Synthesis and Reactivity of "Bismuthinidene" Compounds and the Formation of Bi^I Chelate Complexes

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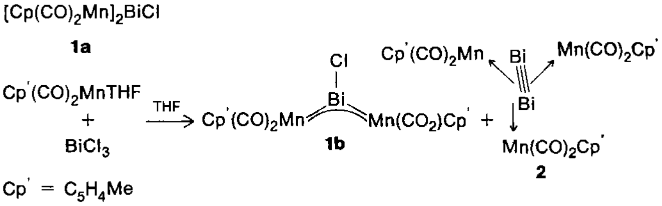
Treatment of $[Cp'Mn(CO)_2THF]$ ($Cp' = C_5H_4Me$) with $BiCl_3$ at 20°C affords the "bismuthinidene" species $[Cp'(CO)_2Mn]_2BiCl$ (**1b**) and very small amounts of the "star-type" compound $[Cp'(CO)_2Mn]_3Bi_2$ (**2**). Higher yields of both compounds are obtained from the reaction of $BiCl_3$ with $[Na][Cp'(CO)_2MnSi(C_6H_5)_3]$. The molecular structure of **1b** has been determined by an X-ray diffraction study, which shows that the bismuth atom, having a trigonal-planar coordination geometry, is bonded to two manganese atoms and one chlorine atom. There are weak interactions between the molecules of **1b** in the solid state thus forming infinite spiral chains of "inidene" complexes. Compound **1b** reacts with NaI to afford the iodine-substituted species $[Cp'(CO)_2Mn]_2BiI$ (**3**). Displacement of the chloride substituent from **1b** by anionic chelating ligands $\widehat{AB}^-$ is also possible; **1b** reacts with tropolonate, 8-oxoquinolate, or 8-mercaptoquinolate to form the bismuth(I) chelate compounds $[Cp'(CO)_2Mn]_2\overline{Bi-\underset{\smile}{AB}}$ (**5a–c**). The molecular structure of **5b** has been determined by X-ray crystallography which shows the bismuth atom in a pseudo trigonal-bipyramidal geometry with the nitrogen atom lying above the plane defined by the two manganese and the oxygen atoms in an apical position. The molecular structure of **5c** has also been determined, and although the numerical values are not very accurate, the coordination geometry of the bismuth atom is seen to be intermediate between pseudo trigonal-bipyramidal and distorted tetrahedral. Abstraction of a chloride ligand from **1b** by $Me_3SiOSO_2CF_3$ affords the cationic cumulene-type complex $[Cp'(CO)_2Mn{=}Bi{=}Mn(CO)_2Cp'][CF_3SO_3]$ (**6a**). Dichloromethane solutions of **6a** are not stable at room temperature but may be treated with 2,2'-bipyridine (bpy) to afford the stable adduct $[\{Cp'(CO)_2Mn\}_2Bi(bpy)][CF_3SO_3]$ (**7**). The molecular structure of **7** has been determined by X-ray analysis, and – similarly to **5c**, although the numerical values are not very accurate – the overall geometry has been determined unequivocally. The bismuth atom is shown to have a distorted tetrahedral geometry, thus being ligated by two manganese atoms and the two nitrogen atoms of the bpy ligands.

Amongst the family of "inidene" compounds $[Cp(CO)_2Mn]_2XR$ (X = P, As, Sb, Bi) ($Cp = C_5H_5$) the "bismuthinidene" species are apparently the least stable members[1,2]. The only complex known is $[Cp(CO)_2Mn]_2BiCl$ (**1a**)[3], and – despite the recent interest in complexes containing transition metals and bismuth atoms[4,5] – only this species and one other "bismuthinidene" compound have been described in the literature[6]. The "chloroinidene" complexes $[L_nM]_2XCl$ (X = P, As, Sb; L_nM = 16-electron fragment) have been shown to be versatile synthetic reagents. When X = As, halide abstraction from $[L(CO)_2Mn]_2AsCl$ ($L = C_5H_4Me$ or C_5Me_5) affords the dimetallacumulenium ions $[L(CO)_2Mn{=}As{=}Mn(CO)_2L]^+$ which can be isolated and which are themselves useful synthetic precursors[7,8]. In this paper we report preparative methods which provide an easier access to "bismuthinidene" complexes and demonstrate that they behave as Lewis acids in forming adducts with Lewis bases in a similar manner to their lighter homologues (P, As, Sb)[9].

Results and Discussion

Synthesis of $[Cp'(CO)_2Mn]_2BiCl$ ($Cp' = C_5H_4Me$) (1b)

The method reported for the synthesis of the first "bismuthinidene" compound $[Cp(CO)_2Mn]_2BiCl$ (**1a**) is readily applicable to the synthesis of its Cp' derivative. The yield of the dark green complex **1b** is only ca. 11% when using this procedure. Purification of **1b** is possible by column chromatography, the main byproduct being – not unexpectedly – $[Cp'Mn(CO)_3]$, a trace amount of the brown complex **2**[10] is also obtained. Compound **1b** is obtained as a black microcrystalline powder by crystallisation from CH_2Cl_2/pentane mixtures at –30°C.



Since relatively poor yields of **1b** were obtained from this procedure an alternative synthesis was developed. As it had been previously reported that the anionic reagent $[Cp'(CO)_2Mn]_2H^-$ will reduce $BiCl_3$ to Bi^0 affording **2**[10], the use of the species $[Cp'(CO)_2MnSi(C_6H_5)_3]^-$ as an anionic starting material was investigated. The propensity of these anions to serve as a source of the fragment $Cp'(CO)_2Mn$ has recently been demonstrated by Schubert et al.[11]. Thus, a red

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THF solution of $[Na][Cp'(CO)_2MnSi(C_6H_5)_3]$ was cooled to −30°C and treated with one equivalent of $BiCl_3$. The red solution immediately turned green, and then quickly changed to dark brown. After one hour, the solvent was removed from the reaction mixture in vacuo, and the black residue was chromatographed on silicated Kieselgel. This procedure afforded both **1b** and **2** in appreciably higher yields, 28 and 10%, respectively. Suitable crystals of **1b** were available, and an X-ray structure analysis was undertaken. The molecular structure is shown in Figure 1, and atomic positional parameters are presented in Table 1.

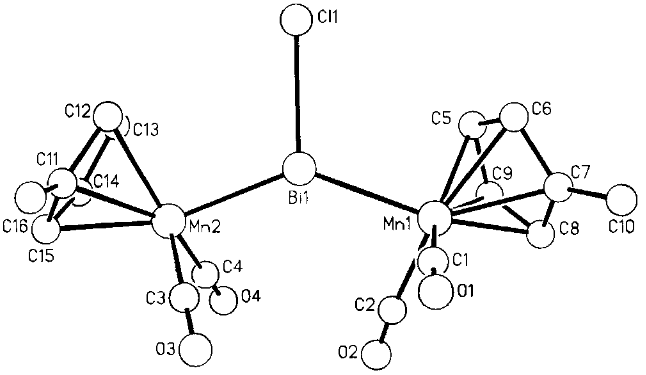


Figure 1. Molecular structure of **1b**; bond lengths [pm] and angles [°]: Bi−Mn(1) 248.3(3), Bi−Mn(2) 247.5(4), Bi−Cl 263(1); Mn(1)−Bi−Mn(2) 138.0(2), Mn(1)−Bi−Cl 110.8(2), Mn(2)−Bi−Cl 109.1(2)

The solid-state structure of **1b** is significantly different to that of $[Cp(CO)_2Mn]_2BiCl$ (**1a**), which in the solid state dimerises by the formation of unsymmetrical Bi−Cl···Cl bridges. In contrast, **1b** is essentially monomeric, and its structure is similar to that of other "inidene" compounds containing P, As, or Sb[1,2] in that the bismuth atom has a trigonal-planar coordination environment. However, there is a slight distortion away from planarity for the atoms Mn(1), Mn(2), Bi, and Cl, with the bismuth atom lying 20.3 pm above the Mn(1), Mn(2), Cl plane. The reason for this distortion will be discussed later. The Bi−Mn bonds are both short (average 247.9 pm), and this value is very similar to that found in **1a** (average 246.9 pm). These distances may be compared with the only other Bi−Mn bond lengths known, those in **2** and in the compound $[(CO)_5Mn]_3Bi$, in which they are very much longer (average 293.2 pm[10] and average 290.4 pm[12], respectively). Similarly, much longer metal−bismuth bond lengths are found in $[\{Cp(CO)_3Mo\}_2BiCl]$ (Mo−Bi average 295.1 pm)[13] and in $[\{[Cp'(CO)_2Fe]_2BiCl\}_3]$ (Fe−Bi average 273.8 pm)[14]. All of these observations are consistent with the Bi−Mn bonds in **1b** showing some multiple-bond character as part of a 3-centre 4-π system. In the solid state compound **1b** is weakly associated, and the configuration adopted is shown in Figure 2. The chlorine atom of one "inidene" molecule interacts weakly with the bismuth atom of an adjacent molecule to form an infinite spiral chain of "inidene" complexes. The distance between the chlorine atom of one molecule and the bismuth of another is long (314 pm) in comparison with the intramolecular Bi−Cl distance of 263 pm. A comparison may be made with **1a**[3] in which the intermolecular interactions are much stronger and involve only two molecules; the chlorine bridges in **1a** are only slightly asymmetric the Bi−Cl distances being 280 and 290 pm. Interestingly, the mean Bi−Cl distance is very similar in both **1a** (285 pm) and **1b** (288 pm). The intermolecular Bi−Cl interaction is orientated so that the weakly coordinated additional chlorine atom is essentially perpendicular to the Mn(1)−Bi−Mn(2) plane; thus, the bonding may be considered to arise from donation from a lone pair at the chlorine atom into an empty p-type orbital at the bismuth atom. This interaction accounts for the deformation out of planarity observed for the atoms Mn(1), Mn(2), Bi, and Cl in each individual molecule.

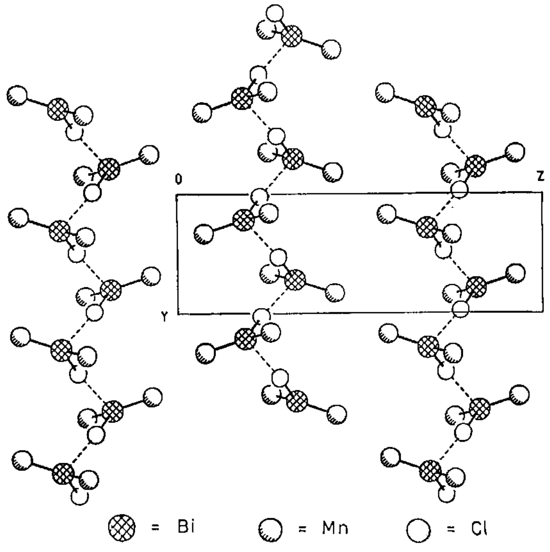
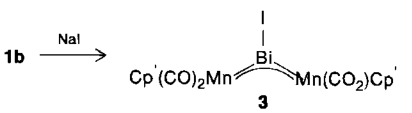


Figure 2. Association of molecules of **1b** in the solid state forming spirals along the 2_1 axes in space group $P2_1/c$

The chlorine substituent in **1b** is readily exchanged for iodine. Stirring **1b** with one equivalent of NaI at room temperature followed by appropriate workup affords $[Cp'(CO)_2Mn]_2BiI$ (**3**) in moderate yield. Significant decomposition is observed during the course of this reaction. Compound **3** is completely characterised by its spectroscopic and analytical data.



$$\mathbf{1b} \xrightarrow{NaI} Cp'(CO)_2Mn{=}\overset{\overset{I}{|}}{Bi}{=}Mn(CO_2)Cp'$$

3

Base Adducts of 1b

"Inidene" compounds $[L_nM]_2XR$ tend to act as Lewis acids adding Lewis bases B:. For (X = P, As, Sb) the trigonal-planar coordination of the main-group element characteristic for "inidene" compounds is transformed into an idealised tetrahedral environment in the base adducts $[L_nM]_2XR{:}B$[1,2,9]. Whether this general behaviour also applies for "bismuthinidene" compounds has not been demonstrated. Many examples are known where phosphines act as Lewis bases **B**: towards “arsinidene” and “stibinidene” compounds[15–17]. Thus, a CH_2Cl_2 solution of **1b** was treated with PPh_3; no instantaneous reaction was observed, however, the solution colour gradually changed from intense green to brown with the precipitation of some black material. The only soluble product isolated was $[Cp'(CO)_2Mn\text{-}PPh_3]$ (**4**).

In contrast to this behaviour when **1b** is dissolved in THF it clearly forms a THF adduct. The THF solutions of **1b** are dark brown, while solutions of **1b** in non-donor solvents are green. The IR absorptions of the brown THF solutions show a long-wavelength shift for the ν(CO) frequencies of ca. 15 cm^{-1} relative to those of **1b** in CH_2Cl_2. If the solvent is evaporated from this adduct the starting material **1b** is regenerated. Unfortunately, attempts to crystallise the THF adduct have been unsuccessful. It is noteworthy that stable base adducts of “inidene” compounds $[L_nM]_2XR$ have thus far only been isolated where $L_nM = M(CO)_5$ (M = Cr, Mo, W) and not where $L_nM = Cp(CO)_2Mn$.

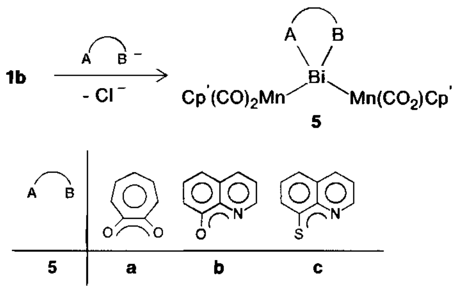
Bi^{I} Chelate Complexes

For simple entropic reasons the stability of base adducts is generally enhanced if the basic centre **B**: is part of the main-group substituent. Thus, chelate compounds $[L_nM]_2\text{-}X-\overset{\frown}{AB}$, derived from “inidene” complexes $[L_nM]_2XR$, are known for X = P, As, Sb[18–20] and are found to be relatively stable compounds. This entropic stabilisation also works for **1b**. When CH_2Cl_2 solutions of **1b** are treated with solutions containing anionic bidentate ligands such as tropolonate, 8-oxoquinolate, or 8-mercaptoquinolate, an immediate colour change from green (**1b**) to red-brown (**5**) is observed.

Evaporation of the solvent followed by extraction, filtration, and recrystallisation affords the compounds **5a–c** as analytically pure, black, crystalline samples. The ^1H-NMR spectra of the new compounds (see Experimental) clearly show the organic groups present in these species. In addition, the pattern and wavelength of the ν(CO) absorptions correspond almost quantitatively to the data obtained for the analogous Sb^{I} chelate compounds[20]. The observation of 4 ν(CO) absorptions clearly indicates the presence of rotameric equilibria for the compounds **5**.

The molecular structure of the compounds **5** was established by an X-ray analysis of **5b** (Figure 3; the atomic positional parameters are presented in Table 2).

The overall structure of **5b** (Figure 3) corresponds to the picture known for the chelate derivatives and base adducts of “inidene” compounds[18–20]. There is, however, a distinct difference with respect to the coordination geometry around the bismuth atom in **5b** when compared with the structurally and chemically related derivatives of the lighter Group-15 elements; whereas the coordination polyhedra around P, As, Sb in the known analogues of **5b** are generally close to a distorted tetrahedron, that around the bismuth atom in **5b** is much closer to a pseudo trigonal-bipyramidal one. The oxygen atom of the chelate ligand in **5b** lies almost in the plane defined by the atoms Mn(1), Bi, Mn(2), and this corresponds to the arrangement usually found in “inidene” compounds[1,2]. On the other hand the Bi–N bond to the 8-oxoquinolate ligand is almost perpendicular to this plane. This pseudo trigonal-bipyramidal coordination is also clearly illustrated in the relevant bond angles. The formally covalent, in-plane Bi–O bond [231.2(6) pm] is noticeably shorter than the formal Bi–N donor bond [246(1) pm]. Thus, the interaction of the N-donor with the planar “inidene”-type fragment may be considered to arise from an almost pure N-σ-donor Bi-π-acceptor interaction. While in an “inidene” compound this Bi-acceptor p-orbital is used to build up an Mn–Bi–Mn 3-centre 4-π system by its interaction with Mn d-type donor orbitals, in **5b** it is used in Bi–N σ-bonding. The π-contribution to Bi–Mn bonds, which is present in “inidene” compounds is effectively quenched in base adducts such as the compounds **5a–c**. Therefore, in comparison with the Bi–Mn bonds present in a free “bismuthinidene” species those in **5b** should be somewhat longer, and indeed the Bi–Mn bond lengths in **1b** (average 247.9 pm) are noticeably shorter than those in **5b** (average 253 pm). The observed lengthening of the Bi–Mn bonds reflects the effective quenching of the p-system by the donor bond in **5b**.



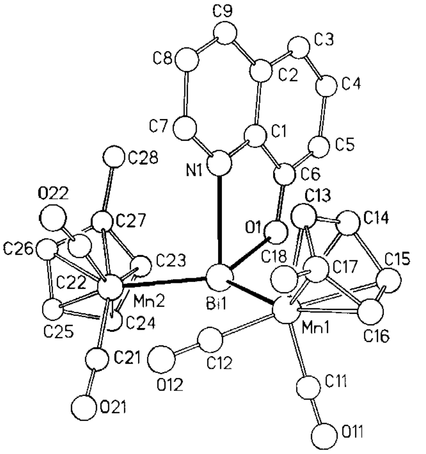


Figure 3. Molecular structure of **5b**; bond lenghts [pm] and angles [°]: Mn(1)–Bi 253.0(2), Mn(2)–Bi 253.0(2), Bi–N(1) 246(1), Bi–O(1) 231.2(6); Mn(1)–Bi–Mn(2) 136.0(1), Mn(2)–Bi–N(1) 97.2(2), Mn(1)–Bi–N(1) 98.0(2), Mn(2)–Bi–O(1) 111.5(2), Mn(1)–Bi–O(1) 112.5(2), N(1)–Bi–O(1) 69.9(2)

An X-ray analysis of **5c** was hampered by obvious twinning problems (see Experimental). However, the overall geometry of this compound was unequivocally determined, and is shown in Figure 4; the atomic positional parameters are presented in Table 6.

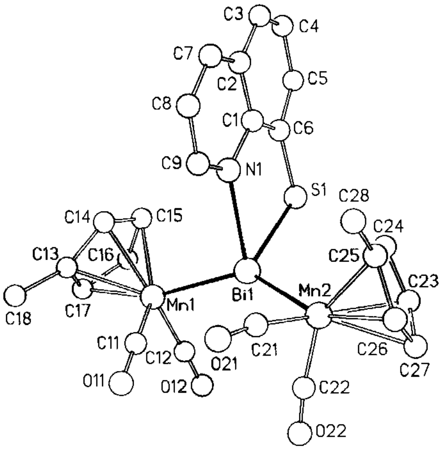


Figure 4. Molecular structure of **5c**. Bond lengths [pm] and angles [°]: Bi−Mn(1) 249.6(5), Bi−Mn(2) 250.4(4), Bi−S(1) 265(1), Bi−N(1) 254(2); Mn(1)−Bi−Mn(2) 135.5(2), Mn(1)−Bi−N(1) 98.5(6), Mn(1)−Bi−S(1) 113.6(2), Mn(2)−Bi−N(1) 104.0(5), Mn(2)−Bi−S(1) 109.2(3), N(1)−Bi−N(2) 74.7(8)

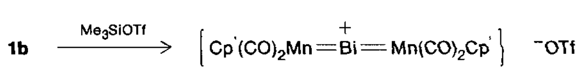
Even though individual numerical values are not very accurate it is clear that the coordination polyhedron around the bismuth atom in **5c** is not as strictly pseudo trigonal-bipyramidal as has been found for **5b**. The sulphur substituent lies at 71 pm from the Mn−Bi−Mn plane, while in **5b** the corresponding oxygen atom lies almost in the plane. Therefore, the structures of **5b** and **5c** differ by the relative rotations of the chelate ligands around an axis parallel to Mn(1)−Mn(2). The geometry around the bismuth atom for **5c** is intermediate between pseudo trigonal-bipyramidal and idealised tetrahedral.

The fact that in the chelate compounds $[L_nM]_2\overline{X-AB}$ the main-group centre has an idealised tetrahedral coordination geometry for the lighter Group-15 elements (X = P, As), while when X = Bi − the heaviest member of this group − it has one close to pseudo trigonal-bipyramidal, demands comment. This structural change might be related to the fact that for the sixth-row elements s-orbitals are not readily available for bonding. This would leave Bi with essentially 3 p-orbitals to interact with the two L_nM fragments and the chelate ligand, making the bonding situation significantly different to that accepted for the homologues containing the lighter elements.

Trapping of the Bismuth Cumulene Species

The green solutions of **1b** gradually turn red-brown when treated with $Me_3SiOSO_2CF_3$, and the IR spectra of these red-brown solutions of **6a** show a short-wavelength shift of the ν(CO) absorptions by ca. 20 cm^{-1} [IR (CH_2Cl_2): **6a**: $\tilde{\nu}$ = 1992 cm^{-1} m, 1962 s, 1938 m, 1878 sh; **1b**: $\tilde{\nu}$ = 1976 cm^{-1} m, 1939 s, 1917 m, 1852 sh].

The IR spectra observed for $[Cp'Mn(CO)_2]_2AsCl$ and $[Cp'(CO)_2Mn]_2As^+$ show a similar relationship [IR (CH_2Cl_2): $\tilde{\nu}$ = 1994 cm^{-1} s, 1951 vs, 1928 s, 1912 sh and $\tilde{\nu}$ = 2037 cm^{-1} s, 2006 vs, 1983 s, 1951 m, respectively), and furthermore the pattern of the absorptions observed in the latter of these two compounds is very similar to that for **6a**[7]. These similarities may be taken as evidence for the formation of the cumulene-type compound **6a**. The species **6a** slowly decomposes at room temperature depositing black insoluble material, the only soluble compound isolable being $[Cp'Mn(CO)_3]$. Evaporation of the solvent from the reaction mixture containing **6a** at low temperatures leaves a black oil, which could not be crystallised. While redissolving this oil in CH_2Cl_2 leads back to the red-brown solution of **6a**, doing so in THF leads to a brown solution [IR (THF): $\tilde{\nu}$ = 1975 cm^{-1} m, 1960 s, 1944 s, 1848 sh). The long-wavelength shift observed for this solution relative to that of **6a** indicates that adduct formation has occured from **6a** by an association of THF donor molecules similar to that observed for **1b** in THF. Evaporation of the solvent from this THF solution regenerates **6a**.

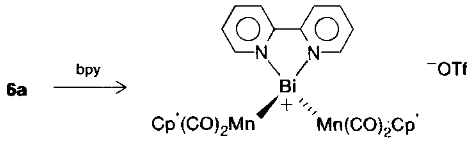


$$\mathbf{1b} \xrightarrow{Me_3SiOTf} \left[Cp'(CO)_2Mn{=}\overset{+}{Bi}{=}Mn(CO)_2Cp'\right]\ {}^{-}OTf$$

6a

Since **6a** has not yet been obtained as a pure crystalline material we tried to trap its cation with chelating donor ligands. It has previously been shown that the dimetallaplumbacumulene $[Cp'(CO)_2Mn{=}Pb{=}Mn(CO)_2Cp']$ adds 2,2′-bipyridine (bpy) to give the stable adduct $[Cp'(CO)_2Mn]_2Pb(bpy)$ (**8**)[21]. Isoelectronic thallium compounds such as $[(CO)_4Fe]_2Tl(bpy)^-$ (**9**) are also stable, even though the parent cumulenes have not yet been isolated[22]. This indicated that stable derivatives of **6a** should also be accessible.

When solutions of **6a** are treated with bpy an immediate colour change from red-brown to red is observed. Appropriate workup (see Experimental) gives the triflate salt **7** as a dark red crystalline material.

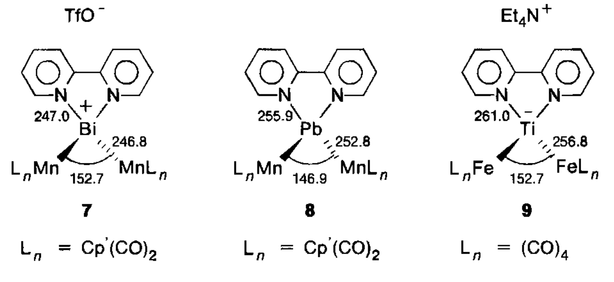


7

The IR spectrum of **7** [IR (CH_2Cl_2): $\tilde{\nu}$ = 1959 cm^{-1} m, 1936 s, 1894 m] displays the expected long-wavelength shift of the ν(CO) absorptions relative to those observed for **6a**, and all of the expected signals for the bpy ligand and the organometallic part of **7** are observed in the ^{1}H-NMR spectrum of this compound. Complex **7** may also be obtained by treating THF solutions of **6a** with bpy, and a further synthetic alternative consists of treating a CH_2Cl_2 solution of **1b** at 20°C with bpy and subsequently with $Me_3SiOSO_2CF_3$.

The structure of **7** was determined by an X-ray analysis, and although the quality of the crystals used and absorption problems connected with its unsuitable shape did not allow for high-quality X-ray analysis, the overall structure has been unequivocally determined. The overall geometry of the cation of 7 corresponds to that observed for **8** and **9** which are formally isoelectronic with the cation of 7. Both the analogous arsenic and antimony compounds $[\{Cp'Mn(CO)_2\}_2Asbpy][CF_3SO_3]$ and $[\{Cp'Mn(CO)_2\}_2Sbbpy][\{Cp'Mn(CO)_2\}_2SbCl_2]$ have recently been prepared and structurally characterised, and a comparison of these two structures with that of 7 has been discussed in the literature[9].

A characteristic feature of the formally isoelectronic compounds 7–**9** (Figure 5) is the large angle subtended at the main-group elements. Another general trend is shown by the fact that the main-group element–nitrogen distances are about the same length or even longer than the main-group element–metal distances (Figure 5). As the radii of nitrogen and metals such as iron and manganese are very different, this equality in the bond lengths N–X and M–X (X = Tl, Pb, Bi; M = Fe, Mn) indicates relatively weak interactions between the main-group centre and the chelate ligand, in comparison with those between the metal centres and the main-group element. If the compounds 7–**9** are conceptually derived from the corresponding cumulene complexes, the assumption of a weak interaction between the chelate ligand and the cumulene is consistent with the large M–X–M bond angles, which would be 180° in the parent cumulenes. Another interesting observation is the decrease in N–X bond length as X is changed from Tl to Pb and then to Bi; this shortening corresponds directly to an increase in the Lewis acidity of the main-group centre as it is changed from Tl^{-I} to Bi^{I}. Obviously, the Lewis base (bpy) will form stronger bonds with a stronger Lewis acid, which is in agreement with the changes in N–X bond lengths observed. This is also reflected in the ^1H-NMR spectra of these compounds. For compound **9** the resonances associated with the bpy group are relatively close to those of the free ligand, the average downfield shift on complexation being only 0.01 ppm, whereas for compound **8** the shift is 0.20 ppm, and for the bismuth-containing compound 7 the shift is 0.52 ppm. This downfield shift of the Lewis base protons on complexation is due to a decrease in proton shielding as electron density is transferred from the Lewis base to the main-group element, this charge transfer is obviously greater in 7 than in **8**, and in both of these species larger than in **9**, an observation that fits well with the structural data, both implying that the bpy ligand is bound most strongly to the main-group centre in 7 and least strongly in **9**.



7 8 9

L_n = Cp'(CO)$_2$ L_n = Cp'(CO)$_2$ L_n = (CO)$_4$

Figure 5. Comparison of the structure of 7 with the geometries of the two formally isoelectronic compounds **8** and **9**; bond lengths [pm], angles [°]

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Experimental

General: All experiments were carried out under oxygen-free nitrogen in freshly distilled solvents, using standard Schlenk techniques. The Kieselgel used for chromatography and the Kieselgur (Merck) used for filtration were degassed under high vacuum at room temperature for 5 d and saturated with nitrogen prior to use. The compounds $[Cp'Mn(CO)_3]$, $BiCl_3$, NaI, $C_7H_6O_2$, C_9H_7NO, C_9H_7NS, $Me_3SiOSO_2CF_3$ and 2,2'-bipyridine were procured commercially and used as supplied. The photochemical reactions were carried out at 12°C in a water-cooled Duran-50 glass apparatus with a mercury lamp (TQ 150 Hanau). – IR: Perkin-Elmer 983 G, CaF_2 cells. – NMR: Bruker AC 200 (standard: TMS internal). – MS: Finnigan MAT 8200, SS 300 Datasystem, ionisation energy 70 eV, ion-source temperature 200°C, CI gas isobutane.

[Cp'(CO)₂Mn]₂BiCl (**1 b**). – *Method* (a): A solution of 4.5 g (22 mmol) $[Cp'Mn(CO)_3]$ in THF (400 ml) was irradiated for 3 h. The dark red solution of $[Cp'Mn(CO)_2THF]$ (70% yield) produced was then added to a slurry of $BiCl_3$ [4.8 g (15.2 mmol)] in THF (10 ml) and the solvent removed in vacuo at 20°C. The oily black residue produced was extracted with CH_2Cl_2, and the extracts were filtered through Kieselgur (8 cm). Silicated Kieselgel (5 g) was added to the dark green eluate obtained, the solvent removed and the adsorbed compound transferred to the top of a cooled (–30°C) Kieselgel column. Unreacted $[Cp'Mn(CO)_3]$ was eluted with pentane, while elution with CH_2Cl_2/pentane (1:1) gave rise to a slow-moving dark green band which was collected. Removal of the solvent form this fraction and recrystallisation from CH_2Cl_2/pentane at –30°C afforded black crystals of **1 b** [yield 1.01 g (11% with respect to $BiCl_3$)]. Elution of the column with CH_2Cl_2 afforded a brown band which was collected. The solvent was removed in vacuo from the eluate and the residue recrystallised from CH_2Cl_2/pentane at –30°C to give black crystals of **2** in less than 1% yield.

Method (b): $[Cp'Mn(CO)_2HSi(C_6H_5)_3]$ [3 g (8.89 mmol)] was dissolved in THF (50 ml) and NaH [1 g (excess)] added to the solution. This mixture was stirred for ca. 12 h, during which time the solution colour changed from yellow to dark red. Filtration of the solution through a Kieselgur pad afforded a dark red eluate, to which was added $BiCl_3$ [2.8 g (8.87 mmol)] at –30°C. The colour of the reaction mixture immediately altered to dark green and then more slowly turned dark brown. The reaction mixture was allowed to warm to room temperature and stirred for 1 h after which time the solvent was removed in vacuo from the reaction mixture, and the black residue obtained was extracted with CH_2Cl_2; these extracts were filtered and then chromatographed as in method (a). This workup procedure afforded black crystals of **1 b** [yield 1.55 g (28%)] and black crystals of **2** [yield 0.80 g (10%)].

1 b: IR (CH_2Cl_2): $\tilde{\nu}$ = 1976 cm^{-1} m, 1939 s, 1917 m, 1852 sh [ν(CO)]. – ^1H NMR (CD_2Cl_2): δ = 1.84 (s, 6 H), 4.75 (m, 4 H), 5.02 (m, 4 H).

$C_{16}H_{14}ClBiMn_2O_4$ (624.59)	Calcd.	C 30.77 H 2.26
	Found	C 30.43 H 2.22

2 was identified by comparison with an authentic sample[10].

$[Cp'(CO)_2Mn]_2BiI$ (**3**): **1 b** [0.20 g (0.32 mmol)] was dissolved in CH_2Cl_2 (20 ml), and to this dark green solution NaI [0.05 g (0.32 mmol)] was added. The reaction mixture was stirred for 1 h, during which time the solution turned green-brown. Filtration of this solution through a pad of Kieselgur (6 cm) afforded a dark green eluate from which the solvent was removed in vacuo. Recrystallisation of the resulting residue from CH_2Cl_2/pentane at −30°C afforded **3** as black crystals [yield 0.06 g (25%)]. – IR (CH_2Cl_2): $\tilde{\nu}$ = 1975 cm^{-1} m, 1939 s, 1917 m [ν(CO)]. – ^1H NMR (CD_2Cl_2): δ = 1.84 (s, 6 H), 4.62 (m, 4 H), 5.01 (m, 4 H).

$C_{16}H_{14}BiIMn_2O_4$ (716.04) Calcd. C 26.84 H 1.97
Found C 26.45 H 1.92

$[Cp'(CO)_2Mn]_2Bi(C_7H_5O_2)$ (**5 a**): A solution of 1.4-diazabicyclo[2.2.2]octane (DABCO) [0.03 g (0.25 mmol)] in CH_2Cl_2 (10 ml) was treated with tropolone ($C_7H_6O_2$) [0.06 g (0.50 mmol)], and the mixture was stirred for 5 min. The colourless solution produced was then added to a dark green solution of **1 b** [0.32 g (0.50 mmol)] in CH_2Cl_2 (10 ml). An instantaneous colour change to red-brown was observed. The resulting solution was stirred for 30 min before the solvent was removed in vacuo to afford a brown residue. This was extracted with pentane/CH_2Cl_2 (1.5:1) (3 × 10 ml), and the extracts were filtered through a Kieselgur pad (5 cm) to give a dark red eluate from which the solvent was removed in vacuo. Recrystallisation of the residue from CH_2Cl_2/pentane at −30°C afforded black crystals of **5 a** [yield 0.23 g (65%)]. – IR (CH_2Cl_2): $\tilde{\nu}$ = 1947 cm^{-1} m, 1924 s, 1885 s [ν(CO)]. – ^1H-NMR ($CDCl_3$): δ = 1.85 (s, 6 H), 4.49 (m, 4 H), 4.80 (m, 4 H), 7.08–7.44 (m, 5 H). – MS (DCI): *m/z* (%) = 711 (1) [M^+], 589 (3) {$[Cp'(CO)_2Mn]_2Bi^+$}, 399 (2) {$[Cp'(CO)_2MnBi]^+$}, 190 (100) {$[Cp'(CO)_2Mn]^+$}.

$C_{23}H_{19}BiMn_2O_6$ (710.25) Calcd. C 38.89 H 2.70
Found C 38.77 H 2.75

$[Cp'(CO)_2Mn]_2Bi(C_9H_6NO)$ (**5 b**): In a similar procedure to that described for **5 a**, compound **1 b** [0.32 g (0.50 mmol)] in CH_2Cl_2 (10 ml) was treated with a mixture of DABCO [0.03 g (0.25 mmol)] and 8-hydroxyquinoline (C_9H_7NO) [0.07 g (0.05 mmol)]. Workup as described for **5 a** afforded black crystals of **5 b** [yield 0.19 g (53%)]. – IR (CH_2Cl_2): $\tilde{\nu}$ = 1948 cm^{-1} m, 1922 s, 1884 s [ν(CO)]. – ^1H NMR ($CDCl_3$): δ = 1.74 (s, 6 H), 4.37 (m, 4 H), 4.78 (m, 4 H), 7.04–8.47 (m, 6 H). – MS (DCI): *m/z* (%) = 733 (5) [M^+], 589 (7) {$[Cp'(CO)_2Mn]_2Bi^+$}, 399 (3) {$[Cp'(CO)_2MnBi]^+$}, 190 (100) {$[Cp'(CO)_2Mn]^+$}.

$C_{25}H_{20}BiMn_2NO_5$ (733.29) Calcd. C 40.95 H 2.75 N 1.91
Found C 40.29 H 2.73 N 2.05

Table 1. Atomic coordinates for **1 b**

ATOM	X/A	Y/B	Z/C
BI1	.5570(1)	.2134(1)	.18189(4)
MN1	.4031(4)	.3265(6)	.0732(1)
MN2	.7908(4)	.1589(5)	.2508(1)
CL1	.4376(7)	.024(1)	.2264(3)
C1	.446(3)	.567(4)	.096(1)
C2	.541(3)	.308(5)	.058(1)
O1	.467(2)	.729(3)	.109(1)
O2	.604(3)	.293(5)	.045(1)
C3	.818(3)	.387(4)	.233(1)
C4	.797(3)	.054(4)	.186(1)
O3	.833(2)	.540(3)	.222(1)
O4	.801(2)	-.021(4)	.1490(9)
C5	.261(2)	.107(2)	.0518(7)
C6	.208(2)	.284(2)	.0534(7)
C7	.204(2)	.403(2)	.0068(7)
C8	.256(2)	.300(2)	-.0235(7)
C9	.292(2)	.117(2)	.0043(7)
C10	.144(3)	.598(4)	-.008(1)
C11	.897(2)	.226(2)	.3497(7)
C12	.788(2)	.114(2)	.3345(7)
C13	.799(2)	-.062(2)	.3101(7)
C14	.914(2)	-.059(2)	.3102(7)
C15	.975(2)	.119(2)	.3347(7)
C16	.927(3)	.410(4)	.380(1)

$[Cp'(CO)_2Mn]_2Bi(C_9H_6NS)$ (**5 c**): Identical reaction conditions and workup procedure produced from the addition of DABCO [0.03 g (0.25 mmol)] and 8-mercaptoquinoline (C_9H_7NS) [0.08 g (0.5 mmol)] to **1 b** [0.32 g (0.5 mmol)] black crystals of **5 c** [yield 0.19 g (50%)]. – IR (CH_2Cl_2): $\tilde{\nu}$ = 1946 cm^{-1} m, 1916 s, 1881 s [ν(CO)]. – ^1H NMR ($CDCl_3$): δ = 1.72 (s, 6 H), 4.41 (m, 4 H), 4.76 (m, 4 H), 7,28–8.85 (m, 6 H).

$C_{25}H_{20}Mn_2BiNO_4S$ (749.36) Calcd. C 40.07 H 2.69 N 1.87
Found C 39.88 H 2.72 N 1.87

Table 2. Atomic coordinates for **5 b**

ATOM	X/A	Y/B	Z/C
BI1	.48963(5)	.35867(4)	.80945(3)
MN1	.6330(2)	.4756(1)	.7439(1)
MN2	.2555(2)	.1906(1)	.6959(1)
N1	.6437(9)	.1965(8)	.8506(8)
O1	.5976(8)	.4218(6)	1.0283(5)
C1	.715(1)	.2318(9)	.9787(8)
C2	.810(1)	.150(1)	1.0196(9)
C3	.888(1)	.194(1)	1.154(1)
C4	.868(1)	.312(1)	1.242(1)
C5	.770(1)	.390(1)	1.1994(9)
C6	.692(1)	.3526(9)	1.0688(8)
C7	.654(1)	.083(1)	.763(1)
C8	.743(1)	-.006(1)	.796(1)
C9	.818(1)	.027(1)	.924(1)
C11	.556(1)	.628(1)	.7722(9)
C12	.498(1)	.379(1)	.5824(9)
O11	.512(1)	.7277(8)	.7885(9)
O12	.417(1)	.3179(9)	.4781(7)
C13	.801(1)	.365(1)	.745(1)
C14	.837(1)	.464(1)	.872(1)
C15	.842(1)	.598(1)	.877(1)
C16	.810(1)	.578(1)	.749(1)
C17	.787(1)	.431(1)	.667(1)
C18	.768(2)	.369(1)	.531(1)
C21	.177(1)	.258(1)	.585(1)
C22	.312(1)	.066(1)	.5887(9)
O21	.120(1)	.2954(9)	.5062(8)
O22	.338(1)	-.0211(9)	.5139(8)
C23	.260(1)	.238(1)	.879(1)
C24	.132(1)	.265(1)	.801(1)
C25	.058(1)	.133(1)	.688(1)
C26	.140(1)	.031(1)	.698(1)
C27	.267(1)	.095(1)	.817(1)
C28	.381(2)	.020(1)	.865(1)

$[\{Cp'(CO)_2Mn\}_2Bi(bpy)][CF_3SO_3]$ (**7**): Treatment of **1 b** [0.20 g (0.32 mmol)] in CH_2Cl_2 (20 ml) at −15°C with $Me_3SiOSO_2CF_3$ [1.0 ml (excess)] resulted in a gradual colour change from dark green to red-brown. Removal of the solvent in vacuo at −10°C gave a black oil which was washed with cold (−20°C) pentane (3 × 10 ml) and dried under vacuum. The resulting residue was redissolved in CH_2Cl_2 (10 ml), and bpy [0.05 g (0.32 mmol)] was added to the red-brown solution. The reaction mixture was allowed to warm to room temperature over the course of 1 h, during which time the colour changed to dark red. Removal of the solvent in vacuo gave a dark red oily residue which was extracted with CH_2Cl_2 (3 × 10 ml), and the residues were filtered through a Kieselgur pad (5 cm). The solvent was removed in vacuo from the dark red eluate obtained and the residue recrystallised from CH_2Cl_2/pentane at −30°C to give red crystals of 7 [yield 0.06 g (22%)]. – IR (CH_2Cl_2): $\tilde{\nu}$ = 1951 cm^{-1} m, 1936 s, 1894 m [ν(CO)]. – ^1H NMR (CD_2Cl_2):

δ = 1.85 (s, 6 H), 4.54 (m, 4 H), 4.78 (m, 4 H), 8.01 (t, 2 H), 8.56 (t, 2 H), 8.80 (d, 2 H), 9.12 (d, 2 H).

$C_{27}H_{22}BiF_3Mn_2N_2O_7S$ (894.39) Calcd. C 36.26 H 2.48 N 3.13
Found C 35.99 H 2.53 N 3.52

Table 3. Atomic coordinates for **5c**

ATOM	X/A	Y/B	Z/C
BI1	.9555(1)	.11966(5)	.23225(7)
MN1	1.0722(4)	.0920(2)	.3846(3)
MN2	.9218(4)	.0816(2)	.0853(3)
S1	.8079(7)	.1900(4)	.2338(7)
N1	1.015(2)	.222(1)	.216(1)
C1	.945(3)	.269(1)	.216(2)
C2	.983(3)	.325(2)	.210(2)
C3	.919(3)	.373(1)	.214(2)
C4	.837(3)	.366(2)	.230(2)
C5	.801(2)	.311(2)	.238(2)
C6	.855(2)	.259(1)	.230(2)
C7	1.071(3)	.329(1)	.197(2)
C8	1.135(3)	.282(2)	.191(2)
C9	1.101(3)	.229(2)	.207(2)
C10	1.155(4)	.053(2)	.342(3)
O11	1.204(3)	.019(2)	.328(2)
C12	.997(3)	.030(2)	.377(2)
O12	.950(2)	-.010(1)	.378(2)
C13	1.211(2)	.125(1)	.488(2)
C14	1.153(2)	.171(1)	.433(2)
C15	1.053(2)	.172(1)	.435(2)
C16	1.051(2)	.126(1)	.491(2)
C17	1.149(2)	.098(1)	.523(2)
C18	1.323(4)	.101(2)	.508(2)
C21	1.060(4)	.080(2)	.112(2)
O21	1.142(2)	.073(1)	.125(2)
C22	.923(3)	.009(2)	.125(2)
O22	.915(3)	-.039(1)	.145(2)
C23	.761(2)	.090(1)	.003(2)
C24	.813(2)	.145(1)	.016(2)
C25	.888(2)	.141(1)	-.018(2)
C26	.883(2)	.084(1)	-.053(2)
C27	.804(2)	.053(1)	-.040(2)
C28	.970(4)	.176(2)	-.037(3)

Table 4. Crystal structure data for **1b**, **5b**, **5c**

	1b	**5b**	**5c**
Crystal-Parameter			
Empirical Formula	$C_{16}H_{14}BiClMn_2O_4$	$C_{25}H_{20}BiMn_2NO_5$	$C_{25}H_{20}BiMn_2NO_4S$
Formula Weight	624.59	733.29	749.36
Crystal System	Monoclinic	Triclinic	Monoclinic
Space Group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a, pm	1227.4(3)	1049.2(5)	1415.8(3)
b, pm	704.6(2)	1079.0(5)	2297.5(7)
c, pm	2499.1(6)	1265.1(6)	1698.5(3)
a, deg		114.76(3)	
b, deg	121.89(1)	113.35(3)	114.60(1)
c, deg		90.06(4)	
V, pm^3	1835.10^6	1179.10^6	5024.10^6
Z	4	2	4
d_{calc}, g cm^{-3}	2.261	2.082	1.982
F(000)	1168	700	2869
mμ(MoKα)mm^{-1}	11.08	8.6	8.09
Temp, °C	25	25	25
Measured Parameters			
Scan	ω	ω	ω
Scan width, ω	0.75	0.75	0.75
$2\Theta_{max}$, deg	50	54	54
Measured reflections	2554	5154	7918
Unique reflections	2002	4342	4128
Structure Solution	Direct Methods	Direct Methods	Direct Methods
Refinement			
Absorption correction	Empirical	Empirical	Empirical
Refined Parameters	147	309	229
R	0.0754	0.0532	0.0917
R_w	0.0673	0.0438	0.0757
Goodness of fit	4.57	3.17	3.00

X-ray Crystallographic Data: Crystal data and important numbers pertinent to data collection and refinement are collected in Table 4. The measurements were carried out with a Siemens/Nicolet P3-Diffractometer [Mo-K_α radiation (λ = 71.069 pm), graphite monochromator, solution and refinement with SHELXTL[23]].

The reflections of **5c** could be consistently indexed in a monoclinic cell, space group $P2_1/c$, a = 1415.8 (3), b = 2297.5 (7), c = 1698.5 (3) pm, β = 114.60 (1)°; this cell may be transformed into an orthorhombic one by the transformation (1,0,0; −1,0,−2; 0,1,0): a = 1415.8, b = 3088.8, c = 2297.5 pm. However, the symmetry of the diffraction pattern did not correspond to an orthorhombic space group. This information together with the information obtained by solving the strcuture of **5c** in the monoclinic space group clearly indicates twinning problems. The solution of the structure in the monoclinic space group is hence not really reliable as far as individual numerical values for the geometric parameters are concerned. The overall geometry of **5c** is nevertheless unequivocally defined as shown in Figure 4. Further details of the X-ray structure determinations for **1b** and **5b** are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, F.R.G., on quoting the depository number CSD-54225, the names of the authors and the journal citation.

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