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Preliminary communication

## Alkyl and aryl dimetalla-bismuthine complexes

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### Abstract

The reaction between  $[\text{BiCl}\{\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)\}_2]$ , **5**, and one equivalent of  $\text{K}[\text{BHET}_3]$  affords, as one of the products, the bismuth ethyl complex  $[\text{BiEt}\{\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)\}_2]$ , **7**, which has been characterised by X-ray crystallography. Aspects of the possible mechanism of this reaction are discussed. The phenyl bismuthine complexes  $[\text{BiPh}\{\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)\}_2]$ , **8**, and  $[\text{BiPh}\{\text{Co}(\text{CO})_3(\text{PPh}_3)\}_2]$ , **9**, have also been synthesised from the reaction between  $\text{PhBiBr}_2$  and two equivalents of  $\text{Na}[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$  and  $\text{K}[\text{Co}(\text{CO})_3(\text{PPh}_3)]$  respectively.

As part of our interest in transition metal–bismuth complexes [1] we wish to report some preliminary results concerning the synthesis of alkyl and aryl dimetalla-bismuthine compounds. Few such compounds have been described in the literature, in contrast to the many examples known for the lighter Group 15 congeners, but two noteworthy reports have appeared. The first by Panster and Malisch [2a] described the synthesis of  $[\text{BiMe}\{\text{M}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)\}_2]$ , **1**, ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) as one of the products resulting from the reaction between  $\text{BiBrMe}_2$  and  $\text{Na}[\text{M}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$  whilst Schmidbaur et al. [3] have reported the synthesis of  $[\text{BiEt}\{\text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)\}_2]$ , **2**, from the reaction between  $[\text{BiX}\{\text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)\}_2]$  ( $\text{X} = \text{Cl}, \text{Br}$ ) and  $\text{AlEt}_3$ . The methyl analogue of **2**, viz  $[\text{BiMe}\{\text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)\}_2]$ , **2a**, has also been prepared by Malisch and coworkers [2b] by a method similar to that used in the synthesis of **1**.

None of the above compounds was characterised crystallographically but structural data are available for  $[\text{Fe}_2(\text{CO})_8(\mu\text{-BiMe})_2]$ , **3**, ( $\text{Bi-Me}$  2.28(1) Å) [4] and  $[\text{W}_2(\text{CO})_8(\mu\text{-}\eta^2\text{-Bi}_2)(\mu\text{-Bi}(\text{Me})\text{W}(\text{CO})_5)]$ , **4**, ( $\text{Bi-Me}$  2.339(1) Å) [5], both of which contain BiMe units bridging di-metal centres.

The reaction between the dimolybdenum-bismuth-chloro complex  $[\text{BiCl}\{\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)\}_2]$ , **5**, [6] and  $\text{K}[\text{BHET}_3]$  was examined as a possible synthetic route to bismuth hydride complexes. Treatment of **5** with one equivalent of  $\text{K}[\text{BHET}_3]$  in THF at  $-78^\circ\text{C}$  led to an immediate colour change from dark green to red-purple and then to red-brown. After warming to room temperature, filtration (Celite) and crystallisation from THF–hexane mixtures (solvent diffusion) at  $-30^\circ\text{C}$ , a dark red-brown powder was isolated which was shown by infrared spectroscopy to be the

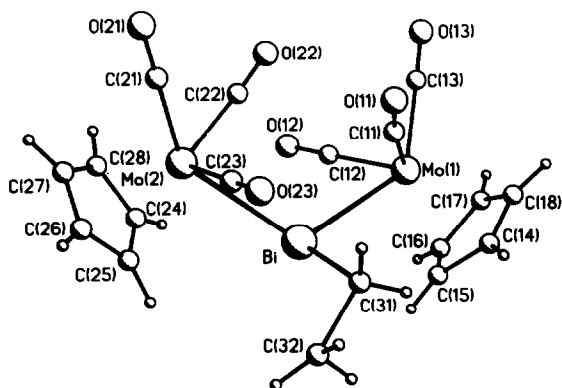


Fig. 1. A view of the molecular structure of **7** showing the atom numbering scheme adopted. Selected bond lengths (Å) and angles (degrees): Bi–Mo(1) 2.994(1), Bi–Mo(2) 2.996(1), Bi–C(31) 2.293(16), C(31)–C(32) 1.541(41) Mo(1)–Bi–Mo(2) 117.8(1), Mo(1)–Bi–C(31) 96.7(5), Mo(2)–Bi–C(31) 107.0(5), Bi–C(31)–C(32) 108.8(13).

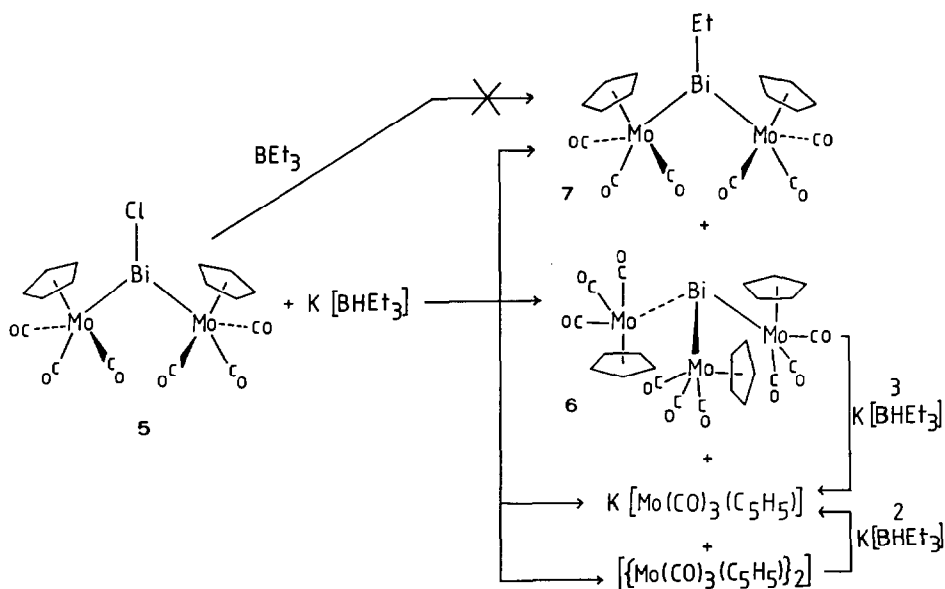
trimolybdenum–bismuth complex  $[\text{Bi}\{\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)\}_3]$ , **6**, [6] together with a small amount of  $[\text{Mo}_2(\text{CO})_6(\eta\text{-C}_5\text{H}_5)_2]$ . However, an infrared spectrum of the mother liquor showed signals attributable to  $\text{K}[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$  and a fourth complex, **7**. After reduction of the solvent volume and further cooling to  $-30^\circ\text{C}$ , a crop of well-formed dark red crystals was obtained which spectroscopic, analytical \* and X-ray crystallographic data \*\* showed to be the ethyl complex  $[\text{BiEt}\{\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)\}_2]$ , **7**, (10.5% yield). The results of the X-ray structure determination are shown in Fig. 1 and revealed a three-coordinate, trigonal pyramidal bismuth centre coordinated to two  $\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$  fragments and an ethyl group. The Bi–C bond length is 2.293(16) Å which is comparable with the values reported for **3** [4] and **4** [5] and also with the trialkyl bismuthine complex  $[\text{Bi}\{\text{CH}(\text{SiMe}_3)_2\}_3]$  (Bi–C 2.306(13), 2.331(14), 2.347(13) Å) described by Power and coworkers [7].

The four products of the above reaction are shown in Scheme 1, and we can partially account for their formation as follows. Previous studies on the reactivity of **5** [8] indicated that this complex readily undergoes a one-electron reduction and

\* Spectroscopic data for  $[\text{BiEt}\{\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)\}_2]$ , **7**: Infrared (THF solution)  $\nu(\text{CO})$  1995s, 1966s, 1910s, 1894s.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  5.36 (s, 5H,  $\text{C}_5\text{H}_5$ ), 3.82 (q, 2H,  $\text{CH}_2$ ,  $^3J(\text{HH}) = 7.8$  Hz), 2.01 (t, 3H,  $\text{CH}_3$ ,  $^3J(\text{HH}) = 7.8$  Hz). Elemental analysis,  $\text{C}_{18}\text{H}_{15}\text{O}_6\text{Mo}_2\text{Bi}$  requires C, 29.69; H, 2.08%. Found C, 30.06; H, 2.02%.

\*\* The atomic coordinates and a complete list of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK.

Crystal data for **7**:  $\text{C}_{18}\text{H}_{15}\text{O}_6\text{Mo}_2\text{Bi}$ ,  $M = 728.17$ , triclinic,  $P\bar{1}$ ,  $a = 8.079(3)$ ,  $b = 11.628(4)$ ,  $c = 12.387(4)$  Å,  $\alpha = 107.66(2)$ ,  $\beta = 98.05(2)$ ,  $\gamma = 105.12(2)^\circ$ ,  $V = 1007.4$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 2.400$  g cm<sup>-3</sup>,  $\lambda(\text{Mo-K}\alpha) = 0.71073$  Å,  $\mu = 9.91$  mm<sup>-1</sup>,  $F(000) = 676$ ,  $T = 295$  K. The structure was determined by Patterson and difference syntheses and refined [13] to a minimum of  $\sum w\Delta^2$  [ $\Delta = |F_o| - |F_c|$ ,  $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + 26 + 107G + 49G^2 - 73H + 49H^2 - 101GH$ ,  $G = F_o/F_{\text{max}}$ ,  $H = \sin \theta / \sin \theta_{\text{max}}$ ] [14] from 3017 reflections with  $2\theta < 50^\circ$  and  $F > 4\sigma_c(F)$  ( $\sigma_c$  from counting statistics only), measured on a Stoe-Siemens diffractometer with on-line profile fitting [15]. Anisotropic thermal parameters were refined for all non-hydrogen atoms. H atoms were constrained. Final  $R = 0.052$ ,  $R_w = (\sum w\Delta^2 / \sum wF_o^2)^{1/2} = 0.065$ ,  $S = 1.06$  for 247 parameters.



Scheme 1

subsequently rearranges to **6**, as the only product containing bismuth and molybdenum, and small amounts of  $[\text{Mo}_2(\text{CO})_6(\eta\text{-C}_5\text{H}_5)_2]$ . The formation of these two products can therefore be rationalised on the basis of  $\text{K}[\text{BHEt}_3]$  acting as a one electron reducing agent. Furthermore, the formation of  $\text{K}[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$  probably arises by reduction of initially formed  $[\text{Mo}_2(\text{CO})_6(\eta\text{-C}_5\text{H}_5)_2]$  and **6** by  $\text{K}[\text{BHEt}_3]$ . The former reaction has been described by Gladysz et al. [9], and we were able to demonstrate in a separate experiment that **6** is reduced to  $\text{K}[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$  quantitatively by reaction with three equivalents of  $\text{K}[\text{BHEt}_3]$  in THF.

Our original thoughts on the formation of **7** were that the  $\text{BEt}_3$  formed on oxidation of  $[\text{BHEt}_3]^-$  reacted with **5** to give **7**. However, in a subsequent experiment we discovered that **5** is completely unreactive to  $\text{BEt}_3$  even when the latter reagent is present in large excess. Thus, the ethyl complex, **7**, is apparently formed by direct ethyl transfer from  $[\text{BHEt}_3]^-$ , a reaction which is unusual for this reagent as discussed in a recent report by Gysling and Luss [10]. Further studies on this and related reactions are in progress.

We were also interested in making aryl derivatives of **5**, and our first attempt involved the reaction between **5** and  $[\text{PhLi}]$ . The major product from this reaction was **6** although small amounts of as yet unidentified materials were also formed. The formation of **6** when attempting direct substitution of the chloride functionality in **5** is something we have frequently observed [8] but the target phenyl complex,  $[\text{BiPh}\{\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)\}_2]$ , **8**, was prepared, with typical yields of 80%, from the reaction between  $\text{PhBiBr}_2$  [11] and two equivalents of  $\text{Na}[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$ . Addition of the molybdenum carbonylate anion to a solution of  $\text{PhBiBr}_2$  in THF at  $0^\circ\text{C}$  led initially to a dark green colour which changed to deep red after complete addition of the reactants. Filtration (Celite) followed by crystallisation by solvent diffusion from THF-hexane mixtures at  $-30^\circ\text{C}$  afforded dark red crystals of **8**,

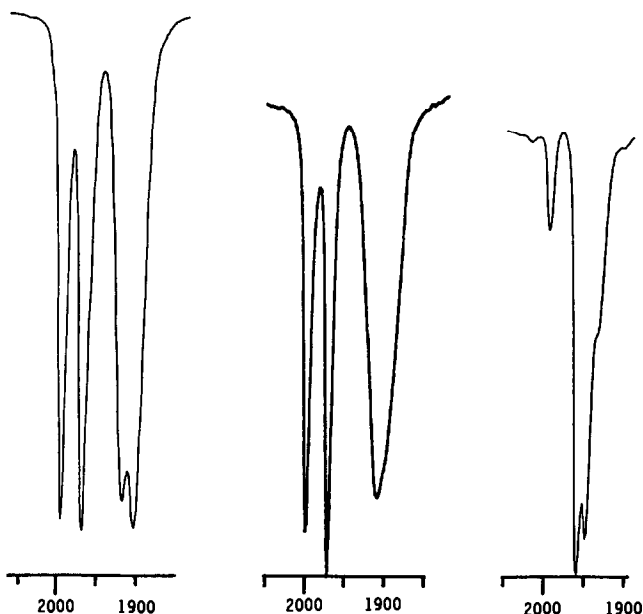
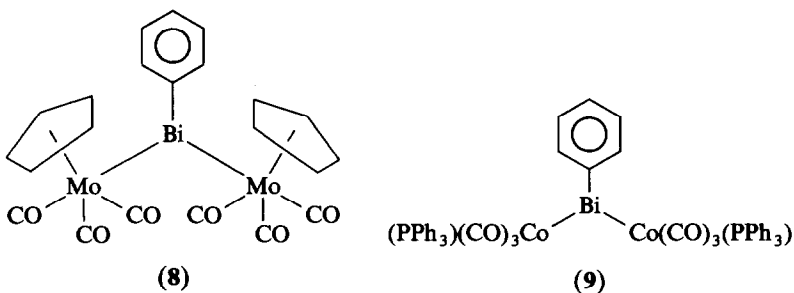


Fig. 2. Solution infrared spectra in THF solution in the carbonyl stretching region. (a), 7; (b), 8; (c), 9.

and although these were not suitable for X-ray diffraction studies, spectroscopic (Fig. 2) and analytical data \* were consistent with the anticipated formula.



We have also synthesised the dicobalt complex  $[\text{BiPh}\{\text{Co}(\text{CO})_3(\text{PPh}_3)\}_2]$ , **9**, from the analogous reaction between  $\text{PhBiBr}_2$  and two equivalents of  $\text{K}[\text{Co}(\text{CO})_3(\text{PPh}_3)]$ , [12] which has been characterised by spectroscopic and analytical methods \*, in 80% yield. We are currently exploring a range of similar reactions with other metal

\* Spectroscopic data for  $[\text{BiPh}\{\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)\}_2]$ , **8**: Infrared (THF solution)  $\nu(\text{CO})$  2000s, 1972s, 1910s, br.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  5.28 (s, 5H,  $\text{C}_5\text{H}_5$ ), 7.25 (m, 3H, Ph), 7.73 (m, 2H, Ph);  $^{13}\text{C}$ - $\{^1\text{H}\}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  92.0 (s,  $\text{C}_5\text{H}_5$ ), 127.3 (s,  $p\text{-C}_6\text{H}_5$ ), 130.0 and 140.8 (s,  $o$  and  $m\text{-C}_6\text{H}_5$ ). Elemental analysis,  $\text{C}_{22}\text{H}_{15}\text{O}_6\text{Mo}_2\text{Bi}$  requires C, 34.04; H, 1.95%. Found C, 33.83; H, 1.92%.

Spectroscopic data for  $[\text{BiPh}\{\text{Co}(\text{CO})_3(\text{PPh}_3)\}_2]$ , **9**: Infrared (THF solution)  $\nu(\text{CO})$  1998m, 1961s, 1950s.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.44 (br, s, Ph);  $^{13}\text{C}$ - $\{^1\text{H}\}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  200.0 (CO), 140.4 (s, *ipso*- $\text{PPh}_3$ ), 133.7 (d, *o*- $\text{PPh}_3$ ,  $^2J(\text{PC})=11.6$  Hz), 130.9 (s, *p*- $\text{PPh}_3$ ), 128.9 (d, *m*- $\text{PPh}_3$ ,  $^3J(\text{PC})=10.1$  Hz), 135.3, 134.4, 126.8 (BiPh);  $^{31}\text{P}$ - $\{^1\text{H}\}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  65.7 [ref. 85%  $\text{H}_3\text{PO}_4(\text{ext})$ ]. Elemental analysis,  $\text{C}_{48}\text{H}_{35}\text{O}_6\text{Co}_2\text{P}_2\text{Bi}$  requires C, 52.57; H, 3.22%. Found C, 52.70; H, 3.39%.

fragments, such high yield routes to phenyl-dimetalla-bismuthine complexes will be important in developing the chemistry of dimetalla-bismuth fragments.

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