Synthetic and Structural Studies on Organotransition Metal–Bismuth Nitrates†

R. John Errington,[a] **Louis J. Farrugia,**[b] **George A. Fisher,**[a] **Anja Niklaus**[a] **and Nicholas C. Norman**[*,a]

[a] *Department of Chemistry, The University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, UK*
[b] *Department of Chemistry, The University, Glasgow G12 8QQ, UK*

The reaction between $Bi(NO_3)_3{\cdot}5H_2O$ and 2 equivalents of $K[Fe(CO)_2(\eta\text{-}C_5H_5)]$ affords the iron–bismuth complex $[Bi(NO_3)\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ **1** which was characterised by X-ray crystallography. Complex **1** comprises a bismuth atom in a trigonal-pyramidal co-ordination geometry bonded to two $Fe(CO)_2(\eta\text{-}C_5H_5)$ fragments and the oxygen atom of a monodentate nitrate group. In addition there is a longer secondary intermolecular contact between the bismuth and a nitrate oxygen of an adjacent molecule which is approximately *trans* to the primary Bi–O bond. The complexes $[Bi(NO_3)(ML_n)_2]$ [ML_n = $Fe(CO)_2(\eta\text{-}C_5H_4Me)$ **2**, $Ru(CO)_2(\eta\text{-}C_5H_5)$ **3**, $Mo(CO)_3(\eta\text{-}C_5H_5)$ **6**, $Mo(CO)_3(\eta\text{-}C_5H_4Me)$ **7**, $W(CO)_3(\eta\text{-}C_5H_5)$ **8**, $W(CO)_3(\eta\text{-}C_5H_4Me)$ **9** or $Cr(CO)_3(\eta\text{-}C_5H_5)$ **10**] have also been prepared and characterised by spectroscopic and analytical methods. Data are also presented on the synthesis and characterisation of the ruthenium complexes $[Bi\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_3]$ **4** and $[BiCl\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2]$ **5** and on the reactions between bismuth nitrate and 2 equivalents of $K[Mn(CO)_5]$ or $K[Co(CO)_3(PR_3)]$ (R = Ph or OPh).

We have previously described the preparation and characterisation of a range of bismuth(III) compounds of the general formula $[BiX(ML_n)_2]$ where X is chloride, bromide or iodide, and ML_n represents a 17-electron organotransition-metal fragment.[1–6] Complexes in which X is an alkyl or aryl function have also been reported.[7] We were interested in extending this range of compounds to other X groups in order to explore the structural consequences of this change and to obtain compounds which were more useful for further reactivity studies. Herein we describe the synthesis and spectroscopic characterisation of a series of organotransition-metal bismuth nitrate species, $[Bi(NO_3)(ML_n)_2]$, together with the crystal structure of one example, which exhibits the same type of intermolecular interactions which are so prevalent in the structures of the halide analogues.

Results and Discussion

The reaction between a suspension of bismuth trinitrate pentahydrate, $Bi(NO_3)_3{\cdot}5H_2O$, hereafter, simply bismuth nitrate, in thf (tetrahydrofuran) with 2 equivalents of $K[Fe(CO)_2(\eta\text{-}C_5H_5)]$ afforded a deep emerald-green solution from which dark green crystals of the complex $[Bi(NO_3)\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ **1** were isolated after work-up. An infrared spectrum in thf solution [Fig. 1(*a*), Table 1] and analytical data (Table 1) were consistent with the proposed and expected formula and this was confirmed by a single-crystal X-ray diffraction study. The results of the crystal structure analysis are shown in Figs. 2 and 3 with selected bond lengths and angles in Table 2 and atomic positional parameters in Table 3. The bismuth centre is bonded to two $Fe(CO)_2(\eta\text{-}C_5H_5)$ fragments with Bi–Fe bonds [both 2.634(2) Å] comparable to, although slightly shorter than, those found in the related complexes $[BiCl\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$,[8] $[BiCl\{Fe(CO)_2(\eta\text{-}C_5H_4Me)\}_2]$[1] and $[N(PPh_3)_2][BiCl_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$[9] (see also ref. 10 for a listing of Bi–Fe bond lengths in general); the Fe–Bi–Fe angle [111.8(1)°] is also similar to the corresponding angles in these three structures. In addition, the bismuth is bonded to a single nitrate ligand with a relatively short Bi–O distance, Bi–O(1), of 2.438(8) Å which is intermediate between those observed in bismuth alkoxides, typically about 2.05–2.10 Å, and those associated with co-ordinate Bi–O bonds (such as thf) which range from about 2.6 to 3.0 Å.[11] The Bi–O(3) distance of 3.088(9) Å is only slightly outside this latter range which implies that a description of the binding of the nitrate ligand as monodentate or highly asymmetrically bidentate is largely a matter of preference but we note that the N–O (Table 2) distances are more in accord with the former. Of more interest, however, is the presence of a secondary, intermolecular interaction [Bi–O(2′) 2.932(8) Å] between the bismuth centre and a nitrate oxygen atom of an adjacent, and symmetry-related, molecule as shown in Fig. 3. The length of this interaction is certainly within the range for co-ordinate Bi–O bonds mentioned above, and the approximately *trans* disposition of the two oxygens [O(1)–Bi–O(2′) 159.4(2)°] is also noteworthy. Exactly similar intermolecular interactions have been noted[1,2,4,5] for the related halide complexes, $[BiX(ML_n)_2]$, and the factors affecting both bond distances and angles have been discussed in detail elsewhere.[5,9,11]

Other bismuth nitrate structures of interest are $[Bi(NO_3)\{SC(NH_2)_2\}_5]^{2+}$,[12] $[Bi(NO_3)_3\{SC(NH_2)_2\}_3]$,[12] $[Bi_6(H_2O)(NO_3)O_4(OH)_4]^{5+}$,[13] $Cs_2[Bi(NO_3)_5(H_2O)]$[14] and $Bi(NO_3)_3(H_2O)_5$ itself,[15] in which the nitrate co-ordination varies from monodentate through asymmetrically bidentate to symmetrically bidentate, and the Bi–O bond distances range from about 2.35 to 2.95 Å, the latter depending both on the denticity of the ligand and the co-ordination number and geometry around the bismuth centre.

The complex $[Bi(NO_3)\{Fe(CO)_2(\eta\text{-}C_5H_4Me)\}_2]$ **2** was prepared similarly as was the ruthenium analogue $[Bi(NO_3)\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2]$ **3** [see Fig. 1(*b*)] and, although we were not able to obtain satisfactory analytical data on these two complexes, the latter indicated that bismuth nitrate might be a useful starting material with which to synthesise additional bismuth–ruthenium compounds. We had previously found that reactions between $BiCl_3$ or $BiBr_3$ and 2 or 3 equivalents of $K[Ru(CO)_2(\eta\text{-}C_5H_5)]$ failed to afford any isolable products containing both bismuth and ruthenium; rather, the only identifiable product, by infrared spectroscopy, was $[Ru_2(CO)_4$-

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Spectroscopic and analytical data for the complexes

Compound	$\nu(CO)^a/cm^{-1}$	Analysis^b (%) C	H	N
1 $[Bi(NO_3)\{Fe(CO)_2(\eta-C_5H_5)\}_2]$	2016s, 1979s, 1956m	26.60 (26.90)	1.40 (1.60)	2.25 (2.25)
2 $[Bi(NO_3)\{Fe(CO)_2(\eta-C_5H_4Me)\}_2]$	2012s, 1977s, 1952m			
3 $[Bi(NO_3)\{Ru(CO)_2(\eta-C_5H_5)\}_2]$	2053m, 2033s, 1993s			
4 $[Bi\{Ru(CO)_2(\eta-C_5H_5)\}_3]$	2018s, 1981m, 1937s	29.40 (28.80)	1.55 (1.70)	
5 $[BiCl\{Ru(CO)_2(\eta-C_5H_5)\}_2]$	2024s, 1993m, 1966s	24.15 (24.40)	1.60 (1.45)	
6 $[Bi(NO_3)\{Mo(CO)_3(\eta-C_5H_5)\}_2]$	2015s, 1979m, 1924s	28.40 (28.85)	1.95 (2.20)	1.50 (1.70)^c
7 $[Bi(NO_3)\{Mo(CO)_3(\eta-C_5H_4Me)\}_2]$	2012s, 1977m, 1921s	28.35 (27.40)	2.05 (1.80)	1.60 (1.75)
8 $[Bi(NO_3)\{W(CO)_3(\eta-C_5H_5)\}_2]$	2010s, 1975m, 1917s	23.30 (23.80)	1.50 (1.80)	1.25 (1.40)^c
9 $[Bi(NO_3)\{W(CO)_3(\eta-C_5H_4Me)\}_2]$	2008s, 1973m, 1916s	21.30 (22.40)	1.55 (1.45)	1.25 (1.45)
10 $[Bi(NO_3)\{Cr(CO)_3(\eta-C_5H_5)\}_2]$	1999s, 1966s, 1900s	28.65 (28.50)	1.85 (1.50)	1.95 (2.10)
12 $[Bi\{Co(CO)_3\{P(OPh)_3\}\}_3]$	2015m, 1983s, 1972s	47.80 (48.25)	3.25 (2.90)	
14 $[Bi(NO_3)\{Mn(CO)_5\}_2]$	2105w, 2078m, 2066m, 2012s, 1948w			

^{a} Measured in thf solution. ^{b} Calculated values in parentheses. ^{c} Calculated values include a molecule of thf.

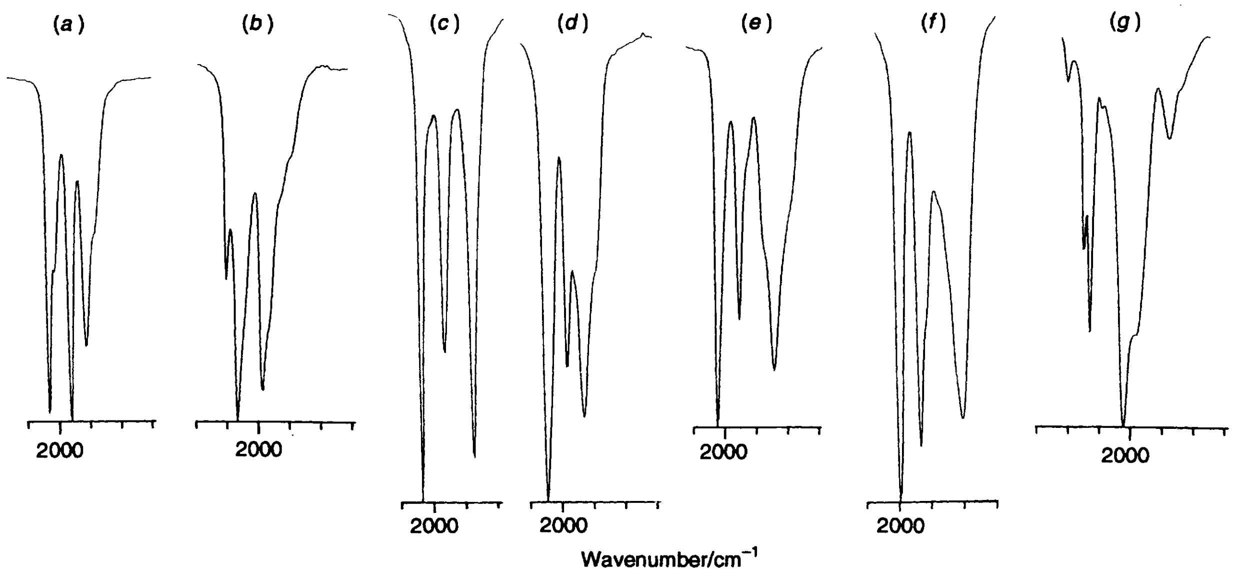


Fig. 1 Infrared spectra recorded in thf solution in CaF_2 cells for selected complexes: (*a*) **1**, (*b*) **3**, (*c*) **4**, (*d*) **5**, (*e*) **7**, (*f*) **10** and (*g*) **14**

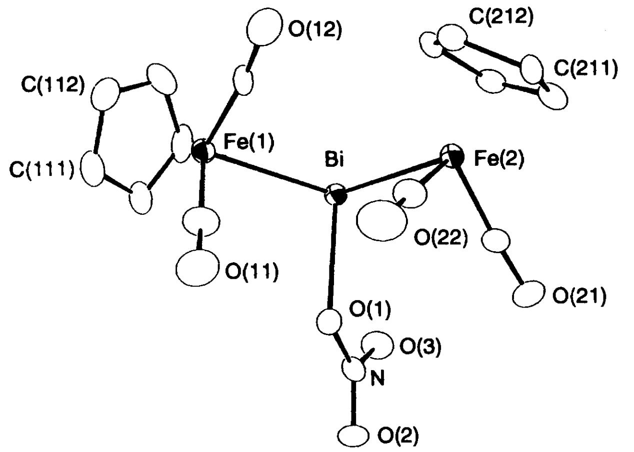


Fig. 2 A view of the monomeric unit of complex **1** showing the atom numbering scheme adopted and with hydrogen atoms omitted

$(\eta-C_5H_5)_2]$ which presumably resulted from an oxidation of the anionic ruthenium reactant. Treatment of bismuth nitrate with 3 equivalents of $K[Ru(CO)_2(\eta-C_5H_5)]$, however, afforded the triruthenium–bismuth complex $[Bi\{Ru(CO)_2(\eta-C_5H_5)\}_3]$ **4** in good yield. A comparison of the infrared spectrum [Fig. 1(*c*), Table 1] with that reported for the analogous iron complex[1,8] and analytical data were in complete accord with the proposed formula. Moreover, the reaction between 2 equivalents of **4** and 1 equivalent of $BiCl_3$ [equation (1)]

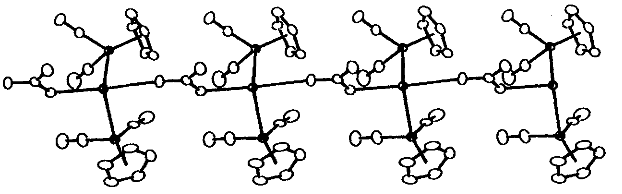


Fig. 3 A view of part of the crystal structure of complex **1** showing the intermolecular Bi ··· O interactions along the crystallographic *a* axis

$$\underset{\mathbf{4}}{2[Bi\{Ru(CO)_2(\eta-C_5H_5)\}_3]} + BiCl_3 \longrightarrow \underset{\mathbf{5}}{3[BiCl\{Ru(CO)_2(\eta-C_5H_5)\}_2]} \quad (1)$$

afforded the chloro complex $[BiCl\{Ru(CO)_2(\eta-C_5H_5)\}_2]$ **5** characterised also by comparison of the infrared spectrum [Fig. 1(*d*), Table 1] with that of the iron analogue,[1,8] and by analytical data. We had previously observed similar

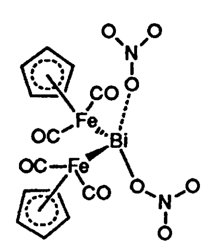
Table 2 Selected bond lengths (Å) and angles (°) for complex **1** *

Bi–Fe(1)	2.634(2)	Bi–Fe(2)	2.634(2)
Bi–O(1)	2.438(8)	Bi–O(2′)	2.932(8)
N–O(1)	1.284(11)	N–O(2)	1.230(13)
N–O(3)	1.231(12)		
Fe(1)–Bi–Fe(2)	111.8(1)	Fe(1)–Bi–O(1)	94.9(2)
Fe(2)–Bi–O(1)	93.5(2)	Bi–O(1)–N	113.9(6)
O(1)–N–O(2)	118.2(10)	O(1)–N–O(3)	118.8(10)
O(2)–N–O(3)	123.0(10)	O(1)–Bi–O(2′)	159.4(2)
Fe(1)–Bi–O(2′)	95.2(2)	Fe(2)–Bi–O(2′)	99.3(2)

* Symmetry operation (′): 1 + *x*, *y*, *z*.

Table 3 Fractional atomic coordinates for compound **1**

Atom	*x*	*y*	*z*
Bi	0.427 86(7)	0.077 05(2)	0.650 13(4)
Fe(1)	0.400 3(2)	0.149 2(1)	0.456 9(2)
Fe(2)	0.543 8(2)	0.122 1(1)	0.892 1(2)
N	−0.005 7(14)	0.034 0(4)	0.647 2(9)
O(1)	0.071 2(12)	0.080 6(3)	0.635 6(8)
O(2)	−0.184 9(12)	0.032 1(4)	0.641 8(9)
O(3)	0.104 1(13)	−0.006 4(3)	0.667 7(10)
O(11)	0.040 2(16)	0.196 2(4)	0.492 1(14)
O(12)	0.661 5(18)	0.226 4(4)	0.635 1(10)
O(21)	0.287 0(15)	0.046 6(5)	0.980 3(10)
O(22)	0.241 9(18)	0.206 1(5)	0.814 7(14)
C(11)	0.180(2)	0.175(1)	0.478(2)
C(12)	0.556 0(19)	0.194 2(5)	0.569 9(11)
C(21)	0.385 4(18)	0.075 6(5)	0.940 1(14)
C(22)	0.362(2)	0.173(1)	0.844(1)
C(111)	0.288(2)	0.152(1)	0.246(1)
C(112)	0.479(3)	0.172(1)	0.289(1)
C(113)	0.606(2)	0.129(1)	0.355(1)
C(114)	0.486(3)	0.084(1)	0.354(1)
C(115)	0.288(3)	0.098(1)	0.286(1)
C(211)	0.759 6(19)	0.160 4(6)	1.053 4(12)
C(212)	0.789 8(19)	0.175 3(5)	0.928 8(12)
C(213)	0.836 1(17)	0.126 4(5)	0.866 8(11)
C(214)	0.824 9(18)	0.083 0(5)	0.951 3(15)
C(215)	0.777(2)	0.105(1)	1.066(2)

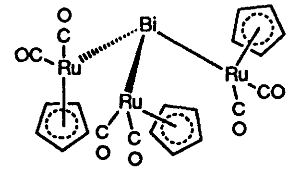


1

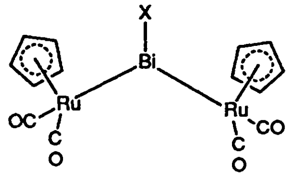
redistribution reactions in the molybdenum and tungsten systems.[2]

The reaction between bismuth nitrate and 2 equivalents of K[Mo(CO)$_3$(η-C$_5$H$_5$)] afforded, after work-up, purple flaky crystals of [Bi(NO$_3$){Mo(CO)$_3$(η-C$_5$H$_5$)}$_2$] **6** and the analogous compounds [Bi(NO$_3$){Mo(CO)$_3$(η-C$_5$H$_4$Me)}$_2$] **7**, [Bi(NO$_3$){W(CO)$_3$(η-C$_5$H$_5$)}$_2$] **8**, [Bi(NO$_3$){W(CO)$_3$(η-C$_5$H$_4$Me)}$_2$] **9** and [Bi(NO$_3$){Cr(CO)$_3$(η-C$_5$H$_5$)}$_2$] **10** were prepared similarly. Infrared spectra of **7** and **10** are shown in Fig. 1(*e*) and 1(*f*) and data for all complexes are presented in Table 1. It did not prove possible to isolate X-ray-quality crystals for any of these complexes.

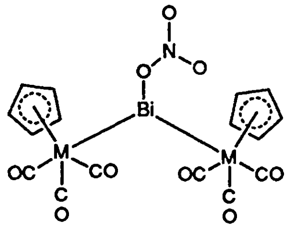
In contrast, the reactions between bismuth nitrate and 2 equivalents of the cobalt carbonylate anions K[Co(CO)$_3$(PPh$_3$)] or K[Co(CO)$_3${P(OPh)$_3$}] did not afford dicobalt bismuth nitrate species; infrared spectra indicated that the complexes formed were the tricobalt bismuth species [Bi{Co(CO)$_3$(PPh$_3$)}$_3$] **11** and [Bi{Co(CO)$_3${P(OPh)$_3$}}$_3$] **12**. The former complex has been previously described[3] whilst the latter is similar in all respects to the antimony analogue.[16] A somewhat similar situation was observed in the reactions between BiCl$_3$ and 2 equivalents of K[Co(CO)$_3$(PPh$_3$)] wherein the tricobalt complex **11** was formed as the initial product which then reacted with unreacted BiCl$_3$ over a period of time to give [BiCl{Co(CO)$_3$(PPh$_3$)}$_2$] by analogy with equation (1).[3] No reaction was observed between **11** and bismuth nitrate and so we suggest that the reaction between bismuth nitrate and 2 equivalents of K[Co(CO)$_3$(PPh$_3$)] proceeds to complex **11** and no further, although we note that the reaction between [Bi{Mo(CO)$_3$(η-C$_5$H$_5$)}$_3$] and bismuth nitrate does yield **6**.



4



X = NO$_3$ **3** or Cl **5**



M = Mo **6**, W **8** or Cr **10**

Finally, we note that, in the reaction between bismuth nitrate and 2 equivalents of Na[Mn(CO)$_5$], mixtures of [Bi{Mn(CO)$_5$}$_3$] **13** and a purple compound which is probably [Bi(NO$_3$){Mn(CO)$_5$}$_2$] **14** were formed. An infrared spectrum of **14** is shown in Fig. 1(*g*) and is very similar to that observed for the analogous chloro complex [BiCl{Mn(CO)$_5$}$_2$],[4] but we were unable to obtain satisfactory analytical data and the compound showed a tendency to decompose in solution as was also found for the chloro species.[4]

In conclusion, we have shown that a range of complexes of the general formula [Bi(NO$_3$)(ML$_n$)$_2$] can be synthesised. Moreover, preliminary reactivity studies show that these species are useful sources of the [Bi(ML$_n$)$_2$]$^+$ fragment, in contrast to the halogeno analogues, full details of which will be the subject of a future publication.

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. Infrared spectra were recorded in thf solution in CaF$_2$ cells on a Nicolet 20 SXB FTIR spectrophotometer and microanalytical data were obtained at the University of Newcastle. The complexes [Ru$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$],[17] [M$_2$-

$(CO)_6(\eta\text{-}C_5H_4R)_2]$ (M = Cr, Mo or W; R = H or Me)[18] and $[Fe_2(CO)_4(\eta\text{-}C_5H_4Me)_2]$[19] were prepared by literature methods; bismuth trinitrate pentahydrate and the other metal carbonyl dimers were procured commercially.

Solutions of the metal carbonylate anions were all prepared by sodium–potassium alloy (NaK) reduction of the corresponding neutral dimers in thf solution (with the exception of cobalt, see later), the excess of NaK being first removed by filtration. For the complexes of Cr, Mo, W and Mn, these reactions are easily monitored, due to the colour change which occurs on reduction, and filtration and use of the anions takes place on completion of the reaction. For the complexes of Fe and Ru, the colour changes are less obvious and the reductions were monitored by infrared spectroscopy; both reactions typically take between 2 and 4 h and it is important not to leave these reductions for longer than is necessary.

Preparations.—$[Bi(NO_3)\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ **1**. A solution of $K[Fe(CO)_2(\eta\text{-}C_5H_5)]$ derived from a NaK reduction of $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.551 g, 1.556 mmol) in thf (20 cm^3) was added to a suspension of $Bi(NO_3)_3{\cdot}5H_2O$ (0.755 g, 1.556 mmol) in thf (10 cm^3) at room temperature. The resulting dark green solution was stirred for 3 h and then filtered through Celite. The volume of the dark green filtrate was reduced to 10 cm^3 and hexane (30 cm^3) was layered over this solution. Solvent diffusion over a period of days at −30 °C afforded a dark green powder. Recrystallisation from CH_2Cl_2 (10 cm^3)–hexane (30 cm^3) mixtures by solvent diffusion at −30 °C afforded dark green X-ray-quality crystals of complex **1** (25%). Compound **2** was prepared in an analogous manner from $[Fe_2(CO)_4(\eta\text{-}C_5H_4Me)_2]$ with similar recrystallised yields.

$[Bi(NO_3)\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2]$ **3**. A solution of $K[Ru(CO)_2(\eta\text{-}C_5H_5)]$ derived from a NaK reduction of $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.280 g, 0.630 mmol) in thf (20 cm^3) was added to a suspension of $Bi(NO_3)_3{\cdot}5H_2O$ (0.310 g, 0.630 mmol) in thf (10 cm^3) at room temperature. The resulting dark purple solution was stirred for 3 h and then filtered through Celite. The volume of the dark purple filtrate was reduced to 10 cm^3 and hexane (30 cm^3) was layered over this solution. Solvent diffusion over a period of days at −30 °C afforded complex **3** as a dark purple powder (20%).

$[Bi\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_3]$ **4**. A solution of $K[Ru(CO)_2(\eta\text{-}C_5H_5)]$ derived from a NaK reduction of $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.589 g, 1.327 mmol) in thf (20 cm^3) was added to a suspension of $Bi(NO_3)_3{\cdot}5H_2O$ (0.429 g, 0.884 mmol) in thf (10 cm^3) at room temperature. The solution immediately turned purple but changed to dark green on complete addition of the $K[Ru(CO)_2(\eta\text{-}C_5H_5)]$. The resulting green solution was stirred for 3 h and then filtered through Celite. The volume of the dark green filtrate was reduced to 10 cm^3 and hexane (30 cm^3) was layered over this solution. Solvent diffusion over a period of days at −30 °C afforded complex **4** as a dark green powder (40%).

$[BiCl\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2]$ **5**. A solution of $BiCl_3$ (0.020 g, 0.061 mmol) in thf (10 cm^3) was added to a green solution of complex **4** (0.107 g, 0.122 mmol) in thf (10 cm^3) resulting in a change in colour to red-purple. The solvent volume was reduced to 10 cm^3 and hexane (30 cm^3) added as an overlayer. Solvent diffusion at −30 °C over a period of days afforded complex **5** as a dark green solid (50%). Although **5** is dark green as a solid, solutions in thf are red-purple.

$[Bi(NO_3)\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ **6**. A solution of $K[Mo(CO)_3(\eta\text{-}C_5H_5)]$ derived from a NaK reduction of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (0.413 g, 0.843 mmol) in thf (20 cm^3) was added to a suspension of $Bi(NO_3)_3{\cdot}5H_2O$ (0.409 g, 0.843 mmol) in thf (10 cm^3) at room temperature. The resulting dark purple solution was stirred for 1 h and then filtered through Celite. The volume of the dark purple filtrate was reduced to 10 cm^3 and hexane (30 cm^3) was layered over this solution. Solvent diffusion over a period of days at −30 °C afforded complex **6** as dark purple flaky crystals (70%) although better-quality crystals were obtained upon recrystallisation by solvent diffusion from thf–Et_2O mixtures. Compound **6** is also formed in the reaction between 2 equivalents of $[Bi\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_3]$[2] and 1 equivalent of bismuth nitrate in thf [in contrast to the corresponding reaction involving the $Co(CO)_3(PR_3)$ fragments, see text], and the complex $[Bi\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_3]$ may be prepared (in addition to previously published routes[2]) from bismuth nitrate and 3 equivalents of $K[Mo(CO)_3(\eta\text{-}C_5H_5)]$ in thf. In many ways, this latter route to $[Bi\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_3]$ is preferable since the KNO_3 by-product is easier to remove than KCl.

The complexes **7**–**10** (**10** is green) were prepared in an analogous manner using the corresponding cyclopentadienyl-metal carbonyl dimers, although recrystallised yields of the tungsten and chromium complexes were only about 20–30%.

$[Bi\{Co(CO)_3\{P(OPh)_3\}\}_3]$ **12**. A solution of $K[Co(CO)_3\{P(OPh)_3\}]$, prepared from $[Co_2(CO)_8]$ (0.540 g, 1.385 mmol) and $P(OPh)_3$ (0.639 g, 2.060 mmol) according to ref. 16, in thf (20 cm^3) was added to a suspension of $Bi(NO_3)_3{\cdot}5H_2O$ (0.500 g, 1.030 mmol) in thf (10 cm^3) resulting in a dark red-brown solution. The solution was stirred for 48 h and filtered through Celite affording a dark red-brown solution which was reduced in volume to about 10 cm^3. Hexane (30 cm^3) was added as an overlayer and solvent diffusion at −30 °C over a period of days afforded dark red-brown crystals of complex **12** (40%).

$[Bi(NO_3)\{Mn(CO)_5\}_2]$ **14**. A solution of $K[Mn(CO)_5]$ derived from a NaK reduction of $[Mn_2(CO)_{10}]$ (0.540 g, 1.380 mmol) in thf (20 cm^3) was added to a suspension of $Bi(NO_3)_3{\cdot}5H_2O$ (0.670 g, 1.380 mmol) in thf (10 cm^3) resulting in a red solution which became brown after stirring for 24 h. Filtration through Celite followed by crystallisation by solvent diffusion from thf–hexane mixtures afforded complex **14** as a purple powder (25%).

X-Ray Crystallography.—*Crystal data for compound* **1**. $C_{14}H_{10}BiFe_2NO_7$, $M = 624.91$, monoclinic, space group $P2_1/n$, $a = 6.9450(4)$, $b = 24.555(2)$, $c = 10.344(1)$ Å, $\beta = 107.304(7)°$, $U = 1684.3(3)$ Å^3, $Z = 4$, $D_c = 2.464$ g cm^{-3}, $F(000) = 1168$, $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-K}\alpha) = 121.28$ cm^{-1}, $T = 298$ K.

Data collection and reduction. A dark green crystal of approximate dimensions 0.73 × 0.16 × 0.13 mm was mounted on a glass fibre and coated in acrylic resin to prevent decomposition in air. Data were collected using the θ–2θ scan mode on a CAD4F automated diffractometer using graphite-monochromated X-radiation. Unit-cell parameters were determined by refinement of the setting angles ($\theta \approx 12°$) of 20 reflections. The intensities of the reflections $\bar{1}\,10\,4$, $2\,0\,4$ and $4\,\bar{4}\,\bar{3}$ were measured every 2 h and a decay in intensities of *ca*. 9% over 45 h of data collection was noted and a linear correction applied. Lorentz, polarisation and absorption/extinction (DIFABS;[20] maximum, minimum corrections 1.46, 0.65 respectively) corrections were also applied; R_{merge} was 0.11 before and 0.034 after the absorption correction. A total of 3311 measured reflections (θ range 2–25°, *h* 0–8, *k* 0–29, *l* − 12 to 12) yielded 2961 independent data of which 2271 reflections having $I > 3.0\sigma(I)$ were considered observed and used in structure determination. The statistics of the normalised structure factors and systematic absences uniquely indicated the centrosymmetric space group $P2_1/n$.

The structure was solved by direct methods (MITHRIL[21]) and subsequent electron-density difference syntheses. Refinement was by full-matrix least squares minimising the function $\Sigma w(|F_o| - |F_c|)^2$ with the weighting scheme $w = [\sigma^2(F_o)]^{-1}$ used and judged satisfactory; $\sigma(F_o)$ was estimated from counting statistics. All non-H atoms were allowed anisotropic thermal motion. The H atoms were included at calculated positions (C–H 1.0 Å) and allowed to ride on their attached C atom. A common refined isotropic thermal parameter was used for all H atoms. Refinement using a total of 227 parameters converged at $R(R') = 0.038$ (0.052) with mean and maximum Δ/σ values of

0.027 and 0.098 respectively in the final cycle. A final electron-density difference synthesis showed no peaks of chemical significance (maximum $\Delta\rho = +1.7$, minimum $\Delta\rho = -1.2$ e Å^{-3} in the vicinity of the Bi atom). The estimated standard deviation (e.s.d.) of an observation of unit weight (S) was 2.6. Neutral atom scattering factors were taken from ref. 22 with corrections applied for anomalous scattering. All calculations were carried out on a Micro VAX 3600 computer using the Glasgow GX suite of programs.[23]

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

Acknowledgements

We thank the SERC for support and BP Research (Sunbury) for a CASE Award (to G. A. F.). N. C. N. also thanks the Royal Society for additional supporting funds, Johnson Matthey for a loan of RuCl$_3$ and Professor S. A. R. Knox for assistance with the preparation of [Ru$_3$(CO)$_{12}$].

References

1 W. Clegg, N. A. Compton, R. J. Errington and N. C. Norman, *J. Chem. Soc., Dalton Trans.*, 1988, 1671.
2 W. Clegg, N. A. Compton, R. J. Errington, N. C. Norman, A. J. Tucker and M. J. Winter, *J. Chem. Soc., Dalton Trans.*, 1988, 2941.
3 W. Clegg, N. A. Compton, R. J. Errington, D. C. R. Hockless, N. C. Norman, M. Ramshaw and P. M. Webster, *J. Chem. Soc., Dalton Trans.*, 1990, 2375.
4 N. A. Compton, R. J. Errington, G. A. Fisher, N. C. Norman, P. M. Webster, P. S. Jarrett, S. J. Nichols, A. G. Orpen, S. E. Stratford and N. A. L. Williams, *J. Chem. Soc., Dalton Trans.*, 1991, 669.
5 W. Clegg, N. A. Compton, R. J. Errington, G. A. Fisher, D. C. R. Hockless, N. C. Norman, N. A. L. Williams, S. E. Stratford, S. J. Nichols, P. S. Jarrett and A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1992, 193.
6 N. C. Norman, *Chem. Soc. Rev.*, 1988, **17**, 269.
7 W. Clegg, N. A. Compton, R. J. Errington, G. A. Fisher, N. C. Norman and N. Wishart, *J. Organomet. Chem.*, 1990, **399**, C21 and refs. therein.
8 J. M. Wallis, G. Müller and H. Schmidbaur, *J. Organomet. Chem.*, 1987, **325**, 159.
9 W. Clegg, N. A. Compton, R. J. Errington, G. A. Fisher, D. C. R. Hockless, N. C. Norman, A. G. Orpen and S. E. Stratford, *J. Chem. Soc., Dalton Trans.*, 1992, 3515.
10 N. A. Compton, R. J. Errington and N. C. Norman, *Adv. Organomet. Chem.*, 1990, **34**, 91.
11 W. Clegg, R. J. Errington, G. A. Fisher, D. C. R. Hockless, N. C. Norman, A. G. Orpen and S. E. Stratford, *J. Chem. Soc., Dalton Trans.*, 1992, 1967 and refs. therein.
12 G. B. Jameson. E. Blaszo and H. R. Oswald, *Acta Crystallogr., Sect. C*, 1984, **40**, 350.
13 F. Lazarini, *Acta Crystallogr., Sect. B*, 1979, **35**, 448.
14 F. Lazarini and I. Leban, *Cryst. Struct. Commun.*, 1982, **11**, 653.
15 P. Herpin and K. Sudarsanan, *Bull. Soc. Fr. Mineral. Crystallogr.*, 1965, **88**, 590.
16 N. C. Norman, P. M. Webster and L. J. Farrugia, *J. Organomet. Chem.*, 1992, **430**, 205.
17 N. M. Doherty and S. A. R. Knox, *Inorg. Synth.*, 1989, **26**, 179.
18 R. Birdwhistell, P. Hackett and A. R. Manning, *J. Organomet. Chem.*, 1978, **157**, 239.
19 R. B. King and F. G. A. Stone, *Inorg. Synth.*, 1963, **7**, 110.
20 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
21 C. J. Gilmore, *J. Appl. Crystallogr.*, 1984, **17**, 42.
22 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
23 P. R. Mallinson and K. W. Muir, *J. Appl. Crystallogr.*, 1985, **18**, 51.

Received 21*st December* 1992; *Paper* 2/06747A