# Bromostibine Complexes of Iron(II): Hypervalency and Reactivity

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S *Supporting Information*

ABSTRACT: The halostibine complexes $[CpFe(CO)_2(SbMe_2Br)][CF_3SO_3]$ and $[CpFe(CO)_2(SbMe_2Br)][BF_4]$ both contain significant interactions between the anion and the formally neutral Sb(III) ligand, which simultaneously displays Lewis acidic and Lewis basic properties. The unexpected secondary product $[CpFe(CO)(Me_2BrSb-\mu-Br-SbBrMe_2)]$ is formed in the presence of excess ligand, the strongly associated Br^- anion bridging the two Sb donors to form a four-membered $FeSb_2Br$ ring.
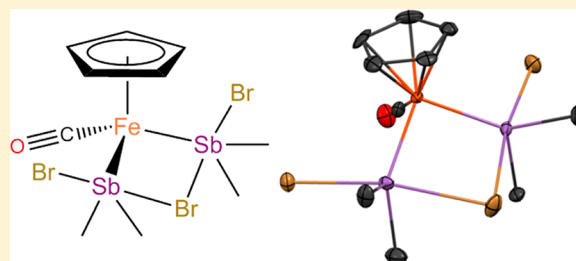
Transition-metal complexes with heavy main-group ligands have been a focus of recent interest due to the propensity of the coordinated heavy p-block donor atom to undergo further bonding interactions or even redox chemistry.[1−4] Gabbaï and co-workers have classed this as "coordination noninnocence" and have exploited such behavior for selective F^- sensing.[3] The fundamental nature of the bonding in such complexes is also an emerging area of study.[5,6] Oxidation of a gold−stibine complex with $PhICl_2$ results in chlorination of the Sb donor; DFT calculations demonstrate that this induces an umpolung of the $Sb{\rightarrow}Au$ bond to $Sb{\leftarrow}Au$.[1] Transition-metal complexes with organostibine ligands, while much rarer than organophosphine complexes, have received considerable study over the past decade.[7,8] The formation of hypervalent interactions between Sb atoms and heterodonor atoms is a well-documented phenomenon which has recently been employed to induce chirality in organostibines.[9] Halostibines SbX_nR_{3-n} ($n = 1, 2$) can have both Lewis acidic and Lewis basic properties. We have reported Mn(I) carbonyl complexes of halostibines in which the coordinated Sb donor atom also acts as an acceptor, forming interactions with nearby $[CF_3SO_3]^-$ anions which significantly distort the geometry of the Sb center.[10] Herein we report the preparation and structures of the first halostibine complexes of iron, each of which displays interactions between the Fe-coordinated Sb atom and the counterion. These interactions are believed to be the driving force for the unexpected formation of the monocarbonyl adduct $[CpFe(CO)(Me_2BrSb-\mu-Br-SbBrMe_2)]$, in which Br^- is strongly associated with both coordinated Sb atoms.

Reaction of $[CpFe(CO)_2(thf)][X]$ ($X = CF_3SO_3$, BF_4) with $SbMe_2Br$ in a 1:1 ratio gives the complexes $[CpFe(CO)_2(SbMe_2Br)][X]$. These two salts were fully characterized by NMR and IR spectroscopy and microanalysis, with $[CpFe(CO)_2(SbMe_2Br)]^+$ observed in the ESI$^+$ mass spectra. The crystal structure of the $[CF_3SO_3]^-$ salt shows disorder of the whole structure, which was successfully modeled in two parts for both the cation and the anion (Figure 1 shows one part of each). The Br substituent on Sb is on the same side of
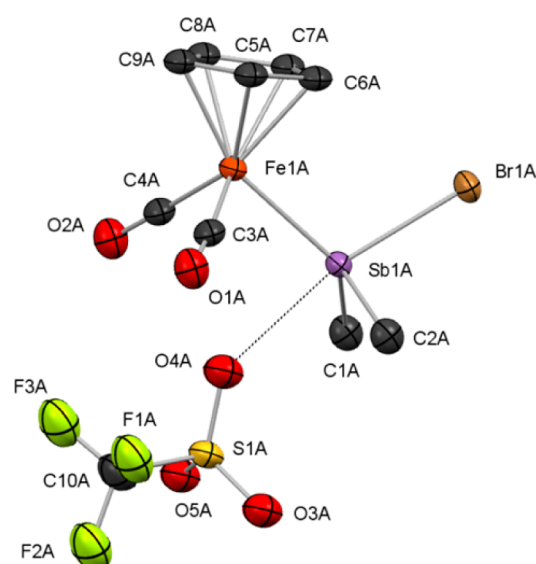
Figure 1. View of one of two disordered cation parts and one of two disordered anion parts of the structure of $[CpFe(CO)_2(SbMe_2Br)][CF_3SO_3]$ showing the atom-numbering scheme. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. The long Sb−O contact is shown as a dotted line.

the molecule as the Cp^- group on Fe, with the anion approaching the Sb from below, trans to the Br substituent. While it is clear that an interaction is present between atom O4A and Sb1A, the two possible positions of each ion mean that the interatomic distance cannot be determined reliably but is in the range 2.59−2.65 Å and, therefore, is certainly shorter than the equivalent $Sb{\cdots}O-SO_2CF_3$ distance of 2.70 Å found in $[Mn(CO)_5(SbMe_2Br)][CF_3SO_3]$.[10]

The crystal structure of the corresponding $[BF_4]^-$ salt is free of disorder, with a somewhat different cation geometry in

comparison to the $[CF_3SO_3]^-$ salt, the Br substituent on Sb eclipsing a CO group on the Fe center rather than the Cp^- group (Figure 2). An interaction is once again observed
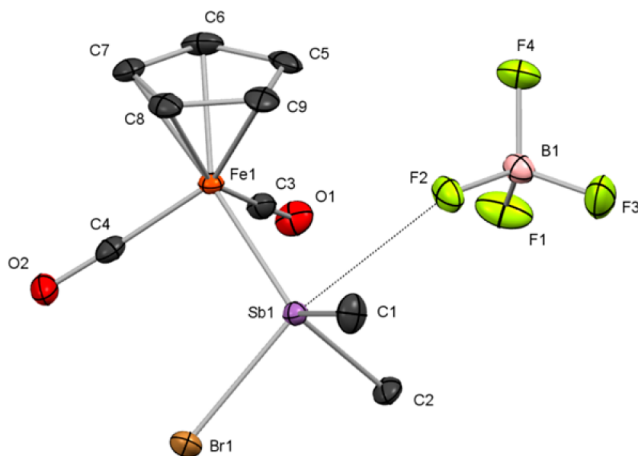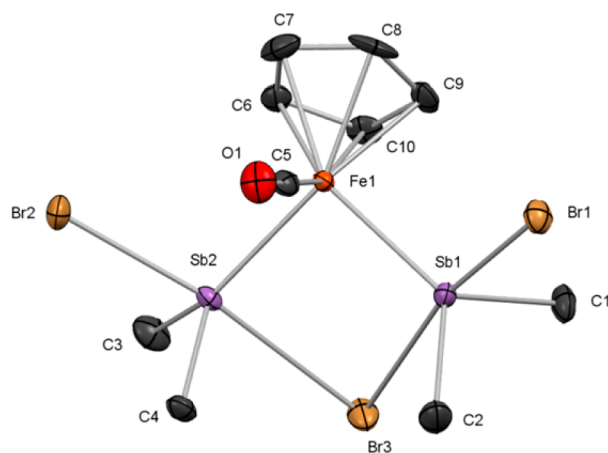

Figure 2. View of the structure of $[CpFe(CO)_2(SbMe_2Br)][BF_4]$ showing the atom-numbering scheme. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. The long Sb–F contact is shown as a dotted line.

between the anion and the cation. One F atom from the $[BF_4]^-$ unit approaches the Sb atom trans to the Br substituent, with a Sb···F distance of 2.825(2) Å, considerably shorter than the sum of the van der Waals radii of these elements (3.93 Å).[11] While $[BF_4]^-$ is generally considered to be a noncoordinating anion, there are many examples of this type of $F_3B–F···M$ bridging to charged s-block and d-block metals and a smaller number with charged p-block metal centers: for example, in $[\{CpFe(CO)_2\}_2SnF][BF_4]$ (Sn···FBF_3 = 2.148 Å).[12] This behavior demonstrates that the coordinated halostibine must possess a significant Lewis acidity.

When, during the synthesis of $[CpFe(CO)_2(SbMe_2Br)]$-$[CF_3SO_3]$, the reaction mixture was left undisturbed at room temperature over a period of days as part of a crystallization process, a few brown, rod-shaped crystals were observed in the reaction vessel. X-ray structure determination showed these to be the 2:1 adduct $[CpFe(CO)(Me_2BrSb-\mu-Br-SbBrMe_2)]$, in which a second ligand replaces one CO group from the Fe center and the $[CF_3SO_3]^-$ anion has been replaced by a Br^- anion, which bridges two Sb atoms, forming a puckered four-membered $FeSb_2Br$ ring (Figure 3).

Several attempts were made to form this monocarbonyl complex directly and exclusively, including treatment of $[CpFe(CO)_2(SbMe_2Br)][CF_3SO_3]$ with HBr, but none were successful. Reacting $[CpFe(CO)_2(thf)][CF_3SO_3]$ with an excess of $SbMe_2Br$ resulted in initial isolation of the 1:1 complex, but subsequent storage of the reaction mixture in the freezer for a period of weeks yielded a significant quantity (26% yield based on Fe) of crystals of $[CpFe(CO)(Me_2BrSb-\mu-Br-SbBrMe_2)]$. IR analysis showed only one peak in the CO region, to low frequency of the two observed in the dicarbonyl complexes, and the $^{13}C\{^1H\}$ NMR resonance for the CO moved ~8 ppm to high frequency, commensurate with a significant increase in electron density on the Fe center. Examination of the structure of this complex showed that the Br^- counterion has a strong interaction with both Sb atoms. The two Sb–Br3 distances are slightly different (Sb1–Br3 = 2.9698(7), Sb2–Br3 = 2.9901(8) Å); both are comparable to

Figure 3. View of the structure of $[CpFe(CO)(Me_2BrSb-\mu-Br-SbBrMe_2)]$ showing the atom-numbering scheme. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.

examples of bridging Br in bromoantimonate polyanions, such as $[Sb_2Br_8]^{2-}$ (Sb–$Br_{bridging}$ = 2.955, 2.972 Å)[13] and $[Sb_2Ph_2Br_7]^{3-}$ (Sb–$Br_{bridging}$ = 3.116 Å)[14] or neutral dimer complexes such as $[SbBr_3(thiocaprolactam)_2]_2$ (Sb–$Br_{bridging}$ = 3.148, 3.159 Å).[15] The geometry around each Sb center is pseudotrigonal bipyramidal, having distorted to accommodate the second Br in an axial position (mean Br–Sb–Br = 170.0°, mean Fe–Sb–$Br_{bridging}$ = 88.8°). Hypervalent interactions in halostibines are generally observed trans to the Sb–X bond, as the low-lying Sb–Br σ^* orbital is the most accessible to accept electron density. The increase in strength of this interaction on going from the $[BF_4]^-$ to Br^- anion is demonstrated by the increase in the Sb–$Br_{terminal}$ bond length (2.51 Å vs mean 2.63 Å) and increased linearity of the donor–Sb–$Br_{terminal}$ angle (mean 170.0° vs 165.9°). Given these observations, a more appropriate description of the Br-bridged species may be as a neutral complex containing a bidentate monoanionic ligand with a Br–Sb–Br–Sb–Br backbone, rather than as a cation and associated anion. The Sb–Fe bond distances (Sb1–Fe1 = 2.4635(9), Sb2–Fe1 = 2.4698(8) Å) are only very slightly shorter than that in the $[CpFe(CO)_2(SbMe_2Br)]^+$ unit, suggesting that, despite the change in the coordination environment of Sb, there is no significant change in the strength of the Sb–Fe bond. The structure can be compared to that of $[RhCl_2\{Ph_2Sb(CH_2)_3SbPh_2\}\{PhClSb(CH_2)_3SbClPh\}]$-Cl, one of several products from the treatment of $[Rh(CO)$-$\{Ph_2Sb(CH_2)_3SbPh_2\}_2][PF_6]$ with excess HCl.[16] The Cl^- ion in this species adopts a position between the two Sb atoms of the coordinated dihalostibine ligand, trans to each Sb–Cl, forming a four-membered ring with the Rh center, reminiscent of that seen with the Fe in $[CpFe(CO)(Me_2BrSb-\mu-Br-SbBrMe_2)]$.

The mechanism by which $[CpFe(CO)(Me_2BrSb-\mu-Br-SbBrMe_2)]$ forms is not immediately evident, and it is clear that other products must be present. The closest analogue, the spectroscopically characterized $[CpFe(CO)(SbPh_3)_2][BF_4]$, was formed via sequential displacement of the thioether ligands from $[CpFe(CO)(SMe_2)_2][BF_4]$ and has an identical CO stretching band (1973 cm^{-1}) in the solution infrared spectrum, demonstrating an approximate equivalence in the net bonding ability for the haloalkyl stibine and triaryl stibine ligands.[17] However, the displacement of a CO group, which we have

shown to be reproducible in this system, has not been observed in analogous reactions of the $[CpFe(CO)_2]^+$ fragment with other stibine ligands, even potentially chelating alkyl-substituted distibines.[18] Conversely, the reaction of $[CpFe(CO)_2X]$ (X = halide) with more strongly σ donating chelating diphosphine ligands does result in the elimination of CO to form $[CpFe(CO)(\text{diphosphine})]X$.[19,20] It is probable that the formation of $[CpFe(CO)(Me_2BrSb-\mu-Br-SbBrMe_2)]$ is driven by the stability of the Br-bridged configuration, arising from the interaction between lone pairs on the central Br and the low-lying Sb−Br σ^* orbital on each $SbMe_2Br$ moiety. In the present case the interaction is strong enough that it could be considered as a three-center−four-electron bond at each Sb center.

This work demonstrates that hypervalency, a phenomenon particularly associated with the heavier elements of group 15, is prevalent in donor complexes of halostibines and can influence the reactivity of these species. In the context of the increasing interest in the bonding and reactivity of heavy p-block transition-metal complexes these revelations suggest that further new reaction chemistry of such complexes remains to be explored.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text giving experimental and crystallographic details and tables and CIF files giving crystallographic data and bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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