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Hybrid Dibismuthines and Distibines: Preparation and Properties of Antimony and Bismuth Oxygen, Sulfur, and Nitrogen Donor Ligands

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The hybrid dibismuthines $O\{(CH_2)_2BiPh_2\}_2$, $MeN(CH_2\text{-}2\text{-}C_6H_4BiR_2)_2$, and $S(CH_2\text{-}2\text{-}C_6H_4BiR_2)_2$ (R = Me, Ph), have been prepared and characterized by microanalysis, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, and FAB mass spectrometry. The X-ray structures of $O\{(CH_2)_2BiPh_2\}_2$ and $S(CH_2\text{-}2\text{-}C_6H_4BiPh_2)_2$ show close to symmetrical hypervalent interactions between the O or S atoms and both bismuth centers. The antimony analogue $S(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2$ is quaternized by MeI to $[S(CH_2\text{-}2\text{-}C_6H_4SbMe_3)_2]I_2$, which also shows a hypervalent S···Sb interaction, but in this case to only a single antimony center. Complexes of these and related ligands with the $CpFe(CO)_2^+$ group, of the type $[\{CpFe(CO)_2\}_2L][BF_4]_2$ (L = $O\{(CH_2)_2BiPh_2\}_2$, $MeN(CH_2\text{-}2\text{-}C_6H_4BiR_2)_2$, $S(CH_2\text{-}2\text{-}C_6H_4BiR_2)_2$, $O\{(CH_2)_2SbR_2\}_2$, $S(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2$, $MeN(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2$, $Ph_2Sb(CH_2)_3SbPh_2$), have been prepared and characterized by microanalysis (antimony complexes only), ^1H and $^{13}C\{^1H\}$ NMR and IR spectroscopy, and ES^+ mass spectrometry. The X-ray crystal structure of $[\{CpFe(CO)_2\}_2\{O\{(CH_2)_2SbMe_2\}_2\}][BF_4]_2$ shows a hypervalent Sb···O contact to one of the antimony centers, whereas no hypervalent contacts are seen in the structure of $[\{CpFe(CO)_2\}_2\{MeN(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}][BF_4]_2$. IR (carbonyl region) and NMR spectroscopy indicate that, uniquely, $[\{CpFe(CO)_2\}_2\{MeN(CH_2\text{-}2\text{-}C_6H_4BiPh_2)_2\}][BF_4]_2$ shows hypervalent N···Bi interactions in both the solid and solution, but for the other dibismuthine complexes, there is evidence for inequivalence of the iron centers (and hence hypervalency) only in the solid state. Spectroscopic data indicate that hypervalent interactions are absent in $[\{CpFe(CO)_2\}_2\{MeN(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}][BF_4]_2$ and $[\{CpFe(CO)_2\}_2\{S(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}][BF_4]_2$, but present in solid $[\{CpFe(CO)_2\}_2\{O\{(CH_2)_2SbR_2\}_2\}][BF_4]_2$. The preparation and X-ray structure of $[CpFe(CO)_2\{BiPh_2(o\text{-}C_6H_4OMe)\}][BF_4]$ is also reported, but attempts to isolate $[CpFe(CO)_2(BiPhMe_2)]][BF_4]$ resulted in rapid scrambling of the substituents at bismuth to give $[CpFe(CO)_2(BiPh_{3-n}Me_n)][BF_4]$ (n = 0−3).

Introduction

The synthesis, coordination and organometallic chemistry of phosphine and, to a rather lesser extent, arsine ligands have been major research areas for the last 70 years. Detailed studies of the heavier analogues, stibines, have only been carried out in the last 25 years or so, the neglect partially reflecting the more difficult syntheses of the ligands but mostly due to the view that they were "similar but poorer" ligands in comparison to phosphines.[1,2] This viewpoint is no longer tenable, and tertiary stibines have a chemistry significantly different from that of their lighter analogues, most clearly demonstrated by the seminal work of Werner,[3] who prepared the first examples of bridging ER_3 (E = P, As, Sb) ligands with Sb^iPr_3 and who showed that metathesis with PR_3 or AsR_3 led to examples of these as bridging ligands, although the latter complexes cannot be obtained directly.[3] It is also clear that the organometallic chemistry supported by tertiary stibines is significantly different from that of the lighter analogues.[2] Although there is an extensive organic chemistry of bismuth,[4] bismuthine ligands have been very little studied, partially due to their poor σ-donor power and to the reactive C−Bi bonds which are prone to fission in the presence of some metals.[2] The majority of bismuthine complexes are with metal carbonyls and contain only symmetrical monodentate BiR_3 ligands;[2,5] only one dibismuthine, $p\text{-}Ph_2BiC_6H_4BiPh_2$, has been complexed (with Cr and W carbonyls),[6] and there are a few hybrid ligands containing bismuth in combination with O, N, P, etc.

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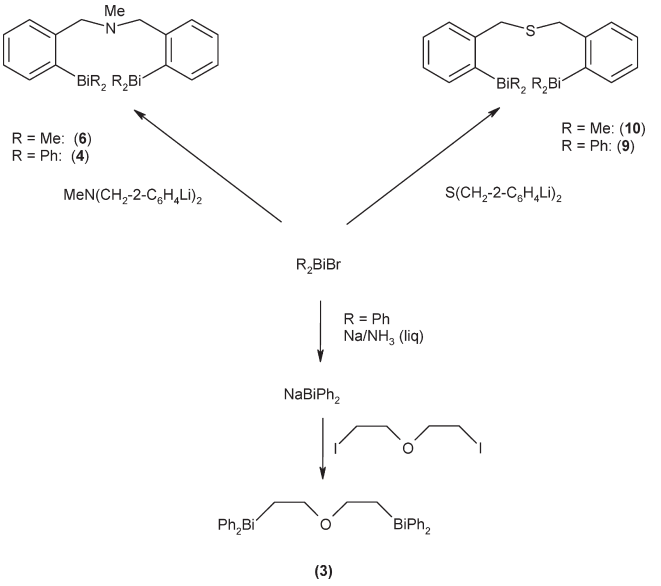
donor atoms,[1,7] although characterization of complexes of the last group has been poor by current standards. Here we report the synthesis of several new ligands containing two bismuthine groups in combination with a single O, N, or S donor atom and some antimony analogues and illustrate their chemistry by complexation to the $[(\eta^5\text{-Cp})Fe(CO)_2]^+$ acceptor unit. There is a great deal of current interest in hypervalent interactions N(O)···Bi(Sb) in organo-antimony and -bismuth compounds and their complexes,[8−10] and there is the possibility of using metal complexes of the bismuth ligands as precursors for bismuth−metal alloys or nanoparticles by thermal deposition techniques.

Results and Discussion

Polydentate Bismuth Ligands. The relative fragility of the Bi−C linkage, which is prone to both fission and scrambling of substituents on the bismuth center, necessitates the introduction of the bismuth groups in the final stage of the ligand syntheses and under carefully controlled (mild) conditions. We found that careful control of the reaction temperature, reagent stoichiometry, and reaction times were all key to obtaining pure samples of the bismuth ligands; relatively minor changes can result in very impure products and low yields. In the introduction of Ph_2Bi- groups, Ph_2BiBr (made by comproportionation of $BiBr_3$ and Ph_3Bi in a 1:2 ratio in diethyl ether solution) is the key reagent; Ph_2BiCl is poorly soluble, especially at low temperatures, and this causes insuperable problems in maintaining control of the reaction stoichiometry. Similarly, we used Me_2BiBr as the preferred source of Me_2Bi- groups; it is not necessary to isolate Me_2BiBr, which was made in situ in thf from $BiBr_3$ and MeLi (1:2) at −78 °C and used immediately. With the R_2BiBr reagents in hand, the two routes to hybrid polybismuthine ligands are either direct reaction with the appropriate lithio derivative or reaction with Na/liquid NH_3 to form $NaBiR_2$[11] and subsequent reaction with an organohalide (Scheme 1); where both routes appear feasible, the former is far preferable and gives higher yields.

Scheme 1. Hybrid Dibismuthine Ligands



$O\{(CH_2)_2BiPh_2\}_2$ (**3**) was obtained in good yield (55%) by reaction of $I(CH_2)_2O(CH_2)_2I$ with $NaBiPh_2$ in liquid ammonia. Use of $X(CH_2)_2O(CH_2)_2X$ (X = Cl, Br) results in incomplete substitution of the halide, indicative of poor nucleophilicity of the bismuthide ion. **3** is a white air-stable solid, but is air-sensitive in solution, readily identified by its ^1H and $^{13}C\{^1H\}$ NMR spectra (Experimental Section), although in contrast to most of the other ligands in this work, it showed only Ph_2Bi^+ and $PhBi^+$ as significant ions in the FAB mass spectrum. In contrast to corresponding P, As, and Sb ligands, neither quaternization with RX nor halogenation (to Bi(V) species) is possible.[4b,c] The structure of **3** (Figure 1) shows a pyramidal arrangement of organic groups about bismuth, with C−Bi−C angles less than 96°, consistent with the Bi−C bonds having high Bi 6p character,[2b,6] and the angle at the oxygen bridge C(15)−O(1)−C(14) is 112.1(4)°. The conformation shows close to symmetric hypervalent interactions between the oxygen and both bismuth atoms, Bi(1)···O(1) = 3.203(3) and Bi(2)···O(1) = 3.126(3) Å, which are within the sum of the van der Waals radii (3.52 Å).[12] Although hypervalent interactions between bismuth and heteroatoms such as O, N, and S are well established,[8] these usually involve a single bismuth center and are, as might be expected, markedly shorter than the present example.

Repeated attempts to isolate $O\{(CH_2)_2BiMe_2\}_2$ from the reaction of $NaBiMe_2$ with $I(CH_2)_2O(CH_2)_2I$ were unsuccessful, the reaction generating large amounts of elemental Bi and a complex mixture of organic fragments. Although $O\{(CH_2)_2SbMe_2\}_2$ is known and is stable in the absence of air, $O\{(CH_2)_2AsMe_2\}_2$ is unstable and cleaves readily at the C−O link on heating or reaction with metal salts to yield 2-(dimethylarsino)ethanol.[10]

Dilithiation of $MeN(CH_2\text{-}2\text{-}C_6H_4Br)_2$[81] with Bu^nLi in thf at −78 °C, followed by warming to room temperature and addition of powdered Ph_2BiBr, after careful workup gave $MeN(CH_2\text{-}2\text{-}C_6H_4BiPh_2)_2$ (**4**) as a pale yellow powder in

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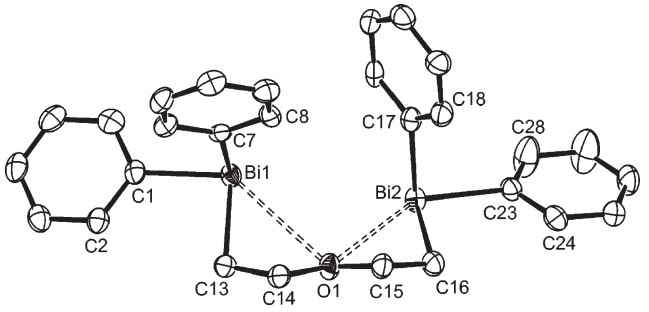

Figure 1. Structure of $O\{(CH_2)_2BiPh_2\}_2$ with the atom-numbering scheme. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Bi1−C1 = 2.254(5), Bi1−C7 = 2.264(5), Bi1−C13 = 2.280(5), Bi2−C17 = 2.256(5), Bi2−C23 = 2.258(5), Bi2−C16 = 2.262(5), O1−C14 = 1.430(6), O1−C15 = 1.421(6), Bi1···O1 = 3.203(3), Bi2···O1 = 3.126(3); C−Bi−C = 89.89(17)−95.27(19), C15−O1−C14 = 112.1(4).

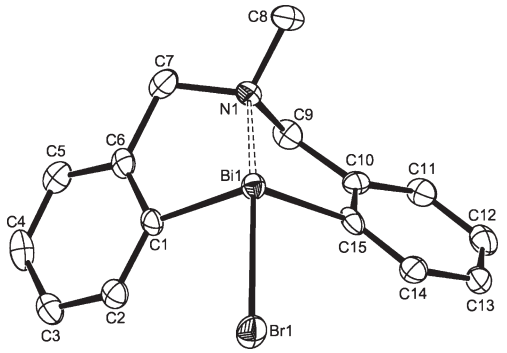

Figure 2. Structure of $MeN(CH_2\text{-}2\text{-}C_6H_4)_2BiBr$ with the atom-numbering scheme. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Bi1−C1 = 2.251(6), Bi1−C15 = 2.240(6), Bi1···N1 = 2.503(5), Bi1−Br1 = 2.8007(7), N1−C7 = 1.479(7), N1−C8 = 1.476(7), N1−C9 = 1.472(7); C15−Bi1−C1 = 99.1(2), C15−Bi1−N1 = 73.9(2), C1−Bi1−N1 = 72.3(2), C15−Bi1−Br1 = 93.4(2), C1−Bi1−Br1 = 91.43(15), N1−Bi1−Br1 = 157.00(11).

modest yield (27%). The identity of the product was confirmed by the ^1H and $^{13}C\{^1H\}$ NMR spectra, the latter showing resonances at δ 42.21 (CH_3N) and 66.95 (CH_2N) and 10 distinct aromatic carbon resonances, including two assigned as BiC_{ipso}. The CI mass spectrum showed the highest significant ion at m/z 857, corresponding to $[P - Ph]^+$. A small amount of white crystalline material isolated from the diethyl ether solution of the crude ligand was found to be the small-ring bromoazabismocine $MeN(CH_2\text{-}2\text{-}C_6H_4)_2BiBr$ (**5**), which probably arises from some residual $BiBr_3$ impurity in the Ph_2BiBr. The structure (Figure 2) is similar to that in other azabismocines[8m] and shows a distorted-trigonal-bipyramidal geometry about bismuth with a vacant equatorial vertex. The hypervalent Bi(1)···N(1) distance (2.503(5) Å) lies at the shorter end of the range in related complexes (2.517(4)−2.764(5) Å).[8m,13]

The corresponding reaction of $MeN(CH_2\text{-}2\text{-}C_6H_4Li)_2$ with Me_2BiBr in thf, initially at −78 °C, followed by warming of the mixture to room temperature and workup, gave $MeN(CH_2\text{-}2\text{-}C_6H_4BiMe_2)_2$ (**6**) as an air-sensitive yellow oil

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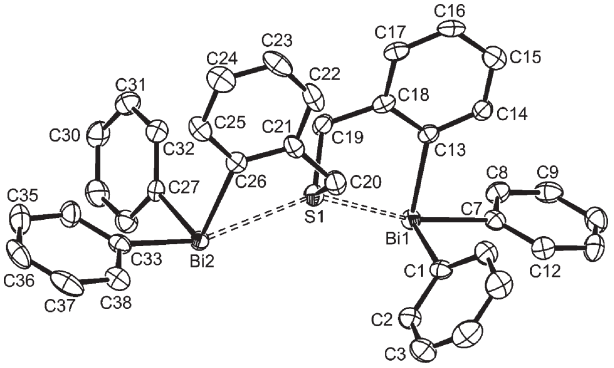

Figure 3. Structure of $S(CH_2\text{-}2\text{-}C_6H_4BiPh_2)_2$ with the atom-numbering scheme. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Bi1−C1 = 2.249(5), Bi1−C7 = 2.267(4), Bi1−C13 = 2.275(4), Bi1···S1 = 3.3254(12), Bi2−C26 = 2.272(4), Bi2−C27 = 2.246(4), Bi2−C33 = 2.259(4), Bi2···S1 = 3.3013(12), S1−C19 = 1.805(5), S1−C20 = 1.811(5); C1−Bi1−C7 = 97.0(2), C1−Bi1−C13 = 92.84(15), C7−Bi1−C13 = 94.06(15), C27−Bi2−C33 = 92.7(2), C27−Bi2−C26 = 94.9(2), C33−Bi2−C26 = 94.86(15), C19−S1−C20 = 101.4(2), Bi2···S1···Bi1 = 147.84(4).

in ~20% yield. The identity in this case was confirmed by the ^1H and $^{13}C\{^1H\}$ NMR spectra, which, in addition to the diagnostic resonances associated with the $-C_6H_4CH_2N(Me)CH_2C_6H_4-$ linker, showed singlet Me_2Bi resonances at δ 1.1 (^1H) and δ 2.91 ($^{13}C\{^1H\}$). The FAB mass spectrum shows $[P]^+$ and $[P - Me]^+$. Careful examination of the NMR spectra showed that some samples contain small amounts (< 5%) of a second species, which was identified as the small-ring azabismocine $MeN(CH_2\text{-}2\text{-}C_6H_4)_2BiMe$ (**7**), i.e. the Me-substituted analogue of **5**, which may result either from scrambling or from some $MeBiBr_2$ in the bismuth reagent.

The sulfur-bridged ligand $S(CH_2\text{-}2\text{-}C_6H_4BiPh_2)_2$ (**9**) was obtained similarly from $S(CH_2\text{-}2\text{-}C_6H_4Br)_2$, MeLi, and Ph_2BiBr as a white solid in 33% yield. The NMR and FAB mass spectra are consistent with the formulation (Experimental Section), and in this case white crystals were obtained from toluene solution. The structure (Figure 3) again shows a pyramidal BiC_3 unit, with angles consistent with predominantly Bi 6p character in the Bi−C bonds.[2b,6] There are hypervalent Bi···S interactions involving both bismuth centers, Bi(1)···S(1) = 3.3254(12) Å, Bi(2)···S(1) = 3.3013(12) Å, and Bi(2)···S(1)···Bi(1) = 147.84(4)°; the Bi···S interactions are, as expected, significantly longer than in thiabismocines containing a single hypervalent link, which are typically < 3.0 Å,[8m] but are still well within the sum of the van der Waals radii (3.8 Å).[12] The corresponding dimethylbismuth ligand $S(CH_2\text{-}2\text{-}C_6H_4BiMe_2)_2$ (**10**) was obtained similarly to **9**, although in rather poor yield, as a very air-sensitive yellow oil.

The antimony analogue of **10**, $S(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2$ (**11**), was obtained as an air-sensitive yellow oil in 68% yield, the much higher yield being typical of ligands with stronger C−Sb bonds, illustrating further the sensitivity of the C−Bi linkages. Ligand **11** was thoroughly characterized by spectroscopy (Experimental Section), and (in contrast with the bismuth ligands) by quaternization with MeI to the distibonium salt $[S(CH_2\text{-}2\text{-}C_6H_4SbMe_3)_2]I_2$ (**11b**). The structure of the latter (Figure 4) confirms the identity of the parent ligand and also reveals the hypervalent interaction Sb(1)···S(1) = 3.555(2) Å,

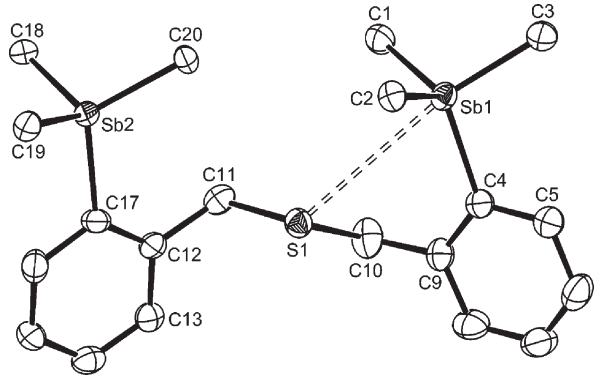

Figure 4. Structure of the dication in $[S(CH_2\text{-}2\text{-}C_6H_4SbMe_3)_2]I_2$ with the atom-numbering scheme. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sb1−C1 = 2.094(6), Sb1−C2 = 2.103(6), Sb1−C3 = 2.102(6), Sb1−C4 = 2.122(6), Sb2−C17 = 2.106(6), Sb2−C18 = 2.097(6), Sb2−C19 = 2.094(6), Sb2−C20 = 2.087(6), S1−C10 = 1.816(6), S1−C11 = 1.837(6), Sb1···S1 = 3.554; C1−Sb1−C2 = 110.7(2), C1−Sb1−C3 = 106.5(3), C2−Sb1−C3 = 106.6(2), C1−Sb1−C4 = 117.3(3), C3−Sb1−C4 = 103.8(2), C2−Sb1−C4 = 111.0(2), C19−Sb2−C20 = 111.8(3), C18−Sb2−C19 = 109.2(2), C18−Sb2−C20 = 108.3(2), C17−Sb2−C18 = 106.9(2), C17−Sb2−C19 = 105.6(2), C17−Sb2−C20 = 114.8(2), C10−S1−C11 = 99.4(3).

whereas Sb(2)···S(1) = 4.419(2) Å; the latter is significantly greater than the sum of the van der Waals radii (3.80 Å). The antimony analogues of **3**, **6**, and also $O\{(CH_2)_2SbMe_2\}_2$ have been described previously.[9,10]

Complexes with $[CpFe(CO)_2]^+$. The [dicarbonyl(η^5-cyclopentadienyl)iron]$^+$ fragment was chosen as the Lewis acid center to explore the coordination of these new bismuthine ligands initially, since it provides a labile binding site (through substitution of the thf ligand in $[CpFe(CO)_2(thf)]^+$) likely to be required for substitution by the bismuthine and contains several reporter groups in the IR and NMR spectra, and also two polymorphs of the relatively stable $[CpFe(CO)_2(BiPh_3)]BF_4$ have been characterized by X-ray crystallography previously, providing an experimental comparison for the present work.[5a,6]

The syntheses involved generation of $[CpFe(CO)_2(thf)]BF_4$ initially from $[CpFe(CO)_2I]$, thf, and $AgBF_4$, in anhydrous CH_2Cl_2 solution (the weak donor bismuthine ligands do not coordinate to the iron in the presence of a large excess of thf, e.g. in thf solution, nor do they displace the iodide from the starting material directly).[5a] The temperature at which the reaction is carried out is also critical; for ligands containing Me_2Bi− donor groups a CH_2Cl_2 solution of the ligand was added to a solution of $[CpFe(CO)_2(thf)]BF_4$ in anhydrous CH_2Cl_2 at −78 °C and the mixture was stirred overnight, as it was slowly warmed to near-ambient temperature. The complex was then quickly isolated and stored in a freezer at −18 °C, although even in a freezer slow decomposition occurs (over a few days). If the reaction was carried out at room temperature, there was extensive decomposition, some black solid precipitate formed (Bi?), and scrambling of the groups on the bismuth center was observed. In contrast, those ligands containing Ph_2Bi− groups did not react with a solution of $[CpFe(CO)_2(thf)]BF_4$ in anhydrous CH_2Cl_2 at −78 °C, and hence the reactions were conducted at room temperature. These complexes were much less prone to decomposition, although measurements were always made on freshly prepared

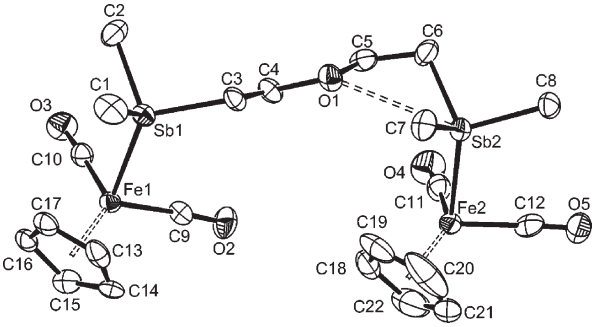

Figure 5. Structure of the dication in $[\{CpFe(CO)_2\}_2\{O\{(CH_2)_2SbMe_2\}_2\}][BF_4]_2$ with the atom-numbering scheme. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe1−C9 = 1.788(12), Fe1−C10 = 1.784(12), Fe1−C(Cp) = 2.065(11)−2.096(11), Fe1−Sb1 = 2.4846(18), Fe2−C11 = 1.778(13), Fe2−C12 = 1.799(14), Fe2−C(Cp) = 2.057(14)−2.091(13), Fe2−Sb2 = 2.4870(19), O1···Sb1 = 4.363(8), O1···Sb2 = 3.184(8); C9−Fe1−C10 = 95.9(5), C9−Fe1−Sb1 = 93.4(4), C10−Fe1−Sb1 = 90.5(4), C11−Fe2−C12 = 95.4(5), C11−Fe2−Sb2 = 94.1(4), C12−Fe2−Sb2 = 88.1(4).

solutions. In contrast, the antimony ligand complexes were prepared at room temperature and are more robust; no significant scrambling of substituents or decomposition was observed even after several hours in solution at room temperature. The bismuthine complexes proved to be too unstable at room temperature to obtain reproducible microanalyses, and the purity of the products was therefore judged by spectroscopic measurements on freshly prepared samples, an approach used by other workers on metal bismuthine complexes.[5a,c,d] In contrast, microanalytical data on the stibine complexes were obtained without problems. The fragility of the hybrid dibismuthine ligand complexes frustrated our attempts to obtain X-ray crystal structures; however, two structures of the complexed distibine analogues were obtained.

The structure of $[\{CpFe(CO)_2\}_2\{O\{(CH_2)_2SbMe_2\}_2\}][BF_4]_2$ (**18**) (Figure 5) shows the antimony ligand bridging two $CpFe(CO)_2$ moieties via Sb, with the hypervalent interaction O···Sb(2) = 3.184(8) Å, whereas the O···Sb(1) distance is 4.363(8) Å, showing no interaction (van der Waals radii sum 3.60 Å). There are no significant differences in the bond lengths of the two iron units, which suggests that the hypervalent interaction is weak and does not lead to significant differences in the electronic environment at the metal centers.

The structure of $[\{CpFe(CO)_2\}_2\{MeN(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}][BF_4]_2$ (**17**) (Figure 6) again shows the ligand coordinated via antimony to two $[CpFe(CO)_2]^+$ units, and in this case there is no hypervalent interaction (Sb···N > 4.85 Å)—the sum of the van der Waals radii in this case is 3.74 Å. Presumably in this case the small energy gain to be made by a hypervalent interaction, which would require some conformational change in the molecule, is less than the energy obtained from packing the molecules in the form found.

The key spectroscopic data for the complexes are summarized in Table 1, the NMR data for the bismuthine complexes being recorded at 223 K to slow decomposition in solution. Apart from those for $[\{CpFe(CO)_2\}_2\{MeN(CH_2\text{-}2\text{-}C_6H_4BiPh_2)_2\}][BF_4]_2$ (**15**), discussed below, the solution spectroscopic data are generally similar, with $\delta(^{13}C)$ of the Cp carbons and the CO groups covering small ranges, although for directly comparable compounds the carbonyl resonances are at higher

frequency in the bismuthine systems compared to in the stibines, consistent with weaker donation by the former. The two carbonyl stretching frequencies ($A_1 + B_1$) of the complexes in CH_2Cl_2 solution show decreases of between 10 and 20 cm^{-1} on replacing Bi by Sb in comparable ligand frameworks, showing the usual trends in group 15 ligand chemistry.[2,5] Much more interesting are the IR spectra in the carbonyl region, recorded as Nujol mulls (Table 1). All of the dibismuthine ligand complexes and the two distibine complexes **18** and **19** show three or four carbonyl stretching vibrations, consistent with the presence of inequivalent iron centers resulting from hypervalent interactions (four stretches are expected—where only three are observed, this is attributed to accidental coincidence). In contrast, complexes **17** and **20** show only two carbonyl stretching vibrations, due to the absence of hypervalent interactions (confirmed for **20** by the X-ray structure above). The model complex $[\{CpFe(CO)_2\}_2\{Ph_2Sb(CH_2)_3SbPh_2\}][BF_4]_2$ (**22**), which contains no heteroatom to make a hypervalent contact, has an IR spectrum in the carbonyl region very similar to those of **17** and **20**, confirming this deduction. The presence of inequivalent iron centers in some of the solid complexes due to hypervalency, which appears to be lost in solution, is further evidence for the weakness of the hypervalent coordination. The complex $[\{CpFe(CO)_2\}_2\{MeN(CH_2\text{-}2\text{-}C_6H_4BiPh_2)_2\}][BF_4]_2$ (**15**) is unique in this series in that it shows hypervalent interactions both as the solid and in solution in CH_2Cl_2. In addition to the presence of four ν(CO) bands in the solution IR spectrum, the $^{13}C\{^1H\}$ NMR spectrum at 223 K shows two carbonyl resonances and two very closely spaced Cp resonances of equal intensity. This is readily explained by a hypervalent N···Bi interaction involving one bismuth center which is retained in solution. Why this complex alone should show the retention of the hypervalent interaction in solution is less clear. The data in Table 1 show that hypervalence is more common (and presumably a stronger interaction) in bismuth systems compared with antimony, but whether the interaction remains in solution will depend upon small differences in energy of the various ligand conformations possible in these bridged systems, only some of which are suitably oriented to retain the interaction. In contrast to the uncomplexed ligand structures described above, it seems that steric factors prevent interaction of the heteroatom with both Sb and Bi centers in the metal complexes.

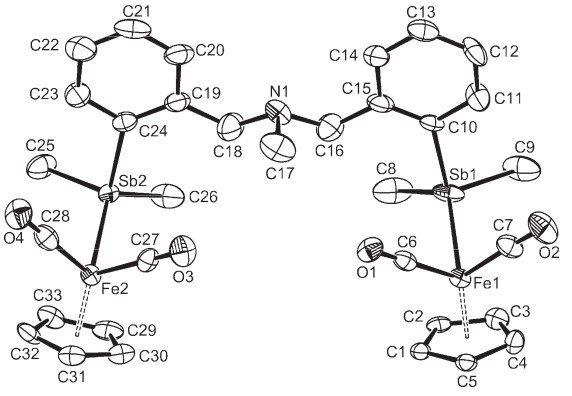

Figure 6. Structure of the dication in $[\{CpFe(CO)_2\}_2\{MeN(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}][BF_4]_2 \cdot {}^1/_2CH_2Cl_2$ with the atom-numbering scheme. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe1−Sb1 = 2.4669(14), Fe1−C6 = 1.777(10), Fe1−C7 = 1.777(10), Fe1−C(Cp) = 2.081(10)−2.103(8), Fe2−Sb2 = 2.4780(14), Fe2−C27 = 1.772(10), Fe2−C28 = 1.771(11), Fe2−C(Cp) = 2.075(10)−2.101(9); C6−Fe1−C7 = 92.8(5), C6−Fe1−Sb1 = 92.2(3), C7−Fe1−Sb1 = 91.2(3), C27−Fe2−C28 = 91.0(4), C27−Fe2−Sb2 = 91.9(3), C28−Fe2−Sb2 = 92.2(3).

$[CpFe(CO)_2L]BF_4$ (L = $SbMe_2Ph$, $BiPh_2(o\text{-}C_6H_4OMe)$, $BiMe_2Ph$, $BiPh_3$). As mentioned in the Introduction, almost all known complexes of tertiary bismuthines contain the symmetrically substituted monobismuthine ligands BiR_3. Since the hybrid dibismuthines described above contain two different substituents at the bismuth, we also briefly explored the reactions of $BiPh_2(o\text{-}C_6H_4OMe)$ and $BiMe_2Ph$ with the $CpFe(CO)_2^+$ acceptor group. $[CpFe(CO)_2(SbMe_2Ph)]BF_4$ (**21**) was made as a model complex for comparison purposes, and its structure (Figure 7) was determined. The bond lengths and angles and the spectroscopic properties are unexceptional, but notably, the complex is stable in CH_2Cl_2 solution.

In contrast, the reaction of $[CpFe(CO)_2(thf)]^+$ with $BiMe_2Ph$ under a variety of reaction conditions, e.g. performing the reaction at temperatures varying from 195 K to ambient, in the dark, and with different reaction times, gave red waxy solids which were found by NMR spectroscopy and ES^+ mass spectrometry (Experimental Section) to be mixtures containing all possible R group combinations on bismuth: viz., $[CpFe(CO)_2(BiMe_2Ph)]^+$, $[CpFe(CO)_2(BiMe_3)]^+$, $[CpFe(CO)_2(BiMePh_2)]^+$,

Table 1. Selected Spectroscopic Data for $[\{CpFe(CO)_2\}_nL][BF_4]_n$

	ν(CO)/cm^{-1}		$^{13}C\{^1H\}$ NMR[a]	
complex	chlorocarbon soln	Nujol	δ(Cp)	δ(CO)
12	2063, 2020	2062, 2021, 2007 (sh)	86.3	209.5
13	2067, 2020	2071, 2055, 2023	85.3	210.0
14	2072, 2020	2068, 2015, 2005	86.2	209.6
15	2070, 2055, 2022, 1998	2065, 2040, 2020, 2003	85.4, 85.5	210.2, 211.1
16	2071, 2024	2071, 2043, 2017, 2004	86.6	209.6
17	2045, 2001	2040, 1992	86.1	209.7
18	2044, 2000[b]	2041, 2034, 2005, 1993	86.3	210.7
19	2050, 2006	2044, 2002 (sh), 1996	86.3	209.2
20	2049, 2002	2039, 1998	86.0	209.0
21	2046, 2002	2041, 1999	85.7	209.3
22	2048, 2005	2042, 1992	85.9	208.9
23	2057, 2001	2041, 2001	86.7	209.4
24	2057, 2013	2044, 1997	86.5	209.3
$[CpFe(CO)_2(thf)][BF_4]$[c]	2065, 2019		85.8	208.9

[a] Conditions: chlorocarbon solution, Bi ligand complexes at 223 K, Sb complexes at 295 K. [b] Spectrum recorded in MeCN due to poor solubility in chlorocarbons. [c] Data from: Reger, D. L.; Coleman, C. *J. Organomet. Chem.* **1977**, *131*, 153.

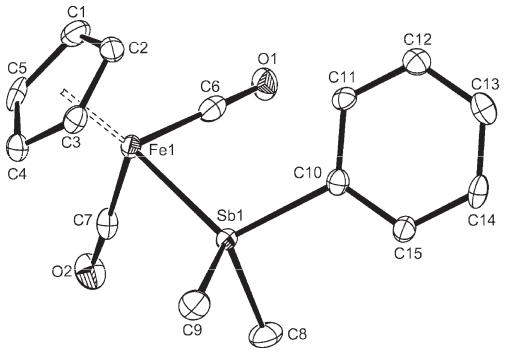

Figure 7. Structure of the dication in $[CpFe(CO)_2(SbPhMe_2)][BF_4]$ with the atom-numbering scheme. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sb1−Fe1 = 2.4846(7), Fe1−C6 = 1.776(4), Fe1−C7 = 1.770(4), Fe−C(Cp) = 2.088(4)−2.118(4); C6−Fe1−C7 = 93.7(2), C6−Fe1−Sb1 = 89.10(13), C7−Fe1−Sb1 = 89.72(13).

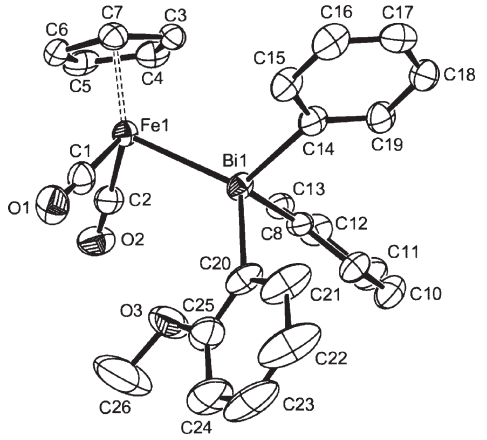

Figure 8. Structure of the dication in $[CpFe(CO)_2\{BiPh_2(o\text{-}C_6H_4OMe)\}][BF_4]\cdot 0.9CH_2Cl_2$ with the atom-numbering scheme. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe1−C1 = 1.780(7), Fe1−C2 = 1.776(7), Fe1−C(Cp) = 2.072(6)−2.112(6), Fe1−Bi1 = 2.5631(9); C1−Fe1−C2 = 92.2(3), C1−Fe1−Bi1 = 92.5(2), C2−Fe1−Bi1 = 91.6(2).

and $[CpFe(CO)_2(BiPh_3)]^+$. Reaction of $[CpFe(CO)_2(thf)]^+$ with $BiPh_2(o\text{-}C_6H_4OMe)$ was more successful in that $[CpFe(CO)_2\{BiPh_2(o\text{-}C_6H_4OMe)\}]BF_4$ was isolated as red crystals, although small amounts of $[CpFe(CO)_2\{BiPh_{3-n}(o\text{-}C_6H_4OMe)_n\}]BF_4$ (n = 0, 2, 3) were also detected in the crude product and scrambling occurred when CH_2Cl_2 solutions of $[CpFe(CO)_2\{BiPh_2(o\text{-}C_6H_4OMe)\}]BF_4$ were allowed to stand. However, the crystal structure of $[CpFe(CO)_2\{BiPh_2(o\text{-}C_6H_4OMe)\}]BF_4$ was determined and shows (Figure 8) the expected geometry; it is the first crystallographically characterized example of a metal complex with an unsymmetrically substituted monodentate bismuthine. In the course of this work we also reprepared $[CpFe(CO)_2(BiPh_3)]BF_4$ as red crystals, which proved to be the dichloromethane solvate (1:1). There are no significant differences in the bond lengths and angles about the Fe and Bi in the present solvate compared to those in the two published polymorphs.[5a,6] The data are presented in the Supporting Information.

Conclusions

Preparative routes to a series of new hybrid dibismuthines and distibines containing O-, N-, and S-donor atoms and bearing either terminal phenyl or methyl substituents have been developed. Reaction of these ligands with $[CpFe(CO)_2(thf)][BF_4]$ leads to coordination via the Bi or Sb donor atoms only, yielding ligand-bridged complexes. Spectroscopic and structural studies reveal hypervalent Bi/Sb···O/N/S interactions in several of the ligands and also in all but two of the complexes. The $[CpFe(CO)_2]^+$ fragment, which is bonded only to Sb or Bi, has allowed us to probe the hypervalent O/N/S···Sb/Bi interactions and particularly whether these are retained in solution. There is considerable disparity in the strength of these interactions, from strong (and evident both in the solid state and in solution) for $[\{CpFe(CO)_2\}_2\{MeN(CH_2\text{-}2\text{-}C_6H_4BiPh_2)_2\}][BF_4]_2$ to weaker (and only observed in the solid state) in the other dibismuthine complexes, while no hypervalency is evident in $[\{CpFe(CO)_2\}_2\{MeN(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}][BF_4]_2$ (X-ray and IR spectroscopic evidence) or $[\{CpFe(CO)_2\}_2\{S(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}][BF_4]_2$ (IR spectroscopic evidence). The bismuthine complexes also represent the first examples with unsymmetrical substituents at Bi.

Experimental Section

Infrared spectra were recorded as Nujol mulls between NaCl plates using a Perkin-Elmer Spectrum 100 spectrometer over the range 4000−500 cm^{-1}, and solution spectra used NaCl solution cells over the range 2200−1800 cm^{-1}. ^1H NMR spectra were recorded from $CDCl_3$ solutions using a Bruker AV300 spectrometer, and ^1H and $^{13}C\{^1H\}$ NMR spectra of the complexes were recorded from $CDCl_3$ or CD_2Cl_2 solutions using a Bruker DPX400 spectrometer and are referenced to the residual solvent signal. NMR spectra of all of the ligands and antimony ligand complexes were recorded at ambient temperature (295 K) unless otherwise stated, but spectra of complexes of the bismuth ligands were routinely run at 223 K, due to the limited solution stability of these complexes, especially over the several hours necessary to obtain $^{13}C\{^1H\}$ NMR data. Microanalyses on new complexes were outsourced to Medac Ltd. The thermal instability of the iron carbonyl complexes of the bismuth ligands precluded outsourced microanalysis. FAB mass spectra (3-NOBA matrix) were obtained from Medac Ltd. and positive ion electrospray (ES^+) in MeCN solution using a VG Biotech platform. Preparations were undertaken using standard Schlenk and glovebox techniques under a N_2 atmosphere. Solvents were dried by distillation from CaH_2 (CH_2Cl_2) or Na/benzophenone ketyl (thf, hexane, and diethyl ether).

$O\{(CH_2)_2SbR_2\}_2$ (R = Me, Ph),[10] $MeN(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2$,[9] $SbPh_2Cl$,[14] $SbMe_2Ph$,[14] $Ph_2Sb(CH_2)_3SbPh_2$,[15] $BiMe_2Ph$,[11b] and $BiPh_2(o\text{-}C_6H_4OMe)$[7b] were made as described previously.

Ph_2BiBr (1). Triphenylbismuth (29.8 g, 67.8 mmol) was dissolved in diethyl ether (100 mL), and bismuth tribromide (15.2 g, 33.9 mmol) in diethyl ether (100 mL) was added. The reaction mixture was stirred for 16 h and concentrated to ∼20 mL, giving a pale yellow solid and a faintly yellow solution. The solids were isolated by filtration and dried in vacuo. Yield: 14.3 g, 95%. ^1H NMR ($CDCl_3$): δ 7.3 (m, [2H], Ph), 7.6 (m, [4H], Ph), 8.1 (m, [4H], Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 129.67, 132.79, 138.12 ($C_{aromatic}$), 157.87 (BiC_{ipso}).

Me_2BiBr (2). For all ligand preparations this was made and used in situ. Bismuth bromide (3.0 g, 6.7 mmol) was dissolved in

(14) Levason, W.; Matthews, M. L.; Reid, G.; Webster, M. *Dalton Trans.* **2004**, 51.
(15) Sato, S.; Matsumura, Y.; Okawara, R. *J. Organomet. Chem.* **1972**, *43*, 333.

Table 2. Crystal Data and Structure Refinement Details[a]

	$\{O(CH_2)_2BiPh_2\}_2$ (**3**)	$MeN(CH_2\text{-}2\text{-}C_6H_4)_2BiBr$ (**5**)	$S(CH_2\text{-}2\text{-}C_6H_4BiPh_2)_2$ (**9**)	$[S(CH_2\text{-}2\text{-}C_6H_4SbMe_3)_2]I_2$ (**11b**)
formula	$C_{28}H_{28}Bi_2O$	$C_{15}H_{15}BiBrN$	$C_{38}H_{32}Bi_2S$	$C_{20}H_{30}I_2SSb_2$
M_w	798.46	498.17	938.66	799.80
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a (Å)	8.0582(10)	8.2155(10)	11.2692(10)	12.047(2)
b (Å)	10.6596(15)	12.371(2)	12.8951(10)	8.0567(15)
c (Å)	15.370(2)	13.950(2)	22.4136(15)	26.471(5)
α (deg)	81.788(10)	90	90	90
β (deg)	86.311(10)	95.362(10)	101.793(4)	100.379(7)
γ (deg)	73.351(10)	90	90	90
U (Å^3)	1251.6(3)	1411.6(4)	3188.3(4)	2527.1(8)
Z	2	4	4	4
μ(Mo Kα) (mm^{-1})	14.06	15.30	11.11	4.67
total no. of rflns	26 661	21 119	45 794	21 722
no. of unique rflns	5713	3238	7317	5737
R_{int}	0.033	0.068	0.054	0.036
no. of params, restraints	280, 0	154, 0	370, 0	232, 0
R1[b] ($I_o > 2\sigma(I_o)$)	0.027	0.036	0.029	0.043
R1 (all data)	0.041	0.048	0.037	0.055
wR2[b] ($I_o > 2\sigma(I_o)$)	0.048	0.069	0.058	0.084
wR2 (all data)	0.053	0.074	0.061	0.090
	$[\{CpFe(CO)_2\}_2\{\{O(CH_2)_2\text{-}SbMe_2\}_2\}][BF_4]_2$ (**18**)	$[\{CpFe(CO)_2\}_2\{MeN\text{-}(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}][BF_4]_2\cdot{}^1/_2CH_2Cl_2$ (**17**)	$[CpFe(CO)_2(SbPhMe_2)][BF_4]$ (**21**)	$[CpFe(CO)_2\{BiPh_2\text{-}(o\text{-}C_6H_4OMe)\}][BF_4]\cdot 0.9CH_2Cl_2$ (**23**)
formula	$C_{22}H_{30}B_2F_8Fe_2O_5Sb_2$	$C_{33.5}H_{38}B_2ClF_8Fe_2NO_4Sb_2$	$C_{15}H_{16}BF_4FeO_2Sb$	$C_{26.9}H_{23.8}BBiCl_{1.8}F_4FeO_3$
M_w	903.28	1082.92	492.69	810.51
cryst syst	monoclinic	triclinic	orthorhombic	triclinic
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_12_12_1$ (No. 19)	$P\bar{1}$ (No. 2)
a (Å)	8.0949(15)	10.5977(10)	6.9012(10)	10.481(2)
b (Å)	14.664(3)	11.799(2)	13.6533(15)	12.3341(15)
c (Å)	25.465(5)	16.732(3)	18.753(3)	12.370(3)
α (deg)	90	78.332(6)	90	88.091(10)
β (deg)	96.009(10)	86.814(8)	90	66.197(10)
γ (deg)	90	85.261(8)	90	82.102(10)
U (Å^3)	3006.2(10)	2040.4(5)	1767.0(4)	1448.8(4)
Z	4	2	4	2
μ(Mo Kα) (mm^{-1})	2.81	2.14	2.39	6.78
total no. of rflns	27 948	36 221	15 822	29 158
no. of unique rflns	5858	9355	4020	6634
R_{int}	0.089	0.064	0.046	0.047
no. of params, restraints	370, 11	500, 0	219, 0	354, 22
R1[b] ($I_o > 2\sigma(I_o)$)	0.084	0.084	0.030	0.044
R1 (all data)	0.123	0.114	0.034	0.054
wR2[b] ($I_o > 2\sigma(I_o)$)	0.144	0.169	0.071	0.098
wR2 (all data)	0.162	0.188	0.074	0.103

[a] Common items: temperature 120 K; wavelength (Mo Kα) 0.710 73 Å; θ(max) = 27.5°. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

thf (40 mL) and the solution cooled to −78 °C, before the dropwise addition of methyllithium (8.3 mL, 13.4 mmol, 1.6 M solution in diethyl ether). The reaction mixture was stirred (15 min, −78 °C) and then warmed to room temperature over the course of 2 h, producing a faintly yellow solution. The solvents were removed in vacuo, toluene (20 mL) was added, and the mixture was filtered. The resulting pale yellow solution was reduced in vacuo to give a yellow oil. Yield: 1.5 g, 70.3%. ^{1}H NMR ($CDCl_3$): δ 1.9 (s, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 27.77 (Me).

O{(CH$_2$)$_2$BiPh$_2$}$_2$ (3). Ph_2BiBr (13.6 g, 31 mmol) was dissolved in liquid ammonia (300 mL) at −78 °C. The addition of small pieces of sodium (1.55 g, 67 mmol) with stirring for 15 min gave a dark green solution. After 30 min the solution had become dark red; a thf solution (10 mL) of bis(2-iodoethyl) ether (4.8 g, 15 mmol) was added and the ammonia slowly evaporated under a flow of N_2, leaving a dark solid residue. Extraction with diethyl ether (60 mL) gave a pale yellow solution, which was reduced in vacuo to yield an off-white crystalline powder. Yield: 6.5 g, 55%. Anal. Calcd for $C_{28}H_{28}Bi_2O$: C, 42.1; H, 3.5. Found: C, 42.1; H, 3.4. ^{1}H NMR ($CDCl_3$): δ 2.3 (t, [4H], CH_2Bi), 4.1 (t, [4H], CH_2O), 7.3 (m, [12H], Ph), 7.7 (m, [8H], Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 34.13 (CH_2Bi), 68.52 (CH_2O), 127.26, 129.37, 137.26 ($C_{aromatic}$), 148.92 (C_{ipso}). FAB MS: m/z 286 $[PhBi]^+$, 363 $[Ph_2Bi]^+$.

MeN(CH$_2$-2-C$_6$H$_4$BiPh$_2$)$_2$ (4). $MeN(CH_2\text{-}2\text{-}C_6H_4Br)_2$ (1.75 g, 4.74 mmol) was dissolved in diethyl ether (60 mL) and cooled to −78 °C, before the dropwise addition of ^{n}BuLi (6.42 mL, 9.96 mmol, 1.55 M solution in hexane). The reaction mixture was stirred for 2 h before it was warmed slowly to room temperature. $BiPh_2Br$ (4.3 g, 9.7 mmol) was added as a solid, and the mixture was stirred at room temperature for 16 h. Degassed, distilled water (60 mL) was added, and the organic layer was separated. The aqueous phase was washed with diethyl ether (2 × 30 mL), and the organic extracts were combined, dried over $MgSO_4$, and filtered to give a pale yellow solution. A small amount of white precipitate formed, which was separated and identified as the small ring $MeN(CH_2C_6H_4)_2BiBr$ (**5**). The solvent was removed in vacuo, giving an off-white/yellow solid. Yield: 1.2 g, 27%. Anal. Calcd for $C_{39}H_{35}Bi_2N$: C, 50.0; H, 3.8; N, 1.5. Found: C, 49.3; H, 3.2; N, 1.7. ^{1}H NMR ($CDCl_3$): δ 1.8 (s, [3H], MeN), 3.5 (s, [4H], CH_2N), 7.1−7.8 (m, [28H], aromatic CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 42.21 (MeN), 66.95 (CH_2N), 128.25, 128.49, 130.86, 131.09, 131.45, 138.30, 140.16, 144.81 ($C_{aromatic}$), 157.2, 159.4 (BiC_{ipso}). CI MS: m/z 857 $[P - Ph]^+$, 496 $[Ph_2Bi(C_6H_4)CH_2N(Me)CH_2]^+$.

[MeN(CH$_2$-2-C$_6$H$_4$)$_2$BiBr] (5). This species was isolated as a minor byproduct from the preparation of **4** as a white powder. Crystals of this material were grown from pentane solution. ^{1}H NMR ($CDCl_3$): δ 2.8 (s, [3H], MeN), 4.0 (d, $^2J_{HH}$ = 15 Hz, [2H], C*H*HN), 4.2 (d, $^2J_{HH}$ = 15 Hz, [2H], CH*H*N), 7.1−7.6 (m, [6H], 3,4,5-Ar), 8.7 (m, [2H], 2-Ar). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 44.30 (MeN), 65.94 (CH_2N), 127.89, 128.27, 131.56, 140.27, 147.77 ($C_{aromatic}$) (BiC_{ipso} unclear).

MeN(CH$_2$-2-C$_6$H$_4$BiMe$_2$)$_2$ (6). MeN(CH$_2$-2-C$_6$H$_4$Br)$_2$ (3.57 g, 9.67 mmol) was dissolved in diethyl ether (50 mL) and cooled to −78 °C, before the dropwise addition of ^{n}BuLi (12.1 mL, 19.4 mmol, 1.6 M solution in hexane). The reaction mixture was stirred for 2 h before it was warmed slowly to room temperature, producing a yellow solution. Simultaneously, Me_2BiBr (6.79 g, 21.3 mmol) was prepared by the addition of methyllithium (24.6 mL, 42.6 mmol, 1.7 M solution in diethyl ether) to a thf (80 mL) solution of $BiBr_3$ (9.55 g, 21.3 mmol), kept at −78 °C. This mixture was stirred for 15 min at −78 °C and then warmed to room temperature over 2 h. The two solutions were cooled to −78 °C, combined, and stirred for 16 h, during which time it was slowly warmed to room temperature. The solvent was removed in vacuo. The solid residues were redispersed in diethyl ether (80 mL), the mixture was filtered, and the resulting yellow solution was treated with distilled, degassed water (60 mL). After separation, the aqueous layer was washed with diethyl ether (2 × 20 mL). The combined organic extracts were dried over $MgSO_4$ and filtered, and the solvent was removed to give a yellow oil. Yield: 1.3 g, 19.6%. ^{1}H NMR ($CDCl_3$): δ 1.1 (s, [12H], MeBi), 1.9 (s, [3H], MeN), 3.5 (s, [4H], CH_2N), 7.0−7.9 (m, [8H], aromatic CH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 2.91 (MeBi), 41.53 (MeN), 66.56 (CH_2N), 127.20, 128.84, 136.00, 142.84, 147.71 ($C_{aromatic}$), 168.81 (BiC_{ipso}). FAB MS: *m*/*z* 687 [P]$^+$, 672 [P − Me]$^+$, 433 [C$_{16}$H$_{18}$BiN]$^+$, 418 [C$_{15}$H$_{15}$BiN]$^+$.

MeN(CH$_2$-2-C$_6$H$_4$)$_2$BiMe (7). This species was also observed as a minor byproduct present in some preparations of **6** (see text). ^{1}H NMR ($CDCl_3$): δ 1.15 (s, [3H], MeBi), 2.4 (s, [3H], MeN), 3.55 (d, $^2J_{HH}$ = 15 Hz, [2H], C*H*HN), 3.75 (d, $^2J_{HH}$ = 15 Hz, [2H], CH*H*N), 7.0−7.3 (m, [6H], 3,4,5-Ar), 7.8 (m, [2H], 2-Ar). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 42.04 (MeN), 61.94 (CH_2N), 127.07, 127.65, 128.98, 136.61, 145.38 ($C_{aromatic}$), (BiC_{ipso} unclear).

S(CH$_2$-2-C$_6$H$_4$Br)$_2$ (8). 2-Bromobenzyl bromide (23.3 g, 0.092 mol) was dissolved in degassed absolute ethanol (300 mL), and sodium sulfide nonahydrate (11.2 g, 0.047 mol) was added, along with sodium hydroxide (four pellets). The reaction mixture was refluxed for 16 h, giving a cream-colored precipitate and an orange solution. The solvent was removed in vacuo, and the resulting solids were treated with a mixture of diethyl ether (200 mL) and degassed water (100 mL). The ether layer was removed and the remaining solution washed with more diethyl ether (2 × 60 mL). The combined organic extracts were dried over $MgSO_4$ before the majority of the solvent was removed in vacuo, precipitating a pale yellow crystalline solid. Yield: 13.3 g, 78%. ^{1}H NMR ($CDCl_3$): δ 3.8 (s, [4H], CH_2S), 7.0 (t, [2H]), 7.2 (t, [2H]), 7.4 (d, [2H]), 7.5 (d, [2H], all aromatic CH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 36.48 (CH_2S), 124.67, 127.48, 128.68, 130.77, 133.10, 137.29 ($C_{aromatic}$).

S(CH$_2$-2-C$_6$H$_4$BiPh$_2$)$_2$ (9). S(CH$_2$-2-C$_6$H$_4$Br)$_2$ (3.0 g, 8.06 mmol) was dissolved in diethyl ether (100 mL) and the solution cooled to −30 °C, before the dropwise addition of *n*-butyllithium solution (10.4 mL, 16.12 mmol, 1.55 M solution in hexane). The reaction mixture was stirred for 3 h at −30 °C before the addition of powdered $BiPh_2Br$ (7.14 g, 16.12 mmol) as a solid. The resulting mixture was stirred overnight when it was slowly warmed to room temperature, giving a yellow solution and some brown solid. The solvent was removed in vacuo, and the solid was extracted with toluene (80 mL) and the extract filtered, giving a yellow solution. Degassed distilled water (60 mL) was added, the organic layer was separated and dried over $MgSO_4$, and the solvent was reduced in volume to give a waxy yellow solid. Washing with degassed acetone (2 × 10 mL) gave a white solid. Crystals were grown from a saturated toluene solution. Yield: 1.5 g, 33%. Anal. Calcd for $C_{38}H_{32}Bi_2S$: C, 48.6; H, 3.4. Found: C, 48.5; H, 3.7. ^{1}H NMR ($CDCl_3$): δ 3.55 (s, [4H], CH_2S), 7.0−7.7 (m, [28H], aromatic CH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 40.74 (CH_2S), 128.61, 128.83, 131.01, 131.40, 138.57, 138.72, 140.99, 144.15 ($C_{aromatic}$), 157.19, 159.30 (BiC_{ipso}). FAB MS: *m*/*z* 961 [P + Na]$^+$, 453 [C$_{19}$H$_{16}$Bi]$^+$, 421 [C$_{14}$H$_{12}$BiS]$^+$, 363 [Ph$_2$Bi]$^+$, 286 [PhBi]$^+$.

S(CH$_2$-2-C$_6$H$_4$BiMe$_2$)$_2$ (10). S(CH$_2$-2-C$_6$H$_4$Br)$_2$ (2.5 g, 6.72 mmol) was dissolved in diethyl ether (80 mL) and the solution cooled to −30 °C, before the dropwise addition of *n*-butyllithium solution (8.82 mL, 14.11 mol, 1.6 M solution in hexane). The reaction mixture was stirred for 3 h at −18 °C, before the addition of bromodimethylbismuth (2.58 g, 23.6 mmol in 80 mL of thf). The resulting mixture was stirred overnight, during which time it was warmed to room temperature, giving an orange solution and some brown solid. The solvent was removed in vacuo, the residue was redissolved in diethyl ether (80 mL), and this mixture was filtered to give a yellow solution. Degassed, distilled water (60 mL) was added and the organic layer extracted, before the aqueous layer was washed with diethyl ether (2 × 10 mL). The combined organic extracts were dried over $MgSO_4$, and the solvent was removed in vacuo, to give a yellow oil. Yield: 0.7 g, 15%. ^{1}H NMR ($CDCl_3$): δ 1.15 (s, [12H], (MeBi)), 3.7 (s, [4H], CH_2S), 7.1−7.9 (m, [8H], aromatic CH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 3.94 MeBi, 42.54 (CH_2S), 128.45, 129.63, 129.69, 138.47, 143.53 ($C_{aromatic}$), 143.68 (BiC_{ipso}). CI MS: *m*/*z* 675 [P − Me]$^+$.

S(CH$_2$-2-C$_6$H$_4$SbMe$_2$)$_2$ (11). S(CH$_2$-2-C$_6$H$_4$Br)$_2$ (1.97 g, 5.31 mmol) was dissolved in diethyl ether (100 mL) and cooled in an ice/ethanol bath (approximately −15 °C). ^{n}BuLi (6.64 mL of 1.6 M in hexane, 10.62 mmol) was added dropwise. A bright yellow precipitate was formed and the mixture stirred for 3 h, maintaining the temperature between −15 and 0 °C. A toluene solution (60 mL) of $SbMe_2Cl$ (1.98 g, 10.62 mmol) was added dropwise to the cooled lithiate, and the reaction mixture was stirred overnight, resulting in a pale yellow solution and white precipitate. Degassed water (100 mL) was added, and after thorough mixing the organic layer was separated, the aqueous layer was washed with diethyl ether (40 mL), and the combined organics were dried over $MgSO_4$. The solution was then filtered, and the volatiles were removed in vacuo, yielding a yellow oil. Yield: 3.8 g, 68%. ^{1}H NMR ($CDCl_3$): δ 0.9 (s, [12H], MeSb), 3.8 (s, [4H], CH_2S), 7.1−7.6 (m, [8H], aromatic CH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ −0.30 (MeSb), 40.15 (CH_2S), 127.98, 128.77, 129.58, 135.32, 139.01, 144.02 ($C_{aromatic}$).

S(CH$_2$-2-C$_6$H$_4$SbMe$_3$)$_2$I$_2$ (11b). A sample of the product (0.3 g) was dissolved in acetone (10 mL), and excess MeI (2 mL) was added. The mixture was stirred for 2 min and then allowed to stand overnight, resulting in the formation of very pale yellow needle crystals, which were isolated by filtration and dried in vacuo. Anal. Calcd for $C_{20}H_{30}I_2SSb_2$: C, 30.0; H, 3.8. Found: C, 30.7; H, 3.8. ^{1}H NMR (d_6-dmso): δ 1.9 (s, [18H], MeSb), 3.8 (s, [4H], CH_2S), 7.4−7.8 (m, [8H], aromatic CH). ^{13}C{^{1}H} NMR (d_6-dmso): δ 4.9 (MeSb), 36.5 (CH_2S), 128.4, 131.2, 131.5, 135.1, 141.3, 146.0 ($C_{aromatic}$). ES$^+$ MS: *m*/*z* 273 [C$_{20}$H$_{30}$Sb$_2$S]$^{2+}$, 529 [C$_{19}$H$_{27}$Sb$_2$S]$^+$.

[{CpFe(CO)$_2$}$_2${O{(CH$_2$)$_2$BiPh$_2$}$_2$}][BF$_4$]$_2$ (12). [CpFe(CO)$_2$I] (0.15 g, 0.50 mmol) was dissolved in a mixture of CH_2Cl_2 (10 mL) and thf (1 drop), and the resulting dark red-brown solution was added to a CH_2Cl_2 (10 mL) solution of $AgBF_4$ (0.098 g, 0.50 mmol) in a foil-wrapped flask. The reaction mixture was stirred for 2 h before filtration. The red filtrate was cooled to −78 °C, O{(CH$_2$)$_2$BiPh$_2$}$_2$ (0.2 g, 0.25 mmol) dissolved in CH_2Cl_2 (10 mL) was added, and the mixture was stirred for 16 h, warming slowly during this period. The solvent was removed in vacuo, leaving a dark red solid which was stored in a freezer. Yield: 0.1 g, 30%. ^{1}H ($CDCl_3$, 223 K): δ 2.5 (s, [4H], CH_2Bi), 4.25 (s, [4H], CH_2O), 5.3 (s, [10H], Cp), 7.3−7.8 (m, [20H], aromatic CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 223 K): δ 34.7 (CH_2Bi), 69.3 (CH_2O), 86.3 (Cp), 128.4, 131.2, 138.2 ($C_{aromatic}$), 149.5 (BiC_{ipso}), 209.5 (CO). ES$^+$ MS: *m*/*z* 975 [{CpFe(CO)$_2$}{O{(CH$_2$)$_2$BiPh$_2$}$_2$}]$^+$. IR

(Nujol/cm^{-1}): 2062 (s), 2021 (s) 2007 (sh) (CO), 1090 (vbr) (BF_4). IR ($CHCl_3$/cm^{-1}): 2063 (s), 2020 (s) (CO).

[{**CpFe(CO)$_2$**}$_2${**S(CH$_2$-2-C$_6$H$_4$BiPh$_2$)$_2$**}][**BF$_4$**]$_2$ **(13).** [CpFe(CO)$_2$I] (0.13 g, 0.43 mmol) was dissolved in a mixture of CH_2Cl_2 (10 mL) and thf (1 drop), and the resulting dark red-brown solution was added to a CH_2Cl_2 (10 mL) solution of $AgBF_4$ (0.083 g, 0.43 mmol) in a foil-wrapped flask. The reaction mixture was stirred for 2 h before filtration. The red filtrate was cooled to −78 °C, a solution of S(CH$_2$-2-C$_6$H$_4$BiPh$_2$)$_2$ (0.2 g, 0.22 mmol), dissolved in CH_2Cl_2 (10 mL), was added, and the mixture was stirred for 16 h at room temperature. The solvent volume was reduced (ca. 10 mL), and hexane (10 mL) was added, precipitating a dark red-brown solid. After filtration, the residues were dried in vacuo, yielding a dark red-brown waxy solid which was stored in a freezer. Yield: 0.05 g, 16%. ^{1}H NMR ($CDCl_3$, 223 K): δ 3.7 (s, [4H], CH_2S), 5.28 (s, [10H], Cp), 7.3−7.9 (m, [28H], aromatic CH). ^{13}C{^{1}H} NMR ($CDCl_3$ 223 K): δ 46.2 (CH_2S), 85.3 (Cp), 128.3, 128.9, 131.0, 131.9, 132.0, 138.0, 138.2 ($C_{aromatic}$), 152.1, 156.7 (BiC_{ipso}), 210.0 (CO). ES$^+$ MS: m/z 1116 [CpFe(CO)$_2$-{S(CH$_2$-2-C$_6$H$_4$BiPh$_2$)$_2$}]$^+$, 647 [{CpFe(CO)$_2$}$_2${S(CH$_2$-2-C$_6$H$_4$-BiPh$_2$)$_2$}]$^{2+}$. IR (Nujol/cm^{-1}): 2071 (s), 2055 (s), 2023 (s) (CO), 1080 (vbr) (BF_4). IR (CH_2Cl_2/cm^{-1}): 2067 (s), 2020 (s) (CO).

[{**CpFe(CO)$_2$**}$_2${**S(CH$_2$-2-C$_6$H$_4$BiMe$_2$)$_2$**}][**BF$_4$**]$_2$ **(14).** [CpFe(CO)$_2$I] (0.176 g, 0.58 mmol) was dissolved in a mixture of CH_2Cl_2 (10 mL) and thf (1 drop), and the resulting dark red-brown solution was added to a CH_2Cl_2 (10 mL) solution of $AgBF_4$ (0.113 g, 0.58 mmol) in a foil-wrapped flask. The reaction mixture was stirred for 2 h before filtration. The red filtrate was cooled to −78 °C, a solution of S(CH$_2$-2-C$_6$H$_4$BiMe$_2$)$_2$ (0.2 g, 0.29 mmol), dissolved in CH_2Cl_2 (10 mL), was added, and the mixture was stirred for 16 h at −78 °C. The solvents were removed in vacuo, leaving a dark red solid. Yield: 0.15 g, 42%. ^{1}H NMR ($CDCl_3$, 223 K): δ 1.76 (s, [12H], MeBi), 3.44 (s, [4H], CH_2S), 5.41 (s, [10H], Cp), 7.4−8.2 (m, [8H], aromatic CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 223 K): δ 7.2 (MeBi), 46.2 (CH_2S), 86.2 (Cp), 128.2, 129.0, 131.8, 132.2, 138.2 ($C_{aromatic}$), 144.5 (BiC_{ipso}), 209.6 (CO). ES$^+$ MS: m/z 523 [{CpFe(CO)$_2$}$_2${S(CH$_2$-2-C$_6$H$_4$BiMe$_2$)$_2$}]$^{2+}$. IR (Nujol/cm^{-1}): 2068 (s), 2015 (s), 2005 (s) (CO), 1085 (vbr) (BF_4). IR (CH_2Cl_2/cm^{-1}): 2072 (s), 2025 (s) (CO).

[{**CpFe(CO)$_2$**}$_2${**MeN(CH$_2$-2-C$_6$H$_4$BiPh$_2$)$_2$**}][**BF$_4$**]$_2$ **(15).** [CpFe(CO)$_2$I] (0.13 g, 0.43 mmol) was dissolved in a mixture of CH_2Cl_2 (10 mL) and thf (1 drop), and the resulting dark red-brown solution was added to a CH_2Cl_2 (10 mL) solution of $AgBF_4$ (0.083 g, 0.43 mmol) in a foil-wrapped flask. The reaction mixture was stirred for 2 h before filtration. A solution of MeN(CH$_2$-2-C$_6$H$_4$BiPh$_2$)$_2$ (0.2 g, 0.21 mmol) dissolved in CH_2Cl_2 (10 mL) was added and the mixture stirred for 16 h at room temperature. The solvent volume was reduced (to ca. 10 mL), and hexane (10 mL) was added, producing a waxy red-brown solid and a light brown-yellow solution. After filtration, the residues were dried in vacuo, giving a dark brown-red solid which was stored in a freezer. Yield: 0.08 g, 26%. ^{1}H NMR ($CDCl_3$, 223 K): δ 3.1 (s, [3H], MeN), 4.5 (s, [2H] CH_2N), 4.6 (s, [2H], CH_2N), 5.18 (s, [5H], Cp), 5.19 (s, [5H] Cp), 7.1−7.8 (m, [28H], aromatic CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 223 K): δ 45.8 (MeN), 68.5, 68.6 (CH_2N), 85.44, 85.47 (Cp), 128.3, 128.9, 129.4, 131.0, 131.6, 132.4, 136.4, 137.4, 138.1 ($C_{aromatic}$), 150.6, 151.2, 155.5 (BiC_{ipso}), 210.2, 211.1 (CO). IR (Nujol/cm^{-1}): 2065 (s), 2040 (s), 2020 (s), 2003(s) (CO), 1084 (vbr) (BF_4). IR (CH_2Cl_2/cm^{-1}): 2070 (s), 2055 (s), 2022 (s), 1998 (s) (CO).

[{**CpFe(CO)$_2$**}$_2${**MeN(CH$_2$-2-C$_6$H$_4$BiMe$_2$)$_2$**}][**BF$_4$**]$_2$ **(16).** This complex was prepared by a method similar to that for **13**, using [CpFe(CO)$_2$I] (0.13 g, 0.44 mmol), $AgBF_4$ (0.085 g, 0.44 mmol), and MeN(CH$_2$-2-C$_6$H$_4$BiMe$_2$)$_2$ (0.15 g, 0.22 mmol). The reaction mixture was kept at −78 °C throughout. After the mixture was stirred for 16 h, the solvent was removed in vacuo, producing a waxy red-brown solid, which was stored in a freezer. Yield: 0.03 g, 13%. ^{1}H NMR ($CDCl_3$, 223 K): δ 1.4 (s, [12H], MeBi), 1.85 (s, [3H], MeN), 3.5 (s, [4H], CH_2N), 5.4 (s, [10H], Cp), 7.3−8.2 (m, [8H], aromatic CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 223 K): δ 5.9 (MeBi), 42.8 (MeN), 62.2 (CH_2N), 86.6 Cp, 127.7, 128.3, 129.5, 129.5, 137.3 ($C_{aromatic}$), 146.0 (BiC_{ipso}), 209.6 CO. ES$^+$ MS: m/z 523 [{CpFe(CO)$_2$}$_2${MeN(CH$_2$-2-C$_6$H$_4$BiMe$_2$)$_2$}]$^{2+}$. IR (Nujol/cm^{-1}): 2071 (s), 2043 (s), 2017 (s), 2004 (s) (CO), 1070 (vbr) (BF_4). IR (CH_2Cl_2/cm^{-1}): 2071 (s), 2024 (s) (CO).

[{**CpFe(CO)$_2$**}$_2${**MeN(CH$_2$-2-C$_6$H$_4$SbMe$_2$)$_2$**}][**BF$_4$**]$_2$ **(17).** This complex was preparted similarly to **15**, using [CpFe(CO)$_2$I] (0.212 g, 0.70 mmol), $AgBF_4$ (0.136 g, 0.70 mmol), and MeN-(CH$_2$-2-C$_6$H$_4$SbMe$_2$)$_2$ (0.15 g, 0.29 mmol). Reduction of the solvent volume to ca. 5 mL and addition of hexane (5 mL) precipitated the complex as a dark orange solid. Yield: 0.08 g, 26%. Crystals were grown from a CH_2Cl_2/hexane (1/1) mixture in the refrigerator. Anal. Calcd for $C_{33}H_{37}B_2F_4Fe_2NO_4Sb_2$: C, 38.1; H, 3.6; N, 1.4. Found: C, 38.6; H, 3.8; N, 1.4. ^{1}H NMR ($CDCl_3$, 223 K): δ 1.9 (s, [12H], MeSb), 2.2 (s, [3H], MeN), 3.8 (s, [4H], CH_2N), 5.4 (s, [10H], Cp), 7.5−7.9 (m, [8H], aromatic CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 223 K): δ 2.2 (MeSb), 44.7 (MeN), 68.6 (CH_2N), 86.1 (Cp), 129.5, 130.2, 131.1, 131.5, 132.3, 133.7 ($C_{aromatic}$), 209.7 (CO). ES$^+$ MS: m/z 434 [{CpFe(CO)$_2$}$_2$-{MeN(CH$_2$-2-C$_6$H$_4$SbMe$_2$)$_2$}]$^{2+}$. IR (Nujol/cm^{-1}): 2040 (s), 1992 (s) (CO), 1080 (vbr) (BF_4). IR ($CHCl_3$/cm^{-1}): 2045 (s), 2001 (s) (CO).

[{**CpFe(CO)$_2$**}$_2${**O{(CH$_2$)$_2$SbMe$_2$}$_2$**}][**BF$_4$**]$_2$ **(18).** This complex was prepared similarly to **15** from [CpFe(CO)$_2$I] (0.162 g, 0.53 mmol), $AgBF_4$ (0.103 g 0.53 mmol), and O{(CH$_2$)$_2$SbMe$_2$}$_2$ (0.100 g, 0.27 mmol). The crude dark orange solid was dissolved in CH_2Cl_2, and after 10 min of stirring a pale orange powder precipitated out and was isolated by filtration. Yield: 0.043 g, 18%. Pale orange platelike crystals were grown from the filtrate. Anal. Calcd for $C_{22}H_{30}B_2F_8Fe_2O_5Sb_2\cdot CH_2Cl_2$: C, 28.0; H, 3.3. Found: C, 27.4; H, 3.0. ^{1}H NMR (CD_3CN): δ 1.5 (s, [12H], MeSb) 2.4 (t, [4H], CH_2Sb) 3.8 (t, [4H], CH_2O), 5.3 (s, [10H], Cp), 5.5 (CH_2Cl_2). ^{13}C{^{1}H} NMR (CD_3CN): δ −0.9 (MeSb), 19.8 (CH_2Sb), 67.8 (CH_2O), 86.3 (Cp), 210.7 (CO). ES$^+$ MS: m/z 817 [{Cp(CO)$_2$Fe}$_2${O{(CH$_2$)$_2$SbMe$_2$}$_2$}BF$_4$]$^+$. IR (Nujol/cm^{-1}): 2041 (s), 2034 (s), 2005 (s), 1993 (s) (CO), 1080 (vbr) (BF_4). IR (MeCN/cm^{-1}): 2044 (s), 2000 (s) (CO).

[{**CpFe(CO)$_2$**}$_2${**O{(CH$_2$)$_2$SbPh$_2$}$_2$**}][**BF$_4$**]$_2$ **(19).** This complex was prepared similarly to **18** from [CpFe(CO)$_2$I] (0.195 g, 0.641 mmol), $AgBF_4$ (0.125 g, 0.641 mmol), and O{(CH$_2$)$_2$SbPh$_2$}$_2$ (0.200 g, 0.321 mmol). The addition of hexane to the reaction mixture precipitated an orange solid. Yield: 0.20 g, 54%. Anal. Calcd for $C_{42}H_{38}B_2F_8Fe_2O_5Sb_2\cdot 2CH_2Cl_2$: C, 40.0; H, 3.2. Found C 39.2, H, 3.6. ^{1}H NMR ($CDCl_3$): δ 2.9 (t, [4H], CH_2Sb), 3.6 (t, [4H], CH_2O), 5.3 (CH_2Cl_2), 5.5 (s, [10H], Cp), 7.4−7.6 (m, [20H], aromatic CH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 22.1 (CH_2Sb), 67.2 (CH_2O), 86.3 (Cp), 128.0, 130.9, 132.2, 135.2 ($C_{aromatic}$), 209.2 (CO). ES$^+$ MS: m/z = 1063 [{Cp(CO)$_2$Fe}$_2${O{(CH$_2$)$_2$-SbPh$_2$}$_2$}BF$_4$]$^+$. IR (Nujol/cm^{-1}): 2044 (s), 2002 (sh), 1996 (s) (CO), 1080 (vbr) (BF_4). IR (CH_2Cl_2/cm^{-1}): 2050 (s), 2006 (s) (CO).

[{**CpFe(CO)$_2$**}$_2${**S(CH$_2$-2-C$_6$H$_4$SbMe$_2$)$_2$**}][**BF$_4$**]$_2$ **(20).** This complex was prepared similarly to **18**, from [CpFe(CO)$_2$I] (0.177 g, 0.58 mmol), $AgBF_4$ (0.113 g, 0.58 mmol), and S(CH$_2$-2-C$_6$H$_4$SbMe$_2$)$_2$ (0.150 g, 0.29 mmol). The title compound was isolated as an orange solid by precipitation with *n*-hexane from a CH_2Cl_2 solution. Yield: 0.39 g, 37%. Anal. Calcd for $C_{32}H_{34}$-$B_2F_8O_4Fe_2SSb_2$: C, 35.1; H, 3.2. Found: C, 35.3; H, 3.0. ^{1}H NMR (CD_2Cl_2): δ 1.9 (s, [12H], MeSb, 3.9 (s, [4H], CH_2S), 5.4 (s, [10H], Cp), 7.3−7.7 (m, [8H], aromatic CH). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ −2.7 (MeSb), 38.1 (CH_2S), 86.0 (Cp), 129.4, 129.6, 132.0, 132.3, 135.0, 142.1 ($C_{aromatic}$), 209.0 (CO). ES$^+$ MS: m/z 957 [{CpFe(CO)$_2$}$_2${S(CH$_2$-2-C$_6$H$_4$SbMe$_2$)$_2$}BF$_4$]$^+$, 435 [{CpFe-(CO)$_2$}$_2${S(CH$_2$-2-C$_6$H$_4$SbMe$_2$)$_2$}]$^{2+}$. IR (Nujol/cm^{-1}): 2039 (s), 1998 (s) (CO), 1080 (vbr) (BF_4). IR (CH_2Cl_2/cm^{-1}): 2049 (s), 2002 (s) (CO).

[**CpFe(CO)$_2$(PhSbMe$_2$)**][**BF$_4$**] **(21).** This complex was prepared similarly to **18**, using [CpFe(CO)$_2$I] (0.096 g, 0.316 mmol), $AgBF_4$ (0.062 g, 0.316 mmol), and $SbPhMe_2$ (0.072 g, 0.316 mmol). The addition of hexane (ca. 10 mL) to the reaction mixture precipitated

a pale orange-pink powder. Yield: 0.05 g, 32%. Crystals were grown from a CH_2Cl_2/hexane (1/1) mixture in the refrigerator. Anal. Calcd for $C_{15}H_{16}BF_4FeO_2Sb$: C, 36.6; H, 3.3. Found: C, 35.8; H, 3.2. ^{1}H NMR ($CDCl_3$, 223 K): δ 1.9 (s, [6H], MeSb), 5.4 (s, [5H], Cp), 7.6 (m, [5H], aromatic CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 223 K): δ 0.8 (MeSb), 85.7 (Cp), 128.7, 130.5, 131.8, 133.7 ($C_{aromatic}$), 209.3 (CO). ES^+ MS: m/z 405 $[CpFe(CO)_2(PhSbMe_2)]^+$. IR (Nujol/cm^{-1}): 2041 (s), 1999 (s) (CO), 1080 (vbr) (BF_4). IR (CH_2Cl_2/cm^{-1}): 2046 (s), 2002 (s) (CO).

$[\{CpFe(CO)_2\}_2\{Ph_2Sb(CH_2)_3SbPh_2\}][BF_4]_2$ (22). This complex was prepared similarly to **18** from $[CpFe(CO)_2I]$ (0.103 g, 0.34 mmol), $AgBF_4$ (0.066 g, 0.34 mol), and $Ph_2Sb(CH_2)_3SbPh_2$ (0.10 g, 0.17 mmol). The reaction mixture was reduced in volume to ca. 10 mL, and the subsequent addition of hexane (5 mL) precipitated a dark orange solid. Yield: 0.082 g, 43%. Anal. Calcd for $C_{41}H_{36}B_2F_8Fe_2O_4Sb_2$: C, 43.9; H, 3.2. Found: C, 43.3; H, 3.2. ^{1}H NMR ($CDCl_3$): δ 1.9 (m, [2H], CH_2), 2.9 (t, [4H], CH_2Sb), 5.4 (s, [10H], Cp), 7.4−7.5 (m, [20H], aromatic CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 22.5 (CH_2Sb), 23.7 (CH_2), 85.9 (Cp), 127.1, 130.7, 132.0, 134.9 ($C_{aromatic}$), 208.9 (CO). ES^+ MS: m/z 474 $[\{CpFe(CO)_2\}_2\{Ph_2Sb(CH_2)_3SbPh_2\}]^{2+}$. IR (Nujol/$cm^{-1}$): 2042 (s), 1992 (s) (CO), 1080 (br) (BF_4). IR (CH_2Cl_2 /cm^{-1}): 2048 (s), 2005 (s) (CO).

$[CpFe(CO)_2\{Ph_2Bi(o\text{-}C_6H_4OMe)\}][BF_4]$ (23). $[CpFe(CO)_2I]$ (0.13 g, 0.425 mmol) was dissolved in a mixture of CH_2Cl_2 (10 mL) and thf (1 drop), and the resulting dark red-brown solution was added to a CH_2Cl_2 (10 mL) solution of $AgBF_4$ (0.083 g, 0.425 mmol) in a foil-wrapped flask. The reaction mixture was stirred at room temperature for 2 h before filtration to give a red solution. A solution of $BiPh_2(o\text{-}C_6H_4OMe)$ (0.3 g, 0.43 mmol, dissolved in 10 mL of CH_2Cl_2) was added and the mixture stirred for 1 h. The solvent was removed in vacuo, and the residue was redissolved in CH_2Cl_2 (20 mL) before further stirring for 18 h. Reduction of the solvent volume to ca. 5 mL and the addition of hexane (5 mL) precipitated the complex as a dark red-brown solid. Yield: 0.15 g, 20%. Crystals were grown from a CH_2Cl_2/hexane (1/1) mixture. ^{1}H NMR ($CDCl_3$, 223 K): δ 3.8 (s, [3H], OMe), 5.5 (s, [5H], Cp), 7.0−7.5 (m, [14H], aromatic CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 223 K): δ 56.5 (OMe), 86.5 (Cp), 114.4, 124.8, 128.4, 131.9, 133.6, 136.2, 146.0, 151.8 ($C_{aromatic}$), 209.3 (CO). ES^+ MS: m/z 647 $[CpFe(CO)_2\{BiPh_2(o\text{-}C_6H_4OMe)\}]^+$. IR (Nujol/$cm^{-1}$): 2044 (s), 1997 (s) (CO), 1080 (vbr) (BF_4). IR (CH_2Cl_2/cm^{-1}): 2057 (s), 2013 (s) (CO). Note: the ^{1}H and $^{13}C\{^1H\}$ NMR spectra always showed weaker resonances, which were attributed to the presence of some $[CpFe(CO)_2\{BiPh_{3-n}(o\text{-}C_6H_4OMe)_n\}][BF_4]$ (n = 0, 2, 3), the amounts varying from preparation to preparation. ES^+ MS ions were also seen at m/z 617 $[CpFe(CO)_2(BiPh_3)]^+$, 677 $[CpFe(CO)_2\{BiPh(o\text{-}C_6H_4OMe)_2\}]^+$, and 707 $[CpFe(CO)_2\{Bi(o\text{-}C_6H_4OMe)_3\}]^+$.

Reaction of $[CpFe(CO)_2(thf)]BF_4$ with $BiPhMe_2$. $[CpFe(CO)_2I]$ (0.096 g, 0.316 mmol) was dissolved in a mixture of CH_2Cl_2 (10 mL) and thf (1 drop) and the resulting dark red-brown solution added to a CH_2Cl_2 (10 mL) solution of $AgBF_4$ (0.061 g, 0.316 mmol) in a foil-wrapped flask. The reaction mixture was stirred for 2 h, before filtration, to give a dark red solution, which was cooled to −78 °C. $BiPhMe_2$ (0.10 g, 0.32 mmol) dissolved in CH_2Cl_2 (10 mL) was added, and the mixture was stirred at −78 °C for 1 h. A 2 mL aliquot was then removed for NMR analysis. The remaining reaction mixture was stirred at −78 °C for 18 h, and a second 2 mL aliquot was removed for NMR analysis. The remaining solvent was removed in vacuo, to give a dark red solid. Selected spectroscopic data on the Fe-containing product (asterisks denote the major species present) are as follows. First aliquot: ^{1}H NMR ($CDCl_3$, 223 K) δ 1.12 (s, Me_3Bi), 1.275 (s, Me_2BiPh)*, 1.45 ($MeBiPh_2$)*, 5.20, 5.40*, 5.42*, 5.60 (Cp), 7.38−7.89 (aromatic CH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 223 K) δ −6.16 ($BiMe_3$), 1.73 ($BiMe_2Ph$)*, 3.36 ($BiMePh_2$)*, 85.47*, 85.73*, 86.20 (Cp), 127.95−147.50 ($C_{aromatic}$), 209.6, 210.0 (CO); EI^+ MS m/z 618 $[CpFe(CO)_2(BiPh_3)]^+$, 555 $[CpFe(CO)_2(BiPh_2Me)]^+$, 493 $[CpFe(CO)_2(BiPhMe_2)]^+$, 431 $[CpFe(CO)_2(BiMe_3)]^+$.

The second aliquot was not significantly different. The final solid isolated was only partially soluble in $CDCl_3$, and the soluble component seemed to contain $[CpFe(CO)_2(BiMe_{3-n}Ph_n)]BF_4$ (n = 1−3), but no detectable amount of the $BiMe_3$ complex.

X-ray Studies. Details of the crystallographic data collection and refinement parameters are given in Table 2. Crystals were obtained as described above. Data collection used a Nonius Kappa CCD diffractometer fitted with monochromated (confocal mirrors) Mo Kα X-radiation (λ = 0.710 73 Å). Crystals were held at 120 K under a nitrogen gas stream. Structure solution and refinement were routine,[16−18] with hydrogen atoms on C added to the model in calculated positions and using the default C−H distance.

CCDC reference numbers 797557−797565 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Supporting Information Available: A table giving crystallographic details for the compound $[CpFe(CO)_2(BiPh_3)]BF_4 \cdot CH_2Cl_2$, together with a figure of the structure, and CIF files for the other crystal structures described. This material is available free of charge via the Internet at http://pubs.acs.org.

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