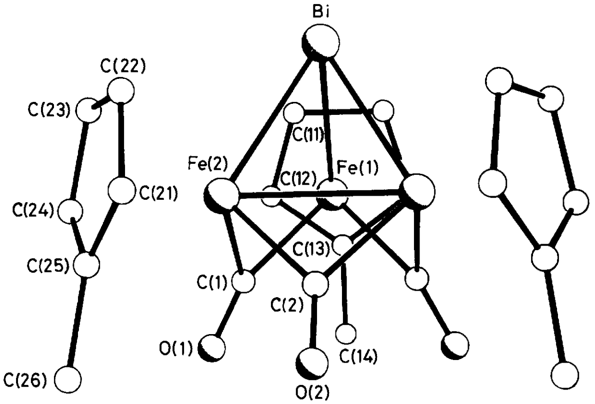
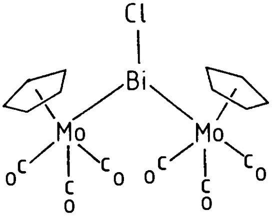
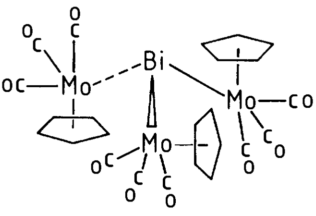


Figure 3 *A view of the molecular structure of* [BiFe$_3$(CO)$_3$(C$_5$H$_4$Me)$_3$], (25)



(26)



(27)

Group VI metals, molybdenum and tungsten.[38,39] The dimolybdenum complex [BiCl{Mo(CO)$_3$(C$_5$H$_5$)}$_2$], (26), has been characterized by *X*-ray crystallography (see Figure 4) and contains bismuth in a trigonal pyramidal coordination

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[38] W. Clegg, N. A. Compton, R. J. Errington, and N. C. Norman, *J. Organomet. Chem.*, 1987, **335**, C1.

[39] W. Clegg, N. A. Compton, R. J. Errington, N. C. Norman, and M. J. Winter, *J. Chem. Soc., Dalton Trans.*, in press.

geometry. In contrast to the di-iron bismuth chloro complex (23), which exists as a cyclotrimer in the solid state, (26) is essentially monomeric. There is, however, some degree of intermolecular association between the chlorine atom and an adjacent bismuth centre resulting in a weakly bonded chain polymeric structure in the solid state. The reasons for such a marked difference between the structures of (23) and (26) are not entirely clear. Steric factors might impose a weaker degree of association in the latter complex but of probably more importance is the greater electron releasing capability of the molybdenum centre which would render the bismuth less Lewis acidic.

The trimolybdenum complex $[Bi\{Mo(CO)_3(C_5H_5)\}_3]$, (27), has also been prepared and is assumed to have a structure similar to (24) as represented in the diagram. However this has not yet been confirmed by *X*-ray crystallography either for (27) or the related tungsten complex $[Bi\{W(CO)_3(C_5H_5)\}_3]$, (28).

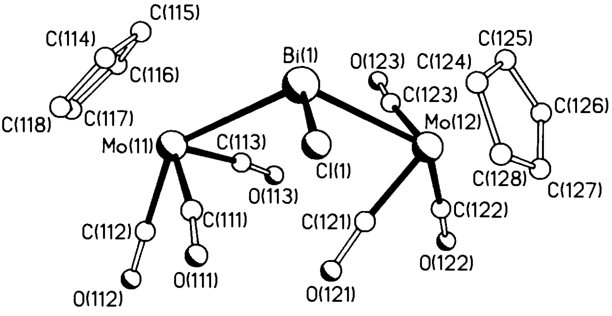


Figure 4 *A view of the molecular structure of* $[BiCl\{Mo(CO)_3(C_5H_5)\}_2]$, (26)

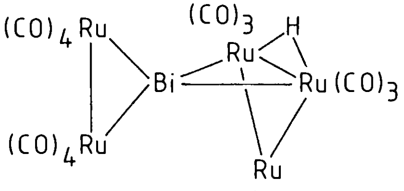
5 Conclusions

This review has concentrated on complexes which are known to contain transition metal–bismuth bonds and, as is evident from the references, this particular area of chemistry has developed only in the last few years, *i.e.* since the late 1970s. The purpose of this account is to illustrate the diversity of structural types that have already been observed including our own recent work in the area of cyclopentadienyl substituted complexes. Little attention has been given to the synthetic methods employed in preparing these compounds nor to examples of their reactivity although in the latter case, very few reports dealing with this aspect have appeared.

It is expected that the synthesis of new compounds in this area will continue apace and that detailed reactivity studies will follow. In this context, the study of transition metal–bismuth complexes fits well into the more general area of transition metal–main group metal chemistry which itself is continuing to attract much current attention.

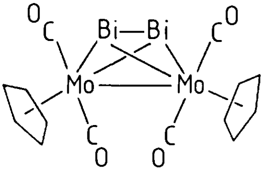
Acknowledgements. First I would like to thank the Society of Maccabaeans and the Royal Society of Chemistry for the award of the Meldola Medal. Thanks are also due to Neville A. Compton for carrying out much of the synthetic work described in Section 4, to W. Clegg for crystal structure determinations, and to R. J. Errington for his collaboration in this area. My thanks also go to Professors M. Green (King's College) and A. H. Cowley (Austin, Texas) for having provided stimulating research environments in which to work and learn. Financial support for our own work described herein has been received from the Research Corporation Trust, Nuffield Foundation, SERC, BP Research (Sunbury) and The University of Newcastle upon Tyne.

Note added in proof. The structure of the M_5Bi cluster, $[HBiRu_5(CO)_{18}]$, described in the text has now been determined (B. F. G. Johnson, J. Lewis, P. R. Raithby, and A. J. Whitton, *J. Chem. Soc., Chem. Commun.*, 1988, 401) and is represented diagramatically below (28). A full paper has also appeared recently with details of other ruthenium carbonyl–bismuth complexes mentioned in the text (C. M. Hay, B. F. G. Johnson, J. Lewis, P. R. Raithby, and A. J. Whitton, *J. Chem. Soc., Dalton Trans.*, 1988, 2091).



(28)

In addition, more recent work (W. Clegg, N. A. Compton, R. J. Errington, and N. C. Norman. *Polyhedron*, 1988, in press) has shown that photolysis of THF solutions of the trimolybdenum bismuth complex (27), affords the dimolybdenum dibismuth complex $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2(\mu_2\text{-}\eta^2\text{-}Bi_2)]$, (29), in which the dibismuth ligand functions as a four-electron donor. The methylcyclopentadienyl derivative has been characterized by *X*-ray crystallography.



(29)

Further studies on the anionic tetracobalt-bismuth complex $[Bi\{Co(CO)_4\}_4]^-$ have also been reported (J. S. Leigh and K. H. Whitmire, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 396, and S. Martinengo, A. Fumagalli, G. Ciani, and M. Moret, *J. Organomet. Chem.*, 1988, **347**, 413).