

### Preliminary communication

---

## The synthesis of some organo-molybdenum and -tungsten complexes containing bismuth

William Clegg, Neville A. Compton, R. John Errington and Nicholas C. Norman

*Department of Inorganic Chemistry, The University, Newcastle upon Tyne, NE1 7RU (Great Britain)*

(Received August 19th, 1987)

### Abstract

The reaction of  $\text{BiCl}_3$  with three equivalents of  $\text{Na}[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$  affords the trimolybdenum complex,  $[\text{Bi}\{\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)\}_3]$  (1). If only two equivalents of the molybdenum carbonylate anion are used the dimolybdenum compound,  $[\{\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)\}_2\text{BiCl}]$  (2) is obtained. A derivative of 2, namely  $[\{\text{Mo}(\text{CO})_2(\text{CN}^t\text{Bu})(\eta\text{-C}_5\text{H}_5)\}_2\text{BiCl}]$  (4) has also been synthesised and characterised by X-ray diffraction. Analogous chemistry involving the tungsten complex  $\text{Na}[\text{W}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$  affords  $[\{\text{W}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)\}_2\text{BiCl}]$  (5) as the only tungsten-bismuth containing product.

---

Compounds containing bismuth and molybdenum are of considerable interest, particularly from an industrial standpoint; for example the SOHIO alkene oxidation and ammoxidation processes involve bismuth molybdate [1,2]. Although the mechanism of this catalytic process is fairly well understood [2], in general the chemistry of bismuth-molybdenum compounds has received little attention. This is particularly the case for complexes containing organomolybdenum fragments, there being only one previous report of which we are aware, which describes the reaction of  $\text{Na}[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$  with  $\text{Me}_2\text{BiBr}$  [3]. The analogous tungsten chemistry is only slightly better developed. In addition to an analogous reaction between  $\text{Na}[\text{W}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$  and  $\text{Me}_2\text{BiBr}$  [3], two other complexes are also known, these being  $[\{\text{W}(\text{CO})_5\}_3(\mu_3\text{-}\eta^2\text{-Bi}_2)]$  [4,5] and  $[\text{W}_2(\text{CO})_8(\mu\text{-}\eta^2\text{-Bi}_2)(\mu\text{-BiMeW}(\text{CO})_5)]$  [5]. As part of a study of organo-transition metal-bismuth complexes we have investigated the reactions of  $\text{Na}[\text{M}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$  ( $\text{M} = \text{Mo}, \text{W}$ ) with  $\text{BiCl}_3$ , and preliminary results are reported herein.

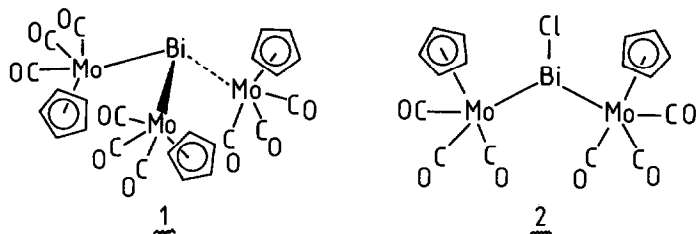
Addition of a THF solution of  $\text{BiCl}_3$  to a THF solution containing three equivalents of  $\text{Na}[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$  initially gives a dark green solution which rapidly becomes deep red. Purification of the resulting mixture (column chromatography on Florisil, THF eluant) affords a deep red solution, from which a red powder may be obtained (THF/hexane,  $-20^\circ\text{C}$ ). This was identified by  $^1\text{H}$  and

Table 1  
Analytical and Spectroscopic Data for the Complexes.

Compound	Colour	IR, $\nu(\text{CO})/\text{cm}^{-1}$ <sup>a</sup>	NMR <sup>b</sup>		Analysis (Found (calcd.)(%))	
			<sup>1</sup> H( $\delta$ ) <sup>c</sup>	<sup>13</sup> C( $\delta$ ) <sup>c,d</sup>	C	H
1	Red	2004m,1966s,1896m	5.52(C <sub>5</sub> H <sub>5</sub> )	93.0(C <sub>5</sub> H <sub>5</sub> )	30.8 (30.5)	1.7 (1.6)
2	Green	2051w,2010s,1978s,1912s	5.57(C <sub>5</sub> H <sub>5</sub> )	94.0(C <sub>5</sub> H <sub>5</sub> )	26.3 (26.2)	1.4 (1.4) <sup>e</sup>
4	Green	1983w,1942s,1921m,1877s <sup>f</sup>	5.37(C <sub>5</sub> H <sub>5</sub> ) <sup>g</sup> 5.36(C <sub>5</sub> H <sub>5</sub> ) 1.28(t-Bu) 1.27(t-Bu)	-	33.6 (34.1)	3.2 (3.3) <sup>h</sup>
5	Purple	2045w,2006s,1973s,1899s	4.99(C <sub>5</sub> H <sub>5</sub> ) <sup>g</sup>	92.1(C <sub>5</sub> H <sub>5</sub> ) <sup>g</sup>	20.9 (21.1)	1.1 (1.1)

<sup>a</sup> Measured in THF solution unless otherwise stated. <sup>b</sup> Chemical shifts ( $\delta$ ) in ppm, measurements at room temperature. <sup>c</sup> Measured in THF-*d*<sub>8</sub> unless otherwise stated. <sup>d</sup> <sup>1</sup>H decoupled, chemical shifts are positive to high frequency SiMe<sub>4</sub>. <sup>e</sup> Chlorine analysis, 5.0(4.8). <sup>f</sup>  $\nu(\text{CN})$  for the CN<sup>t</sup>Bu ligands: 2114 cm<sup>-1</sup> (broad with shoulder at ~ 21 cm<sup>-1</sup>). <sup>g</sup> Measured in C<sub>6</sub>D<sub>6</sub>. <sup>h</sup> Nitrogen analysis, 3.2(3.3).

<sup>13</sup>C NMR and IR spectroscopy and elemental analysis (Table 1) as the trimolybdenum bismuth complex, **1**. The observation of an initial green colour in the



synthesis of **1** suggested the possibility of an intermediate. This was confirmed in a separate reaction in which two equivalents of Na[Mo(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] were added to a solution of BiCl<sub>3</sub>. An immediate green colour developed and persisted throughout the addition of the molybdenum carbonylate anion. Filtration (Celite, THF) followed by crystallisation (CH<sub>2</sub>Cl<sub>2</sub>/hexane) afforded dark green crystals of **2**, identified as the dimolybdenum bismuth chloride by analytical and spectroscopic methods (Table 1). Not only is **2** an intermediate in the synthesis of **1**, but if an excess of BiCl<sub>3</sub> is added to a solution of **1**, immediate formation of **2** occurs, an indication of facile exchange processes. Similar types of exchange reactions have been observed by Malisch [3] in the reaction of Na[Mo(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] with Me<sub>2</sub>BiBr, one of the products of this reaction being the bromo analogue of **2**, [(Mo(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>))<sub>2</sub>BiBr] (**3**). The reported IR spectrum of **3** is essentially identical to that obtained for **2** (Table 1), but neither this nor the analytical data gave any indication as to whether these complexes are monomeric or oligomeric in the solid state. This question was of interest, since in the analogous iron system, [(Fe(CO)<sub>2</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>))<sub>2</sub>BiCl]<sub>3</sub> [6,7], cyclotrimerisation via Bi-Cl bridges occurs due to the Lewis acidity of bismuth. No structure of **3** was reported, and crystals of **2** proved unsuitable for X-ray diffraction. However, suitable single crystals of a related compound, **4**, were obtained, and a structure determination by X-ray diffraction was carried out (Fig. 1). Compound **4**

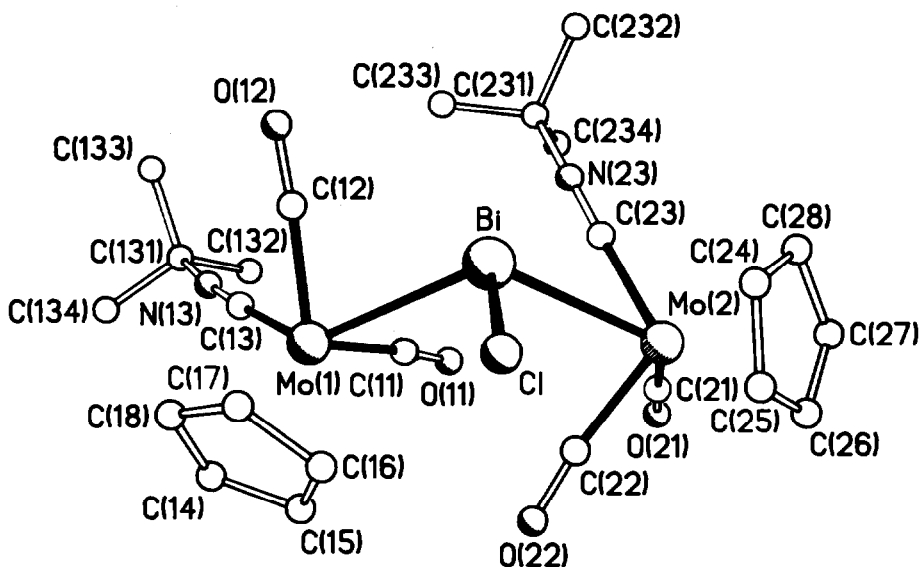
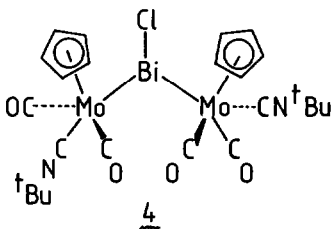


Fig. 1. The molecular structure of **4** with H atoms omitted. Selected bond lengths (Å) and angles (degrees): Bi–Mo(1) 2.978(1), Bi–Mo(2), 2.931(1), Bi–Cl 2.610(2), Mo(1)–C(11) 1.975(4), Mo(1)–C(12) 1.956(5), Mo(1)–C(13) 2.064(5), Mo(2)–C(21) 1.961(6), Mo(2)–C(22) 1.967(7), Mo(2)–C(23) 2.065(5); Mo(1)–Bi–Mo(2) 114.8(1), Mo(1)–Bi–Cl 102.3(1), Mo(2)–Bi–Cl 98.8(1), Bi–Mo(1)–C(11) 75.9(2), Bi–Mo(1)–C(12) 70.8(2), Bi–Mo(1)–C(13) 132.4(2), C(11)–Mo(1)–C(12) 105.3(2), C(11)–Mo(1)–C(13) 77.7(2), C(12)–Mo(1)–C(13) 79.1(2), Bi–Mo(2)–C(21) 123.5(2), Bi–Mo(2)–C(22) 74.8(1), Bi–Mo(2)–C(23) 67.4(1), C(21)–Mo(2)–C(22) 78.6(3), C(21)–Mo(2)–C(23) 78.4(3), C(22)–Mo(2)–C(23) 112.0(2).

was synthesised in an exactly analogous manner to **2** by using the molybdenum complex,  $\text{Na}[\text{Mo}(\text{CO})_2(\text{CN}^t\text{Bu})(\eta\text{-C}_5\text{H}_5)]$  prepared by sodium amalgam reduction of the corresponding dimer  $[\text{Mo}_2(\text{CO})_4(\text{CN}^t\text{Bu})_2(\eta\text{-C}_5\text{H}_5)_2]$ .

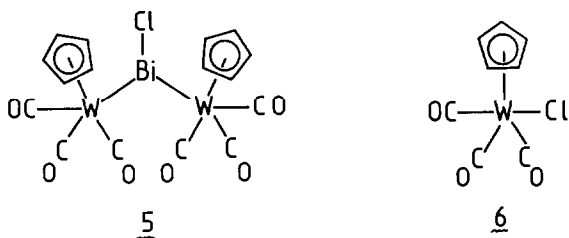


*Crystal data for 4*:  $\text{C}_{24}\text{H}_{28}\text{BiClMo}_2\text{N}_2\text{O}_4$ ,  $M = 844.8$ , monoclinic, space group  $Cc$ ,  $a$  21.256(2),  $b$  11.539(1),  $c$  13.589(1) Å,  $\beta$  117.810(6)°,  $U$  2948.1 Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.903$  g cm<sup>-3</sup>. Intensities of 10428 reflections (a whole sphere of data with  $2\theta_{\text{max}} 50^\circ$ ) were measured on a Siemens AED2 diffractometer with graphite monochromated Mo- $K_\alpha$  radiation ( $\lambda$  0.71073 Å) and on-line profile fitting [8], and corrected semi-empirically for absorption ( $\mu$  6.88 mm<sup>-1</sup>). 5083 independent reflections with  $|F| > 4\sigma(F)$  ( $R_{\text{int}} = 0.015$ ) were used in the structure analysis by Patterson methods and blocked-cascade least-squares refinement on  $F$ ; H atoms were included in calculated positions, and anisotropic thermal parameters were assigned to other atoms. The final  $R$  is 0.0171 ( $R_w = 0.0201$ ). The absolute structure

was determined by refinement of  $\eta = 1.05(1)$  [9]. Selected bond lengths and angles are given in Fig. 1\*.

The structure reveals a monomeric system and this contrasts with the result for the previously mentioned iron complex. The bismuth is bonded to a single chlorine (Bi(1)–Cl(1) 2.610 Å) and two molybdenum atoms (av. Bi–Mo 2.955 Å), these values being consistent with single bonding. In the case of the Bi–Mo bond lengths, this assumption is based on the sum of the covalent radii (2.8 Å) since **4** is the first structurally characterised example of a complex containing a Bi–Mo bond. The coordination geometry around the bismuth is trigonal pyramidal (slightly distorted, sum of angles 315.9°) consistent with the expected presence of a stereochemically active lone pair. In addition to bismuth, each molybdenum is also bonded to one cyclopentadienyl, one *t*-butylisocyanide and two carbonyl ligands, the overall ligand geometry being of the familiar CpML<sub>4</sub> “piano stool” type. Of interest, however, is the stereochemistry at each molybdenum centre. This is arranged such that on one molybdenum the isocyanide is *cis* to the bismuth while on the other it is *trans*. Why this should be so remains unclear, but examination of the <sup>1</sup>H NMR spectrum (Table 1) suggests that this structure is maintained in solution since separate resonances are observed for the C<sub>5</sub>H<sub>5</sub> and CN<sup>*t*</sup>Bu ligands on each molybdenum centre.

The corresponding reactions with tungsten proceed slightly differently. Thus in the reaction between BiCl<sub>3</sub> and two or three equivalents of Na[W(CO)<sub>3</sub>(η-C<sub>5</sub>H<sub>5</sub>)] only the ditungsten-bismuth complex (**5**) is formed. There is no evidence for the



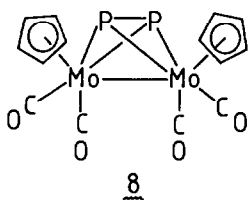
formation of a tritungsten complex analogous to **1** even when a large excess of the tungsten carbonylate anion is present. Compound **5** was identified by the usual methods (Table 1), particularly IR spectroscopy, which revealed a pattern in the carbonyl region almost identical to that for **2**.

The formation of **5** is accompanied by that of small quantities of [WCl(CO)<sub>3</sub>(η-C<sub>5</sub>H<sub>5</sub>)] (**6**) [10], which suggests that for tungsten, unlike molybdenum, electron transfer processes occur in solution in competition with the desired nucleophilic substitution.

Finally we note that the EI mass spectra of both **1** and **2** are identical, and indicate that the species in the gas phase is [Mo<sub>2</sub>Bi<sub>2</sub>(CO)<sub>4</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] (**7**) as confirmed by high resolution mass measurement studies. This suggests that **7** may be isolable, and this possibility is being investigated. A compound such as **7** would

\* The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

be interesting since it is a bismuth analogue of the known diphosphorus species **8** [11]. Mass spectra of the tungsten complex **5** give similar results.



### Acknowledgments

We thank the SERC for financial support and BP Research (Sunbury) for a CASE award (NAC). NCN also thanks the Research Corporation Trust and Nuffield Foundation for additional supporting funds. We are grateful to Dr. M.J. Winter for supplying a sample of  $[\text{Mo}_2(\text{CO})_4(\text{CN}^t\text{Bu})_2(\eta\text{-C}_5\text{H}_5)_2]$ .

### References

- 1 R.K. Grasselli, and J.D. Burrington, *Adv. Catal.*, 30 (1981) 133.
- 2 R.K. Grasselli, *J. Chem. Ed.*, 63 (1986) 216.
- 3 P. Panster, and W. Malisch, *J. Organomet. Chem.*, 134 (1977) C32.
- 4 G. Huttner, U. Weber, and L. Zsolnai, *Z. Naturforsch.*, 37b (1982) 707.
- 5 A.M. Arif, A.H. Cowley, N.C. Norman, and M. Pakulski, *J. Am. Chem. Soc.*, 107 (1985) 1062; A.M. Arif, A.H. Cowley, N.C. Norman, and M. Pakulski, *Inorg. Chem.*, 25 (1986) 4836.
- 6 W. Clegg, N.A. Compton, R.J. Errington, and N.C. Norman, *Polyhedron*, 6 (1987) in press; W. Clegg, N.A. Compton, R.J. Errington, and N.C. Norman, *J. Chem. Soc., Dalton Trans.*, submitted for publication.
- 7 J.M. Wallis, G. Müller, and H. Schmidbaur, *J. Organomet. Chem.*, 325 (1987) 159.
- 8 W. Clegg, *Acta. Crystallogr. A*, 37 (1981) 22.
- 9 D. Rogers, *Acta. Crystallogr. A*, 37 (1981) 734.
- 10 C.E. Coffey, *J. Inorg. Nucl. Chem.*, 25 (1963) 179.
- 11 O.J. Scherer, H. Sitzmann, and G. Wolmershäuser, *J. Organomet. Chem.*, 268 (1984) C9.