Neutral Organoantimony(III) and Organobismuth(III) Ligands as Acceptors in Transition Metal Complexes – Role of Substituents and Co-ligands.

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Contents   **Page**

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Keywords: antimony, bismuth, stibine, bismuthine, transition metal complexes, X-ray structures, 'hypervalency'

Highlights: Transition metal stibine and bismuthine complexes with simultaneous donor and acceptor properties reviewed.

Lewis acid and Lewis base properties of halostibines and halobismuthines reviewed.

Effects of substituent types on structural properties reviewed.

Abstract

This article reviews work up until mid-2014 on the synthesis and properties of transition metal complexes containing the heavier Group 15 Sb(III) and Bi(III) ligands, of general formula ER_3 (E = Sb or Bi; R = alkyl, aryl etc, and may include a pendant donor group such as amine or ether) and $ER_{(3-n)}X_n$ (E = Sb or Bi; R is an organic substituent such as alkyl, aryl, *etc.*; X is an electronegative substituent such as halide; n = 0-3) in which these ligands function as a donor to a transition metal fragment, while simultaneously participating as an acceptor to another electronegative group such as an anionic or metal-coordinated halide, or an amine, ether, *etc.*, leading to Sb/Bi centres bearing more than eight valence electrons ('hypervalent'). The Lewis acid properties of the halostibines and halobismuthines, $ER_{(3-n)}X_n$, are also reviewed.

Abbreviations:

py = pyridine;

thf = tetrahydrofuran;

2,2'-bipy = 2,2'-bipyridine;

1,10-phen = 1,10-phenanthroline;

DFT = density functional theory;

Cp = η^5-$C_5H_5^-$;

dmpu = N,N'-dimethylpropylene urea;

VdW = Van der Waals

1. Introduction

Stibines (SbR_3) and bismuthines (BiR_3) are the heavier Group 15 analogues of the very widely studied phosphine and arsine ligands. Although they are generally regarded as weaker donor ligands, stibines and bismuthines confer a number of interesting features that are often much less evident in the lighter analogues. These heavy Group 15 neutral donor ligands are usually described π-acids or σ-donor π-acceptor ligands, which mainly bond to d-block metals by σ-donation of the lone pair on the Sb or Bi atom, supplemented to some extent by π-acceptance of d-electron density into either Sb/Bi−C σ*-orbitals or a combination of Sb/Bi-C σ*-orbitals and empty Sb/Bi d-orbitals. The relative importance of the σ- and π-components vary with the metal oxidation state and d-electron density.

The trihalides of the Group 15 elements, in particular, PX_3, AsX_3, SbX_3 and BiX_3 (X = F, Cl, Br, I), usually behave as weak acceptors towards other ligands, with the Lewis acidity increasing down the Group for a given X.[1] PF_3 was shown in the early literature[2] to be an effective Lewis base towards (usually) low valent transition metal species. This behaviour is less common for the heavier Group 15 trihalides, notable examples being adducts of nickel dithiocarbamates with coordinated AsI_3 and SbI_3 ligands.[3]

This article reviews recent work on the properties of complexes containing the heavier Group 15 Sb(III) and Bi(III) ligands, of general formula $ER_{(3-n)}X_n$ (E = Sb or Bi; R is an organic substituent such as alkyl, aryl, *etc.*; X is an electronegative substituent such as halide, amide, alkoxide *etc.*; n = 0-3). Specifically, the review is concerned with complexes in which these ligands function as a donor to a transition metal fragment, while simultaneously participating as an acceptor to another electronegative group such as a halide, amine, ether, *etc.*, although it also covers the literature concerning compounds in which halostibines and halobismuthines function as Lewis acids. These types of interaction, often referred to as 'hypervalent', are usually not seen in lighter Group 15 analogues. The term 'hypervalency' has become somewhat controversial, and hence it is pertinent to be clear what is meant by it in the context of the present article, *i.e.* Sb(III) and Bi(III) compounds containing greater than eight valence electrons. These species tend to take the form of additional M−Sb/Bi···X interactions, and can span a significant bond length scale from very long,

weak interactions lying close to the sum of the van der Waals radii for Sb or Bi♦[4] and X, through to much shorter interactions, which are more akin to typical covalent bonds.

The coordination chemistry of triorgano-stibine and -bismuthine ligands has been reviewed previously,[5,6,7,8] whilst Braunschweig and co-workers have reviewed the synthesis, structure and properties of complexes containing a transition metal-bismuth bond.[9] Much of work relevant to the present article is quite disparate and has emerged only over the last decade and is not reviewed elsewhere. A recent review by Raţ, Silvestru and Breunig[10] concentrated on 'hypervalency' in organo-stibine and -bismuthine compounds bearing pendant arm donor groups, focusing primarily on compounds which do not contain a coordinated metal ion. This provides an excellent platform for the present article, which will focus mainly on compounds in which the ER_3 or $ER_{(3-n)}X_n$ ligand is coordinated to a transition metal centre. The Lewis acid properties of the halostibines and halobismuthines, $ER_{(3-n)}X_n$, is also reviewed. Coverage is focused on complexes based upon Sb and Bi formally in oxidation state III only, including literature up to mid-2014. The presence of 'hypervalency' in these systems is often most readily evident from crystallographic analyses, and the majority of the species structurally characterised to-date are based on stibine ligands, hence these dominate the discussion below. However, where these interactions are stronger and if there is a suitable 'reporter' group in the complex, such as CO ligands, they can lead to doubling up of peaks either in the solid state or solution IR spectra, or in the NMR spectra – as discussed in some cases below. The aim of the review is to stimulate experimental and computational investigations in this developing field in order to establish a broader understanding of the bonding, properties and potential applications of complexes containing 'hypervalent' interactions involving Sb(III) and Bi(III) species of this type.

2. Lewis Acid Behaviour of SbR₃ and BiR₃ Ligands

2.1 Donation from neutral ligands towards metal-coordinated SbR₃ and BiR₃

As discussed above, species of the form SbR_3 (triorganostibines) are generally considered as Lewis bases, and their donor behaviour towards transition metals has been well studied,[5,6,8] though the number of stibine complexes still represents a tiny fraction compared to number of phosphine complexes reported. Less well explored is their Lewis acidic character, which, while weak, allows the formation of long intra- or inter-molecular contacts, often referred to as 'hypervalent' interactions,

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♦ van der Waals radii for Sb and Bi are 2.47 and 2.54 Å, respectively.[4]

with a range of donor atoms. A significant amount of work in recent years has focused on organostibines with pendant-arm substituents bearing heteroatoms (usually N or O), many of which display intramolecular 'hypervalent' behaviour of this kind, and have been recently reviewed.[10] In such cases X-ray structural characterisation demonstrates that, in the solid state, a conformation is adopted which allows close approach of the other donor atom to a Sb centre to well within the sum of the Van der Waals radii of the two atoms, indicating the presence of an interaction. These interactions can stabilise unusual species[11] and induce chirality in otherwise achiral molecules.[12]

It is only in a small number of stibine and bismuthine complexes, all reported within the last decade, that these two behaviours (Lewis basic donation towards a transition metal and Lewis acidic acceptance of an intramolecular ligating group) have been observed to occur simultaneously. Electronically it is not surprising that the Sb/Bi ligand, having given up electron density to a transition metal, is all the more ready to behave as an acceptor, though an increase in steric crowding around Sb/Bi may hinder access, especially for bulky substituents. Ligands which can access this behaviour often contain both SbR_3 (or BiR_3) groups and other donor moieties connected by a flexible backbone, and are generally prepared by well-established synthetic routes to organo-stibines or -bismuthines (Figure 1).

Y = S, NMe
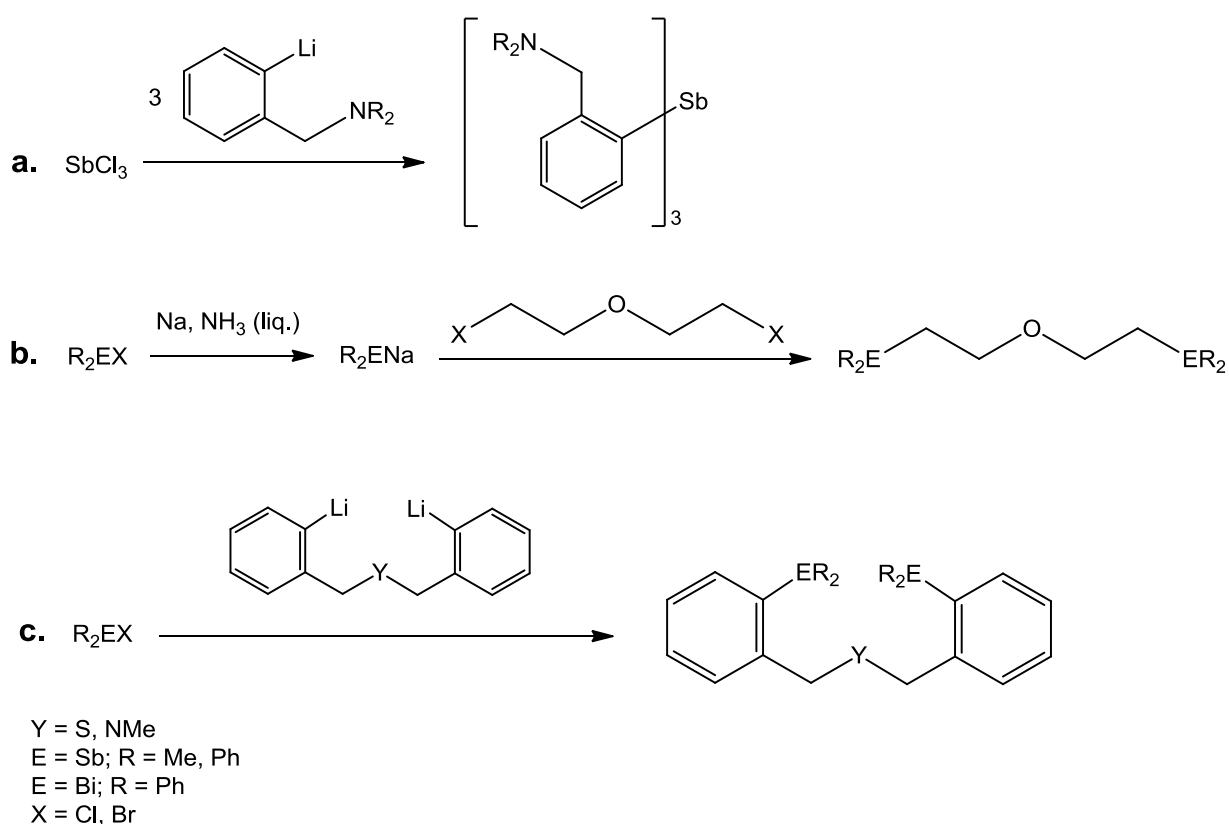E = Sb; R = Me, Ph
E = Bi; R = Ph
X = Cl, Br

Figure 1 Synthetic schemes for some typical hybrid stibine and bismuthine ligands.

'Hypervalent' interactions are often observed in the solid state structures of the uncoordinated hybrid ligands.[10] The first examples of their complexes with transition metals are Pt(II) and Pd(II) chloride derivatives of stibines with pendant amine substituents, a class of organostibines which has been widely investigated for their intramolecular 'hypervalency' (Figure 1a).[13,14] Complexation with transition metal centres has been used to help characterise these organostibines, and can be used to enantiomerically resolve Sb-chiral species.[15] In such complexes the 'hypervalent' interactions observed in the free ligands are often maintained, meaning that the Sb atom acts as a donor (towards the Pt centre) and an acceptor (towards pendant amine substituents) simultaneously. Several structurally characterised examples are known; in [PtCl$_2$\{Sb(C$_6$H$_4$-2-CH$_2$NMe$_2$)$_3$\}], for example, the three identical substituents on the coordinated Sb centre each behave differently, with one amine coordinated to Pt cis to Sb, one amine folded so as to weakly coordinate to Sb (Sb$\cdots$N = 3.24(1) Å), and the third uncoordinated (Figure 2).[13]
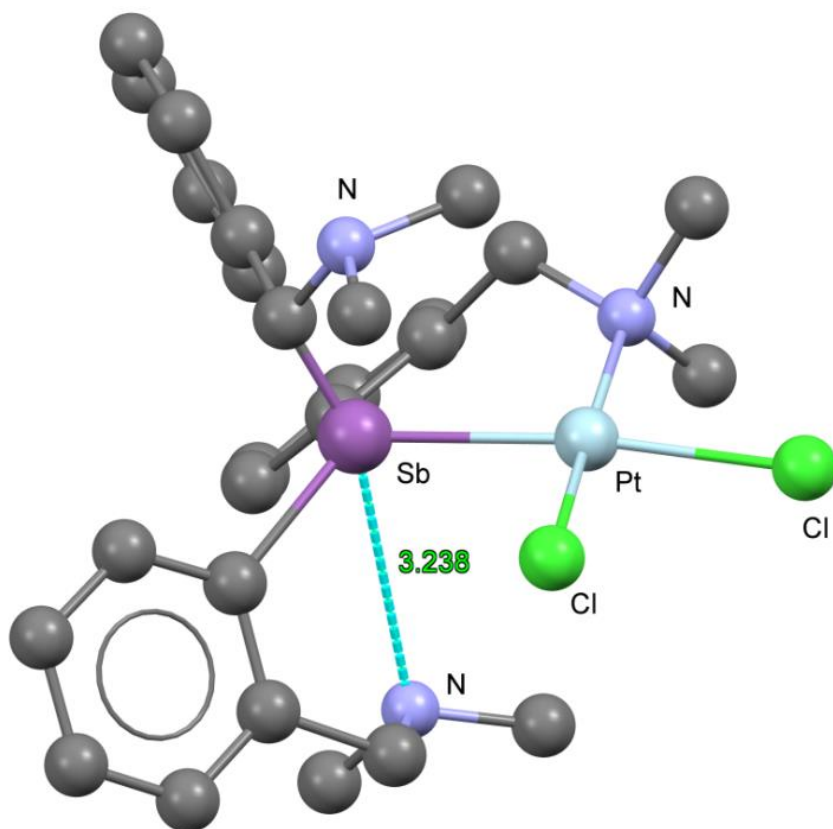

Figure 2 View of the structure of [PtCl$_2$\{Sb(C$_6$H$_4$-2-CH$_2$NMe$_2$)$_3$\}] showing the long-range intramolecular Sb$\cdots$N 'hypervalent' interaction through donation of the lone pair on N to the coordinated Sb donor. Redrawn from reference 13.

The similar complex, [PtCl$_2$\{SbPh$_2$(C$_6$H$_4$-2,6-(CH$_2$NMe$_2$)$_2$)\}], which also contains one amine group coordinated to Pt and one to Sb, was investigated as a cis-platin analogue, however its low

solubility in water hindered cytotoxicity testing.[14] The reaction of the O-bridged $\{R_2Sb\}_2O$ (R = C_6H_4-2-CH_2NMe_2) with [W(CO)$_5$(thf)] in air gives the unusual complex, [W(CO)$_5$(R$_2$SbOH)], in moderate yield, which also displays a 'hypervalent' interaction of one pendant amine with the Sb centre, which is itself coordinated to W (d(Sb$\cdots$N) = 2.860(9) Å), the other amine forming an intramolecular H-bond with the OH substituent.[16]

These intramolecular interactions are not confined to amine donor groups. In [PtCl$_2$(Sb{C$_6$H$_4$-2-CH(OEt)$_2$}$_3$)$_2$] each of the *trans* stibine ligands contains one intramolecular contact to Sb by an O atom from one of three pendant acetal groups (d(Sb$\cdots$O) = 3.126(6) Å).[17] A shorter Sb$\cdots$O interaction (3.000(4) Å) is seen with a pendant ether moiety in an organometallic Pd(II) complex of the chiral {Sb(1-naphthyl)(*p*-tolyl)(C$_4$H$_6$-2-CH$_2$OMe)} ligand ((1), Figure 3), which contains both Sb and C chirogenic centres.[18]
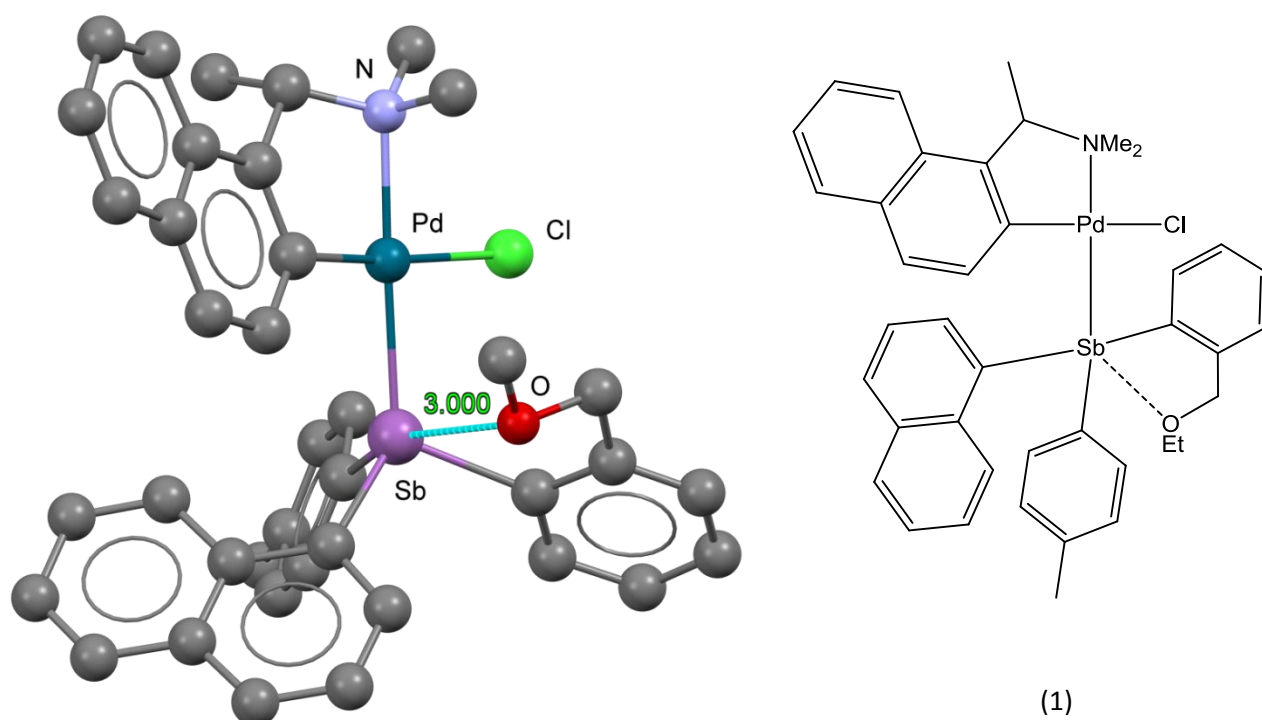

(1)

Figure 3 View of the structure of complex (1) showing the long-range intramolecular Sb$\cdots$O 'hypervalent' interaction through donation of the lone pair on O to the coordinated Sb donor. Redrawn from reference 18.

Recent work in our group has explored hybrid bi- and poly-dentate stibine ligands incorporating two or more Sb donors as well as one hetero-donor (O, S, or N) within the di- or tri-stibine ligand backbone (Figures 1b and c).[19,20,21] These were originally of interest as ligands which could present a mixed donor set to a transition metal fragment, allowing examination of stibine

coordination within a more robust, chelating ligand framework. As part of this work, complexes with low-valent metal carbonyls were pursued as appropriate acceptors for the soft stibine donors. Where multiple coordination sites are available, ligands with Sb_2E donor sets coordinate in a tridentate manner, for example in $[Mn(CO)_3\{E(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}]^+$ (E = S, NMe), and hence no 'hypervalent' interactions are present.[22] However, where available coordination sites at the metal are limited, coordination of the Sb donors to the metal carbonyl is typically preferred, leaving an uncoordinated heteroatom in the ligand backbone. In complexes of this type the formation of an intramolecular interaction between this heteroatom and one or both of the coordinated Sb donors is often observed. For example, the crystal structure of $[\{CpFe(CO)_2\}_2\{O\{(CH_2)_2SbMe_2\}_2\}]^+$ shows an asymmetric conformation of the coordination ligand, allowing an interaction between the central O atom and one of the two Sb–Fe moieties (Sb$\cdots$O = 3.184(8) Å) (Figure 4).[21] In this case the solid state IR spectrum confirms that the two otherwise identical -FeCp(CO)$_2$ groups are in different electronic environments, causing a splitting of the v(CO) bands. Thus, while two bands are expected for the $-FeCp(CO)_2$ units, in practice these are split into two pairs in the binuclear complex cation, though such splitting is not observed in the solution state IR spectrum, indicating that the interaction is not present (or much weaker) in solution (Table 1). IR spectroscopic data on the CO stretching vibrations also support the assignment of Sb$\cdots$O/N 'hypervalent' interactions in other similar complexes.[21]

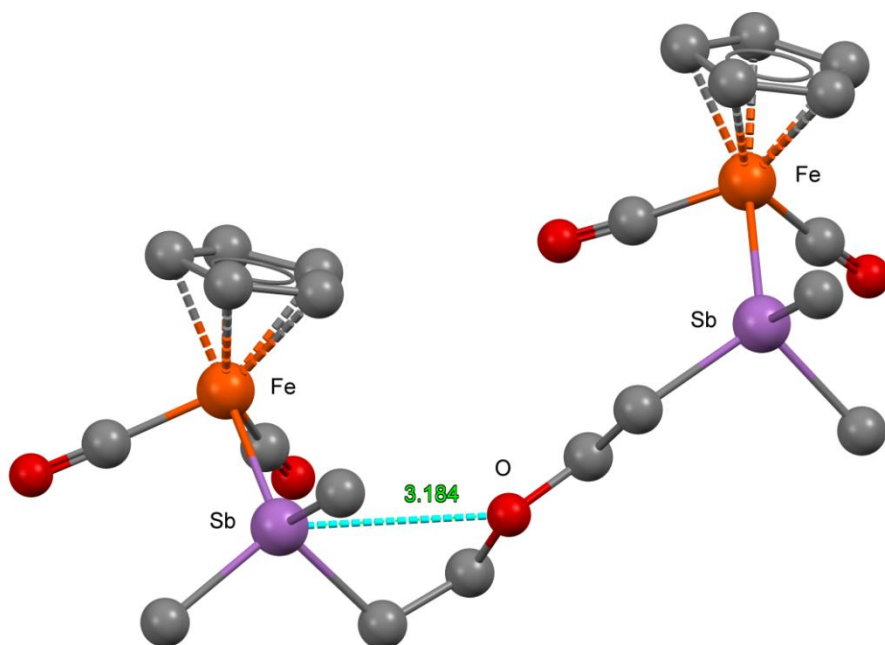Figure 4 View of the structure of the cation in $[\{CpFe(CO)_2\}_2\{O\{(CH_2)_2SbMe_2\}_2\}][BF_4]_2$ showing the long range intramolecular Sb$\cdots$O interaction on one side of the ligand only. Redrawn from reference 21.

[{CpFe(CO)$_2$}$_2$\{O\{(CH$_2$)$_2$SbMe$_2$\}$_2$\}][BF$_4$]$_2$	v(CO) /cm^{-1}
Solid state (Nujol mull)	2041, 2034, 2005, 1993
Solution state (MeCN solution)	2044, 2000

Table 1 Infra-red spectroscopic data for [{CpFe(CO)$_2$}$_2$\{O\{(CH$_2$)$_2$SbMe$_2$\}$_2$\}][BF$_4$]$_2$, demonstrating splitting of the CO bands due to intramolecular interactions in the solid state.[21]

In [Ag\{O\{(CH$_2$)$_2$SbMe$_2$\}$_2$\}$_2$]$^+$ the same ligand chelates the Ag centre *via* the two Sb donors, while the remaining ether is able to form weak intramolecular interactions with both Sb atoms (Sb···O = 3.033(3) to 3.247(4) Å).[19] The analogous arsine complex is structurally very similar, and is a rare example of intramolecular contacts of this type being formed with the less Lewis acidic As centre, possibly an indication that the effects of crystal packing or optimisation of backbone geometry play a role in directing the position of the O donor atom with respect to the heavy atom in these complexes.[19] In some complexes of these ligands, 'hypervalent' interactions are not obviously present, and the factors governing their formation are too subtle to be easily predictable at the present time. One such case is that of the related compounds [M(CO)$_4$\{MeN(CH$_2$-2-C$_6$H$_4$SbMe$_2$)$_2$\}] (M = Cr, Mo, W); in the W and Mo compounds there is an intramolecular N···Sb interaction on one side of the molecule (d(N···Sb) = 2.997(3) and 3.050(4) Å respectively), whereas in the Cr compound no such weak N···Sb interactions are observed, the N atom being roughly equidistant between the two Sb centres and close enough to neither to form a significant interaction (3.643(6) and 3.467(6) Å).[20,22] The presence of this interaction induces a significant distortion of the ligand backbone in the W complex in comparison to the otherwise almost structurally identical Cr complex (Figure 5).[22] The reasons for the different structures across this series are not known, but may in part reflect their different packing arrangements.
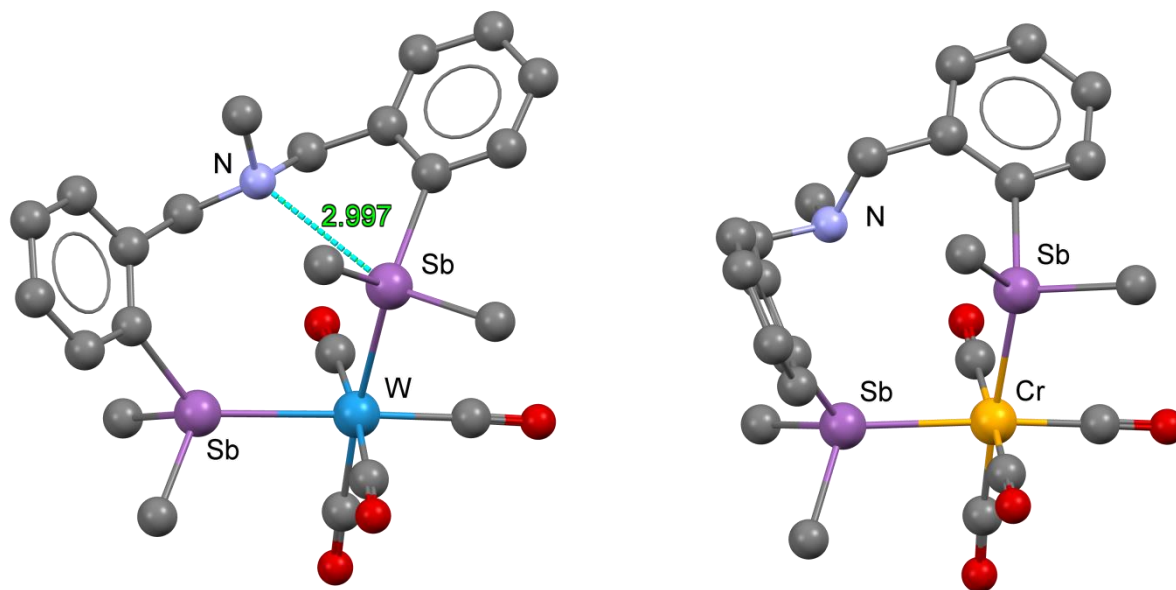
Figure 5 View of the structures of [M(CO)$_4${MeN(CH$_2$-2-C$_6$H$_4$SbMe$_2$)$_2$}] (M = W, left; M = Cr, right) showing the presence or absence, respectively, of a Sb···N interaction, and the resulting differences in ligand conformation. Redrawn from reference 22. The figures have been aligned with respect to the coordination sphere at the metal centre.

While examples of organobismuthines containing intramolecular 'hypervalency' are plentiful, there are only 12 structurally characterised transition metal complexes of BiR$_3$ ligands (CCDC accessed Nov. 2014).[23] Of these, most feature bulky substituents at the Bi centre, and none provide an appropriate intramolecular donor group, therefore there are no authenticated examples of coordinated BiR$_3$ ligands with 'hypervalent' interactions at present. Bismuth analogues of several of the hybrid antimony ligands discussed above have been synthesised (Figure 1, above) and coordinated to a limited number of transition metal centres.[21,22] In complexes of these hybrid dibismuthines with the [CpFe(CO)$_2$]$^+$ fragment, a splitting of the (expected) two v(CO) bands is clearly observed in the solid state IR spectra (Table 2), suggesting the presence of an interaction between the heteroatom in the ligand backbone and one of the two coordinated bismuthines, generating inequivalence of the two Fe centres, as is seen in some of the analogous distibine complexes. In most cases these splittings were not evident in the solution IR spectra, except in the case of [{CpFe(CO)$_2$}$_2${MeN(CH$_2$-2-C$_6$H$_4$BiPh$_2$)$_2$}][BF$_4$]$_2$ where they do remain. Doubling up of resonances is also observable in the ^{13}C{^{1}H} NMR resonances in some of the hybrid dibismuthine complexes, suggesting that the interaction is retained in solution (Table 2).[21] Without structural information it is difficult to probe these interactions fully, although on the basis of the spectroscopic data available, it

seems probable that they are equally, if not more, prevalent in these dibismuthine complexes as compared with complexes of the analogous distibines.

Complex	υ (CO)/cm^{-1} (chlorocarbon solution)	υ (CO)/cm^{-1} (Nujol)	^{13}C{^{1}H} NMR[a] δ(Cp)	^{13}C{^{1}H} NMR[a] δ(CO)
[{CpFe(CO)$_2$}$_2${O{(CH$_2$)$_2$BiPh$_2$}$_2$}][BF$_4$]$_2$	2063, 2020	2062,2021, 2007(sh)	86.3	209.5
[{CpFe(CO)$_2$}$_2${S(CH$_2$-2-C$_6$H$_4$BiPh$_2$)$_2$}]-[BF$_4$]$_2$	2067, 2020	2071, 2055, 2023	85.3	210.0
[{CpFe(CO)$_2$}$_2${S(CH$_2$-2-C$_6$H$_4$BiMe$_2$)$_2$}]-[BF$_4$]$_2$	2072, 2020	2068, 2015, 2005	86.2	209.6
[{CpFe(CO)$_2$}$_2${MeN(CH$_2$-2-C$_6$H$_4$BiPh$_2$)$_2$}][BF$_4$]$_2$	2070, 2055, 2022, 1998	2065, 2040, 2020, 2003	85.4, 85.5	210.2, 211.1
[{CpFe(CO)$_2$}$_2${MeN(CH$_2$-2-C$_6$H$_4$BiMe$_2$)$_2$}][BF$_4$]$_2$	2071, 2024	2071, 2043, 2017, 2004	86.6	209.6

Table 2 Infra-red and ^{13}C{^{1}H} NMR spectroscopic data for some hybrid dibismuthine complexes, demonstrating splitting of the bands due to intramolecular Bi$\cdots$O/N/S interactions, from reference 21.

2.2 Donation from a coordinated halide ligand towards SbR$_3$ and BiR$_3$

Halides represent another class of potential donor atoms towards Lewis acidic Sb centres (*vide infra*). Organoantimony species containing pendant halide substituents have not so far been investigated, probably due to synthetic considerations. However, re-examination of structural data from some complexes of specific SbR$_3$ ligands with transition metal halides does reveal unexpected behaviour. For example, in [PtCl$_2$\{1,2-C$_6$H$_4$(CH$_2$SbMe$_2$)$_2$\}] weak intermolecular contacts are present between one Cl ligand on Pt and both Sb centres in the distibine ligand of a neighbouring molecule, forming a supramolecular polymeric chain (Figure 6) (Sb$\cdots$Cl = 3.644(2) and 3.684(2) Å; ΣVdW radii = 4.29 Å[4]).[24]

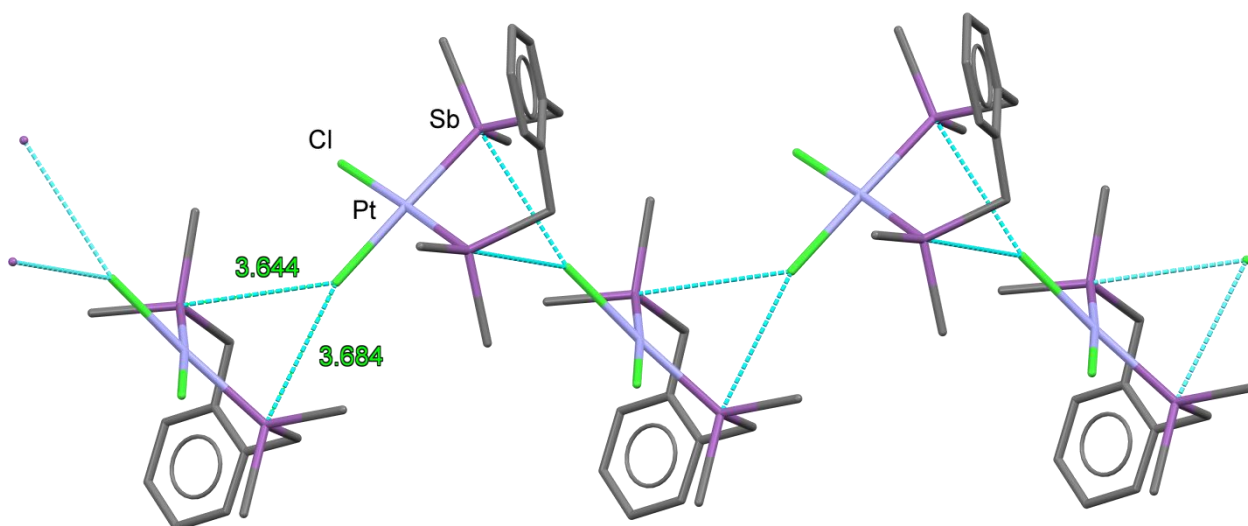Figure 6 View of a section of the supramolecular chain structure of [PtCl$_2$\{1,2-C$_6$H$_4$(CH$_2$SbMe$_2$)$_2$\}] showing long, intermolecular Sb···Cl contacts. Redrawn from reference 24.

The analogous complex of the wide-angled distibine ligand L = \{CH$_2$(2-C$_6$H$_4$CH$_2$SbMe$_2$)\}$_2$ dimerises in the solid state, giving [PtCl$_2$L]$_2$ (Figure 7).[25] The increased flexibility of the ligand backbone allows the formation of a Pt···Pt interaction (3.176(1) Å), with each coordinated Sb directly opposite a Cl ligand in the square plane of the neighbouring Pt centre (Sb···Cl = 3.525(3) and 3.440(3) Å). The organisation of the dimer into this centrosymmetric configuration is likely to be aided by the formation of the favourable Sb···Cl interactions. Examples of Pt(II)···Pt(II) bonded dimers without bridging ligands are known, but are not common; of the two structurally identified polymorphs of [PtCl$_2$\{N(H)C(OH)^{t}Bu\}$_2$]$_2$ for example, one has a comparable d(Pt···Pt) = 3.165(2) Å, although the ligands are staggered with respect to the Pt···Pt bond, whereas in the second polymorph the ligands are held in the eclipsed position by H-bonding between Cl and OH groups, but d(Pt···Pt) (3.3986(7) Å) in this case is considerably longer.[26]

Figure 7 View of the structure of [PtCl$_2${{CH$_2$(2-C$_6$H$_4$CH$_2$SbMe$_2$)}$_2$ }] showing the weakly associated dimer stabilised *via* both long-range Pt···Pt contacts and intermolecular Sb···Cl 'hypervalent' interactions. Redrawn from reference 25.

This type of Sb···X−M behaviour is limited to these few examples at present and in the case of the dimer in Figure 7 it is difficult to separate the magnitude of the effect derived from the Sb···Cl interaction from that of the metallophilic interaction. However, it should be noted that in each case the substituents at Sb are sterically undemanding, whereas other recorded complexes of stibine ligands with transition metal halides generally carry more sterically demanding (often aryl) substituents at Sb, which are likely to hinder the formation of this type of acceptor interaction.

3. Halostibines and halobismuthines

Halostibines and halobismuthines (ER$_{(3−n)}$X$_n$, R = alkyl, aryl; X = halide), which are frequently encountered as intermediates in the preparations of bi- and poly-dentate triorgano-stibines and -bismuthines, are usually prepared by partial alkylation of EX$_3$ using organolithium or Grignard reagents, comproportionation of ER$_3$ and EX$_3$ in the appropriate molar ratio, or *via* E−C(aryl) (usually) bond scission by reaction in a solvent such as diethyl ether, benzene or toluene, saturated with HX.[1,5-8] Halostibines and halobismuthines are expected to fall between the two extremes of Lewis acid and Lewis base behaviour due to the presence of both substituent types. Examples of these compounds acting as Lewis acids are rather rare and, unsurprisingly, complexes of ERX$_2$, bearing two electronegative halide substituents, with other neutral ligands tend to be more prevalent than those with ER$_2$X.

3.1 Lewis acidic behaviour

The halostibines, $SbRX_2$ (X = Cl or Br), readily complex with neutral bidentate ligands such as 2,2'-bipy and 1,10-phen, as well as monodentate O- N- and P-donor ligands. Specific examples include $[SbMeX_2(2,2'-bipy)]$, $[SbPhX_2(2,2'-bipy)]$, $[SbMeX_2(1,10-phen)]$, $[SbPhX_2(thf)_n]$ (n = 1 or 2), $[SbMeBr_2(OPMe_3)_2]$ (Figure 8) and $[SbMeBr_2(OPPh_3)_2]$, all of which appear to be discrete monomers containing distorted square pyramidal coordination at Sb, with the Ph or Me group apical.[27,28,29] Reacting $SbPhCl_2$ with PMe_3 in a 1:1 ratio gives $[SbPhCl_2(PMe_3)]$ which forms a very loosely associated dimer (Figure 9). The corresponding reaction with PPh_3 gives $[SbPhCl_2(PPh_3)]$, which consists of a more closely associated dimer with slightly longer P–Sb coordinative bonds, commensurate with the lower donor power of the arylphosphine.[30] Also isolated from this reaction was the *bis*-ligand complex $[SbPhCl_2(PPh_3)_2]$ which is a monomer (Figure 10), the increased coordination number apparently inhibiting dimer formation here. The complexes $[SbPh_2X(2,2'-bipy)]$ (X = Cl or Br) constitute rare examples containing the more weakly Lewis acidic $SbPh_2X$.[29]
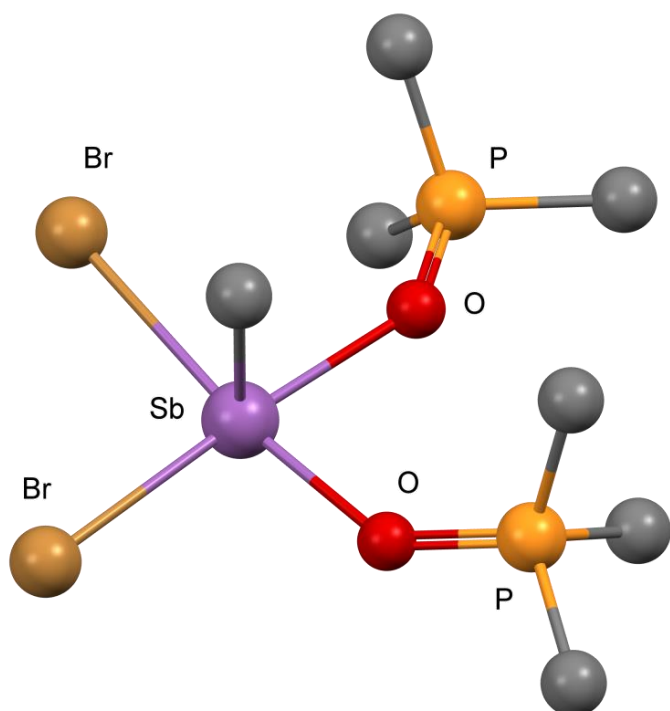

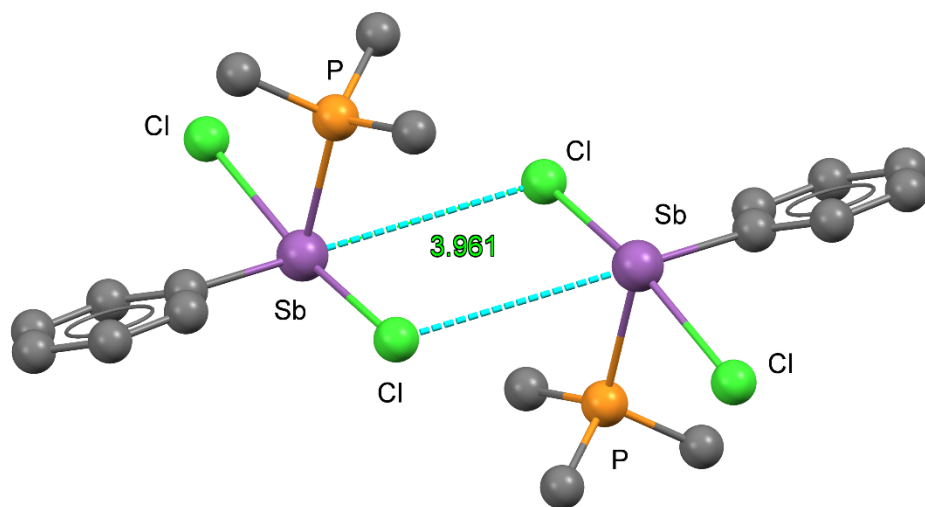Figure 8 View of one of two molecules in the asymmetric unit of $[SbMeBr_2(OPMe_3)_2]$. Redrawn from reference 28.

Figure 9 View of the loosely associated dimer present in the structure of [SbPhCl$_2$(PMe$_3$)]. Redrawn from reference 30.
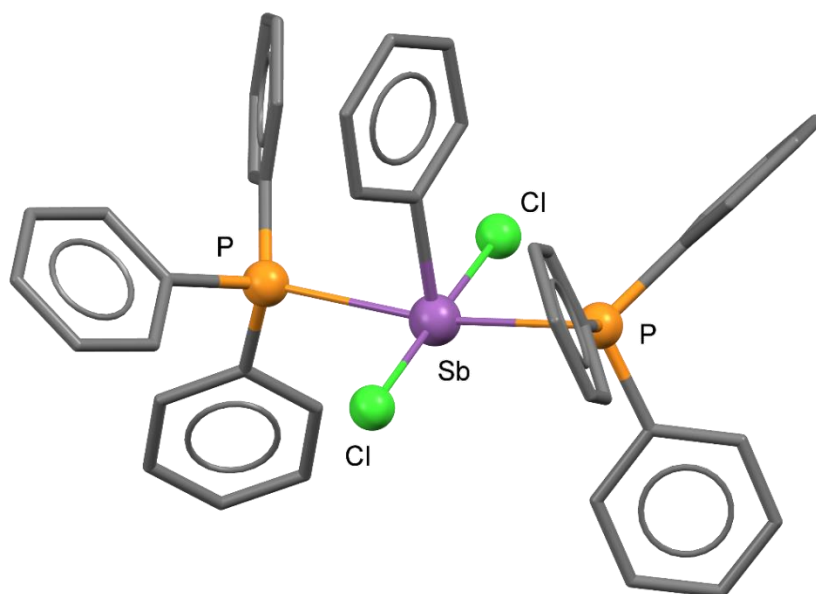

Figure 10 View of the structure of the [SbPhCl$_2$(PPh$_3$)$_2$] monomer. Redrawn from reference 30.

Arylhalobismuthine complexes of the form [BiPhX$_2$(L–L)] (X = Cl, Br or I; L–L = 1,10-phen, 2,2'-bipy) and [BiPhX$_2$L] (L = thf, py, OPR$_3$) have also been known for some years.[31,32,33,34,35] Structural

studies on [BiPhX$_2$(thf)] (X = Cl, Br, I) each reveal one-dimensional polymers in which one halide ligand bridges between adjacent bismuth atoms (Figure 11), similar to the structure of [BiPhCl$_2$(2,2'-bipy)].[34,35,36]

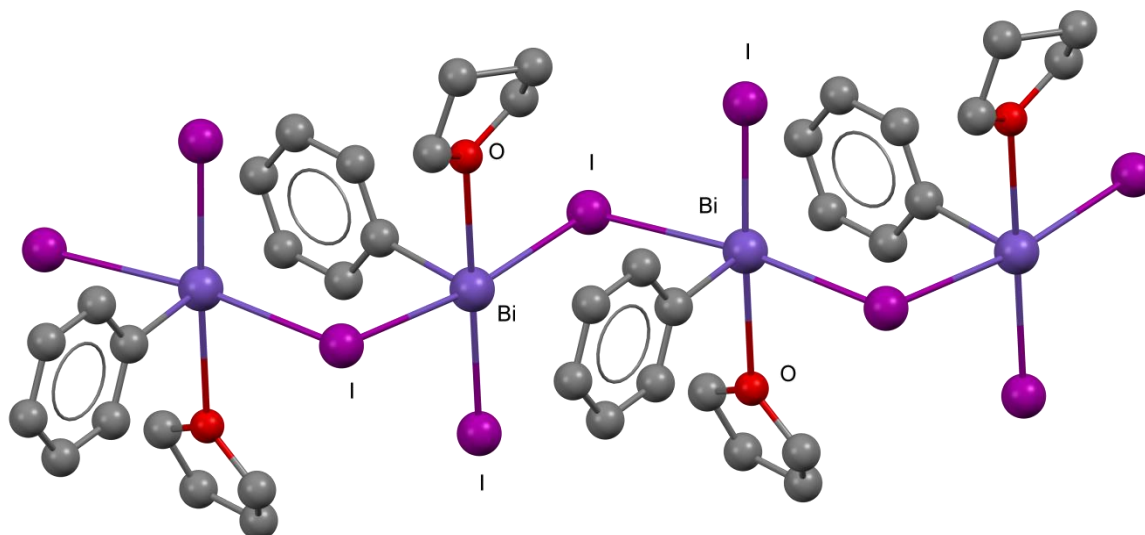Figure 11 View of part of the chain structure of [BiPhI$_2$(thf)]. Redrawn from reference 34.

In contrast, [BiPhBr$_2$(OPPh$_3$)] and [BiPhBr$_2$(dmpu)] (dmpu = N,N'=dimethylpropylene urea) adopt dimer arrangements with two asymmetrically bridging B**r**$^-$ ligands, *anti* apical Ph groups and one terminal OPPh$_3$ or dmpu ligand per bismuth ion (Figure 12), while the *bis* ligand complex [BiPhBr$_2$(dmpu)$_2$] is a monomer.[33]
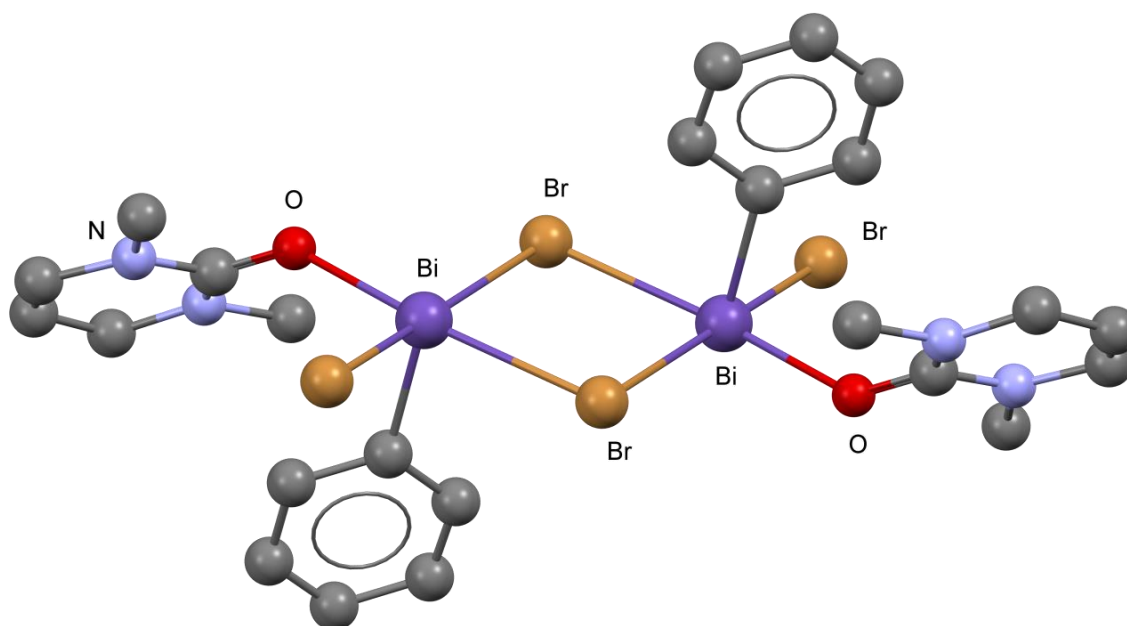
Figure 12 View of the structure of the [BiPhBr$_2$(dmpu)]$_2$ dimer. Redrawn from reference 33.

The corresponding methyldihalobismuthines, BiMeX$_2$ (X = Cl or Br), also behave as modest Lewis acids towards neutral bidentate ligands such as 1,10-phen, 2,2'-bipy or Me$_2$N(CH$_2$)$_2$NMe$_2$ (L-L). The crystal structure of [{BiMeCl$_2$(2,2'-bipy)}$_2$] adopts a weakly associated dimer formed through long range Bi$\cdots$Cl contacts.[27] In contrast, BiMeBr$_2$ forms the five-coordinate, distorted square pyramidal monomers, [BiMeBr$_2$(L–L)], in good yield. Structural analyses on several of these species show the Me group (like the Ph in the earlier examples) always occupies the apical coordination site (Figure 13), and the Bi–C bonds in these species appear to be less susceptible to breaking compared to the parent BiMeX$_2$ compounds. Similar reaction of L–L with BiMe$_2$X leads to disproportionation, driven by the stability of the [BiMeX$_2$(L–L)] complex formed (with BiMe$_3$ the other product).[37]
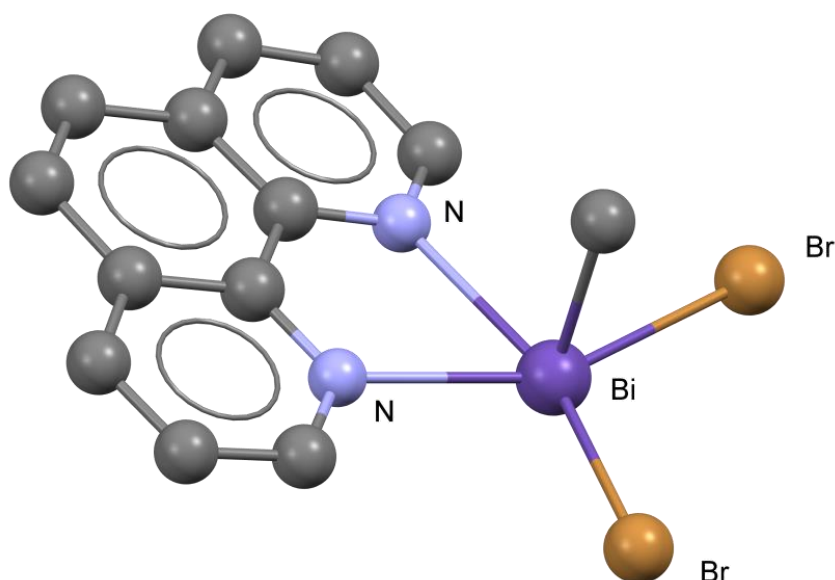

Figure 13 View of the structure of [BiMeBr$_2$(1,10-phen)] redrawn from reference 37.

3.2 Dual donor and acceptor behaviour of halostibines and halobismuthines in transition metal complexes

As noted earlier, as organic substituents at Sb are replaced with halide substituents the Lewis acidity of organostibines increases, and their Lewis basicity decreases. We have recently made an effort to draw the boundaries of these behaviours,[28] and have found that the mixed alkylhalostibines prove a fertile ground for unusual coordination chemistry in which both behaviours are often observed simultaneously. Low valent Group 6 carbonyl complexes with SbR$_2$X ligands (R = Me, Ph, ^{t}Bu; X = Cl,

Br, I) are well established, as well as two examples with the dibromostibine ligand SbMeBr$_2$ ligand, [M(CO)$_5$(SbMeBr$_2$)] (M = Cr, W).[28,38,39,40,41] These complexes are readily prepared by combining photolytically-generated [M(CO)$_5$(thf)] (M = Cr, Mo, W) with the appropriate halostibine. As Breunig and co-workers were the first to observe, weak intermolecular interactions are found in the solid state structures of these compounds between Sb centres and O atoms from CO groups on neighbouring molecules, linking them into dimers or networks.[28,39] These contacts are long, although within the sum of the Van der Waals radii (3.97 Å),[23] but are directional, being persistently observed approximately *trans* to the halide substituent on Sb. In [W(CO)$_5$(SbPh$_2$Cl)] two molecular units are linked into a dimer by these Sb···O contacts (Figure 14), with the bond dissociation energy of these interactions estimated to be 18.7 kJ mol^{-1}.[39] A charge decomposition analysis of the bonding between Sb and W atoms in this compound concluded that both donor and acceptor character was present.[39] Comparing the bond lengths and spectral data for the series [W(CO)$_5$(SbMe$_n$Br$_{3-n}$)] (n = 1, 2, 3) leads to the conclusion that π-acceptance by Sb increases with increasing halide substitution in these complexes, given that d(Sb−W) becomes shorter as the number of halide substituents increases, while at the same time ν(CO) increases and δ(CO) decreases. Overall, this indicates a reduced electron density on the metal centre.[28] Treatment of [W(CO)$_5$(SbMe$_2$Br)] with one mol. equiv. of MeLi or ^{n}BuLi forms the corresponding [W(CO)$_5$(SbMe$_3$)] and [W(CO)$_5$(SbMe$_2$^{n}Bu)], respectively, providing a potential route to di- and poly-stibine formation on a metal ion template.[28]
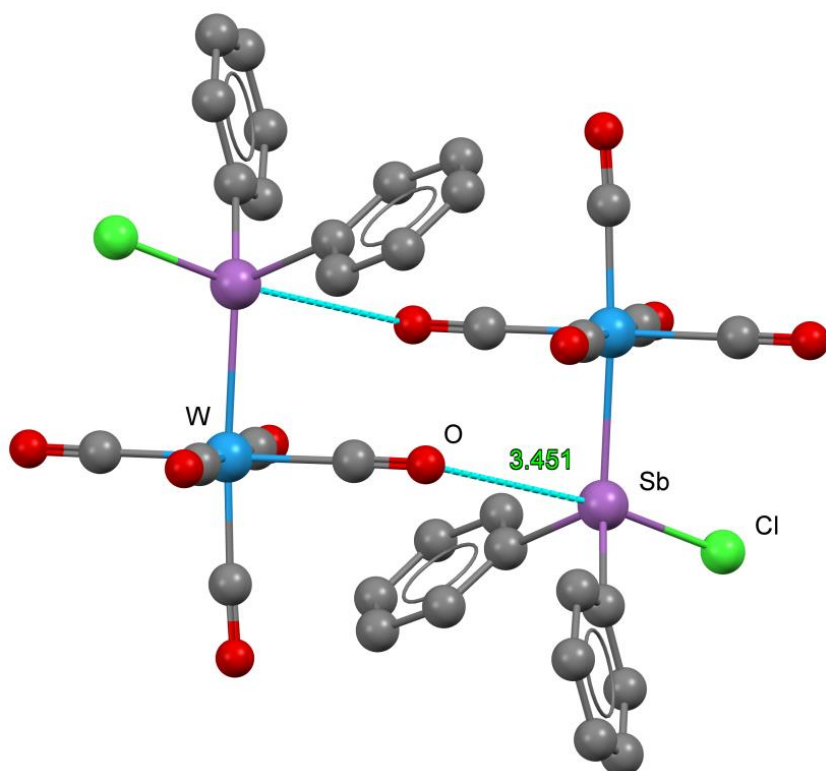
Figure 14 View of the structure of [W(CO)$_5$(SbPh$_2$Cl)] showing the weakly associated dimer formed *via* long-range intermolecular Sb···OC interactions. Redrawn from reference 39.

Cationic metal carbonyl complexes with the SbMe$_2$Br ligand reveal significant interactions between Sb and electronegative atoms in the counteranion, in which the approach of the donor group is always observed approximately *trans* to the Br substituent at Sb. In [Mn(CO)$_5$(SbMe$_2$Br)][CF$_3$SO$_3$] and [Mn(CO)$_3$(SbMe$_2$Br)$_3$][CF$_3$SO$_3$], prepared by reaction of SbMe$_2$Br with [Mn(CO)$_5$(CF$_3$SO$_3$)] or [Mn(CO)$_3$(Me$_2$CO)$_3$][CF$_3$SO$_3$] in the appropriate ratio, O atoms from the triflate anion form contacts with one or, in the latter case, up to two of the Sb centres.[28] The latter complex is an unusual example of multiple halostibine ligands coordinating to a single transition metal centre, and contains two slightly different coordination environments at Sb, with one triflate O atom bridging two halostibines, and the third halostibine forming an interaction with O from a neighbouring anion, forming a loosely associated 1D chain structure (Figure 15). Again, it is notable that these interactions always approach Sb *trans* to the Br substituent, which results in differences in conformation of the three halostibine ligands, two having their Br substituents aligned within the *fac* Sb$_3$ plane, and the other roughly perpendicular.
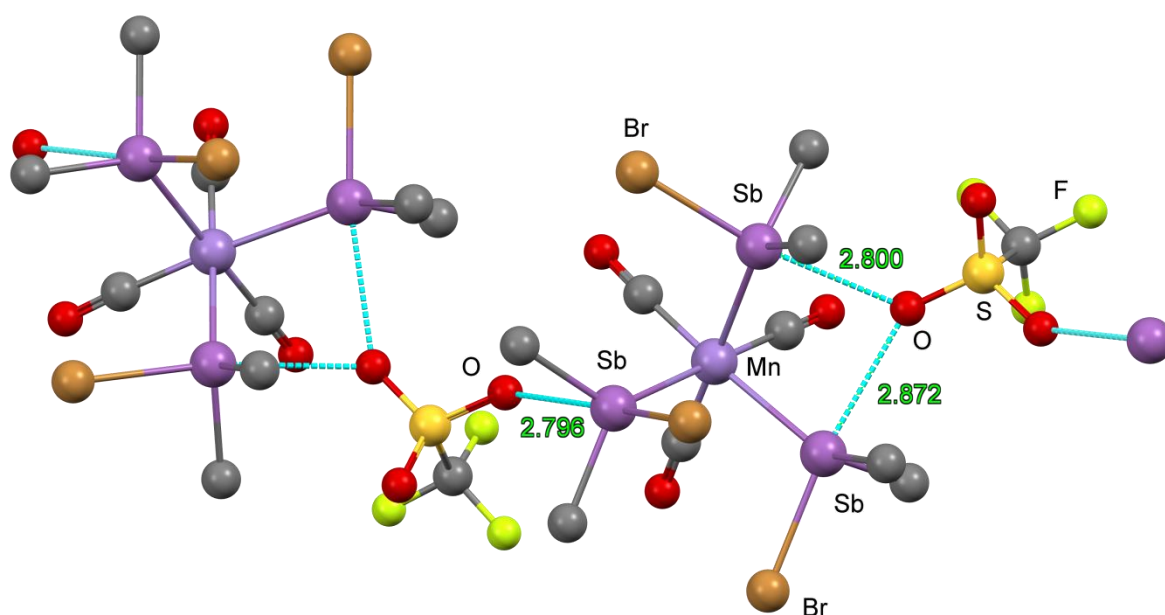

Figure 16 View of part of the chain structure of [Mn(CO)$_3$(SbMe$_2$Br)$_3$][CF$_3$SO$_3$] showing the Sb···O interactions linking the cations and anions. Redrawn from reference 28.

Similar cation-anion interactions are seen in [FeCp(CO)$_2$(SbMe$_2$Br)][X] ([X]$^-$ = [CF$_3$SO$_3$]$^-$ or [BF$_4$]$^-$), between the coordinated Sb and O or F donor atoms from the anion, respectively (Figure

17).[42] The Sb⋯O distances lie between 2.696(5) and 2.874(2) Å, considerably shorter than the weaker associations with carbonyl groups discussed above, and the Sb⋯F distance in [FeCp(CO)$_2$(SbMe$_2$Br)][BF$_4$] is 2.825(2) Å (ΣVdW = 3.93 Å [4]). These interactions affect the geometry at Sb, distorting the usual *pseudo*-tetrahedral arrangement of a coordinated stibine towards a *pseudo*-trigonal bipyramid with Br and O (or F) in axial positions. Interactions of this sort are not observed in analogous complexes of triorganostibine ligands.
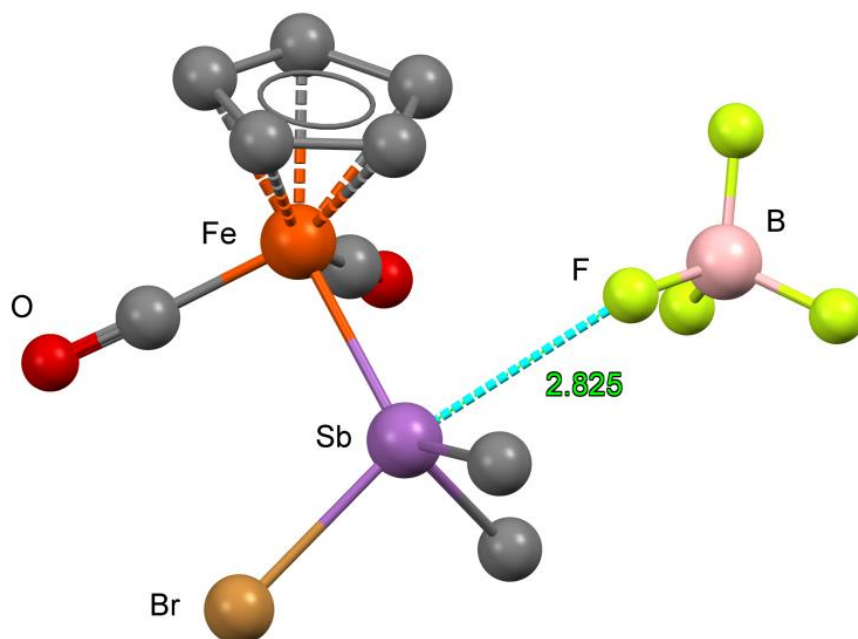

Figure 17 View of the structure of [FeCp(CO)$_2$(SbMe$_2$Br)][BF$_4$] showing the weak, long-range interaction between the Sb atom of the coordinated SbMe$_2$Br ligand and an F atom from the BF$_4^-$ anion. Redrawn from reference 42.

These are relatively rare examples of traditionally 'weakly-coordinating anions' forming significant interactions. Moving to halide anions results in stronger interactions, as seen in [CpFe(CO){Me$_2$BrSb(μ-Br)SbMe$_2$Br}], a by-product from the synthesis of [FeCp(CO)$_2$(SbMe$_2$Br)][X].[42] In the solid state structure the Br$^-$ anion sits closely between two *cis*-coordinated Sb centres, roughly *trans* to the Br substituent on each Sb (mean Br–Sb⋯Br$_{bridging}$ = 170 °) (Figure 18). The interactions are short enough (Sb⋯Br$_{bridging}$ = 2.9698(7), 2.9901(8) Å) that the Br$^-$ can alternatively be considered as a bridging group in a monoanionic Me$_2$BrSb–Br–SbMe$_2$Br ligand.
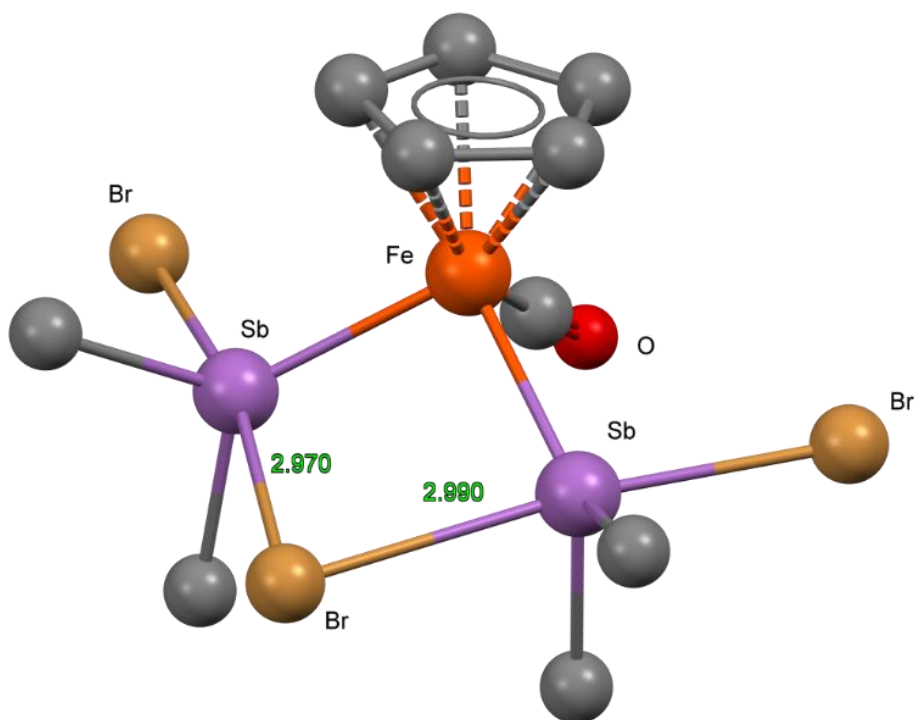
Figure 18 View of the structure of [CpFe(CO){Me$_2$BrSb(μ-Br)SbMe$_2$Br}] showing the presence of the Br$^-$ ion bridging between the two coordinated SbMe$_2$Br ligands. Redrawn from reference 42.

A similar configuration, in which the Cl$^-$ anion sits between the two Sb atoms of the coordinated PhClSb(CH$_2$)$_3$SbClPh ligand, is seen in [RhCl$_2$\{Ph$_2$Sb(CH$_2$)$_3$SbPh$_2$}{PhClSb(CH$_2$)$_3$SbClPh}]Cl, one of several products from the treatment of [Rh(CO){Ph$_2$Sb(CH$_2$)$_3$SbPh$_2$}$_2$][PF$_6$] with HCl (Figure 19).[43] This Rh(III) species appears to be the only structurally characterised complex containing a coordinated bidentate halostibine ligand. The PhClSb(CH$_2$)$_3$SbClPh derives from HCl induced cleavage of a Sb−C(Ph) group on each Sb atom in the parent Ph$_2$Sb(CH$_2$)$_3$SbPh$_2$. It is likely that in both cases the formation of these unexpected products is driven at least in part by the stability of this 'four-membered ring' configuration, with a central halide stabilising two halostibine ligands coordinated *cis* to a transition metal centre.
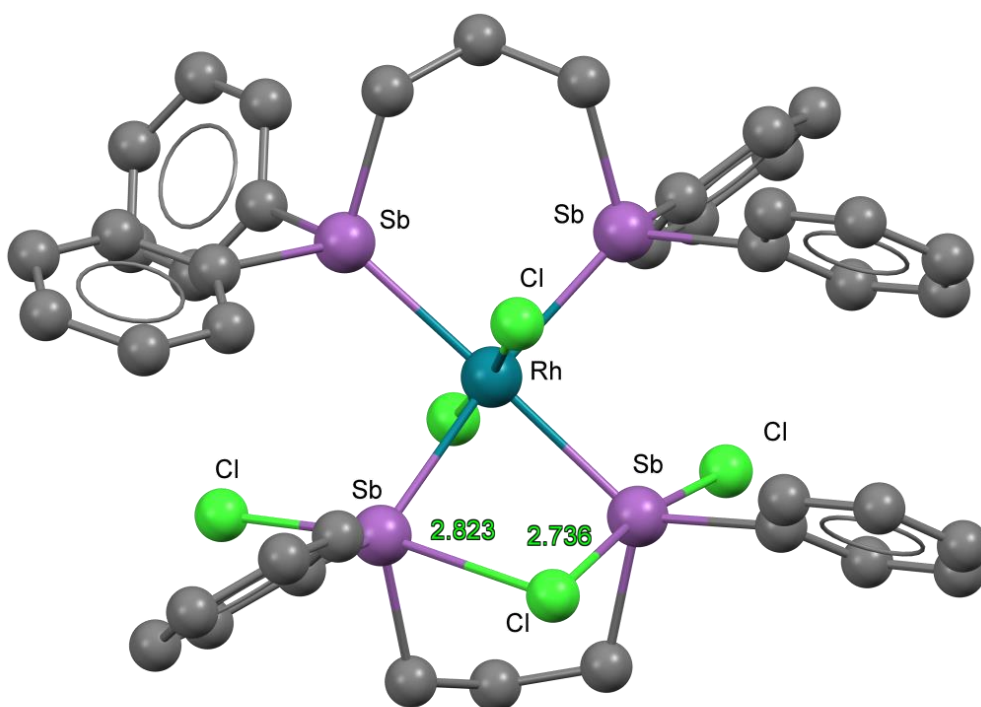
Figure 19 View of the structure of [RhCl$_2$\{Ph$_2$Sb(CH$_2$)$_3$SbPh$_2$\}\{PhClSb(CH$_2$)$_3$SbClPh\}]Cl showing the presence of the Cl$^-$ ion bridging between the two Sb atoms present in the coordinated PhClSb(CH$_2$)$_3$SbClPh ligand. Redrawn from reference 43.

In the last five years a significant body of work has focussed on the reactivity of the mixed ligands E(C$_6$H$_4$-2-PPh$_2$)$_3$ and EPh(C$_6$H$_4$-2-PPh$_2$)$_2$ (E = Sb, Bi) (Figure 20). The phosphine moieties, together with the *o*-phenylene linkers, provide a robust ligand framework which readily chelates to transition metal centres, enabling investigation of reactivity and 'ligand non-innocence' at the heavy p-block atom. One example is [PtCl\{SbClPh(C$_6$H$_4$-2-PPh$_2$)$_2$\}] (Figure 21), formed from the reaction of [PtCl$_2$(SEt$_2$)$_2$] with the *bis*(phosphino)stibine ligand, SbPh(C$_6$H$_4$-2-PPh$_2$)$_2$.[44] As for the halostibine complexes, the unusual reactivity is presumably driven by the Lewis acidity of the Sb centre, as well as the formation of the stable PSbP-chelated square planar configuration at Pt. The resulting species has been formulated as containing a monoanionic Sb ligand, though the environment around Sb is not dissimilar to that in the halide-bridged halostibine complexes discussed above, d(Sb–Cl) = 2.753(2) Å being fairly long for a covalent bond, and very comparable to d(Sb–Cl$_{bridging}$) = 2.736(3), 2.823(3) Å found in the Cl$^-$ bridged species.

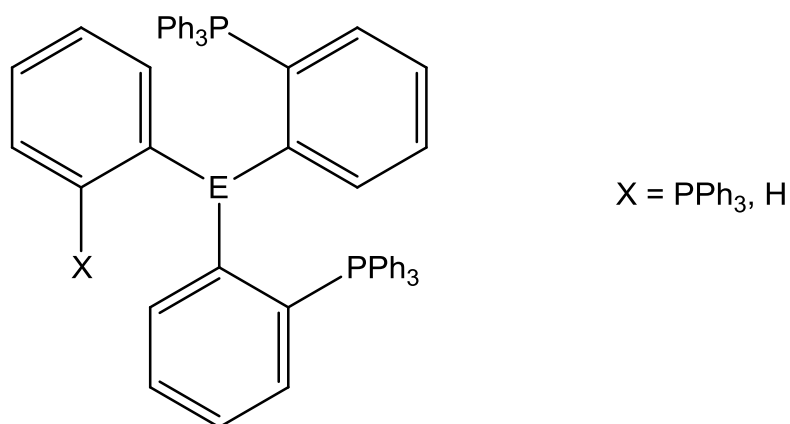Figure 20 Ligands $E(C_6H_4-2-PPh_2)_3$ and $EPh(C_6H_4-2-PPh_2)_2$ (E = Sb, Bi)

Figure 21 View of the structure of $[PtCl\{SbClPh(C_6H_4-2-PPh_2)_2\}]$. Redrawn from reference 44.

The related Ni complex, $[NiCl\{SbCl(C_6H_4-2-PPh_2)_3\}]$, formed from the reaction of $[Ni(PPh_3)\{Sb-(C_6H_4-2-PPh_2)_3\}]$ with $PhICl_2$, features a slightly shorter d(Sb−Cl) of 2.6835(9) Å.[45] Computational natural bond order analyses suggest that in this complex Sb is behaving as an 'X-ligand' towards Ni, i.e. an anionic ligand which forms a covalent bond, and this gives weight to the consideration of the Sb−Cl bond as covalent. Also related are $[PdCl\{SbFPh(C_6H_4-2-PPh_2)_2\}]$ and $[PdCl\{SbF(C_6H_4-2-PPh_2)_3\}]$, formed from anion exchange of $[PdCl\{SbPh(C_6H_4-2-PPh_2)_2\}][BPh_4]$ or $[PdCl\{Sb(C_6H_4-2-PPh_2)_3\}][BPh_4]$

respectively with [NBu$_4$]F (Figure 22).[46] Once again the halide, in this case fluoride, reacts with the Sb centre rather than the transition metal, forming a Sb–F bond. In the latter compound, this leads to a rearrangement of the geometry at Pd from square planar to trigonal bipyramidal, caused by coordination of the (previously uncoordinated) third phosphine moiety. This rearrangement is presumably as a result of the lower σ-donor power of the fluorostiborane compared to the stibine, and can be monitored by UV spectroscopy, meaning this complex can be used as a fluoride ion sensor with ppm sensitivity.
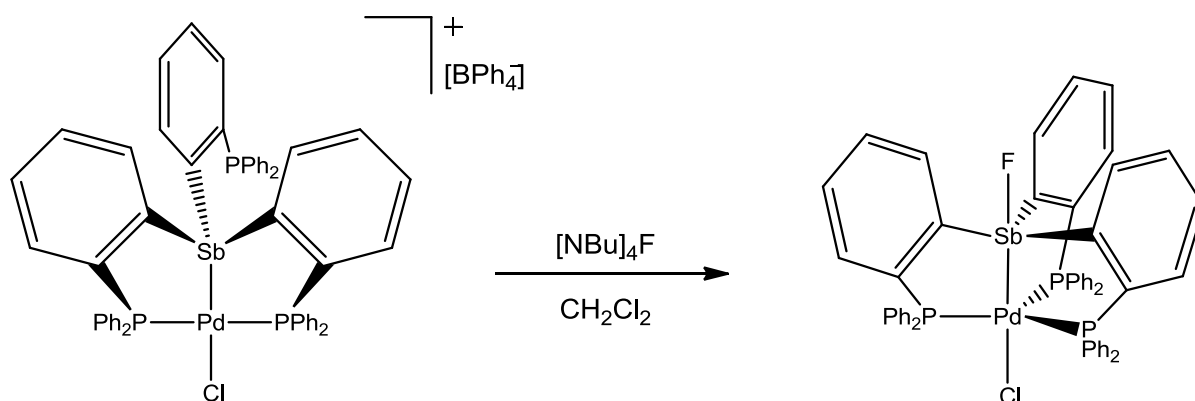

Figure 22 Scheme showing anion exchange in [PdCl{Sb(C$_6$H$_4$-2-PPh$_2$)$_3$}]$^+$, leading to a change in geometry from square planar to trigonal bipyramidal. Redrawn from reference 46.

The corresponding halobismuthines, BiR$_2$X, are considered to be not sufficiently Lewis basic to act as donors towards transition metals, and attempts to coordinate them to metal carbonyl fragments have to-date ended in failure. For example, reaction of [M(CO)$_5$(thf)] (M = Cr or W) with BiMe$_2$Br causes disproportionation to BiMeBr$_2$ and [M(CO)$_5$(BiMe$_3$)].[37] However, reaction of the hybrid BiP$_3$ donor ligand Bi(C$_6$H$_4$-2-PPh$_2$)$_3$ with Au(I), Pd(II) and Pt(II) chlorides results in substitution at the Bi centre, in which one -C$_6$H$_4$-2-PPh$_2$ group is eliminated and replaced with a Cl substituent to form complexes of BiCl(C$_6$H$_4$-2-PPh$_2$)$_2$, for example [AuCl{BiCl(C$_6$H$_4$-2-PPh$_2$)$_2$}] (Figure 23).[47,48] These complexes are structurally very similar to the halostibine complexes discussed above, however detailed DFT studies have demonstrated that the interaction between the metal and the nearby Bi centre (2.974(17) [47] and 2.9979(3) Å [48]) is in fact dative from the transition metal towards Bi. In other words, the chlorobismuthine acts as a Lewis acid towards these transition metal centres, though this interaction is likely to be stabilised by the bidentate phosphine donor framework which holds it in place. The authors suggest that this unusual bonding type has potential uses in catalytic systems, as a method of tuning electron density at the transition metal centre.

The difference in reactivity of transition metal halides with the analogous Sb and Bi ligands, namely that Sb accepts a halide, increasing its coordination number, whereas Bi substitutes the halide for an organic substituent, can be rationalised by the very weak nature of the Bi-C bond and the lower Lewis basicity of Bi.
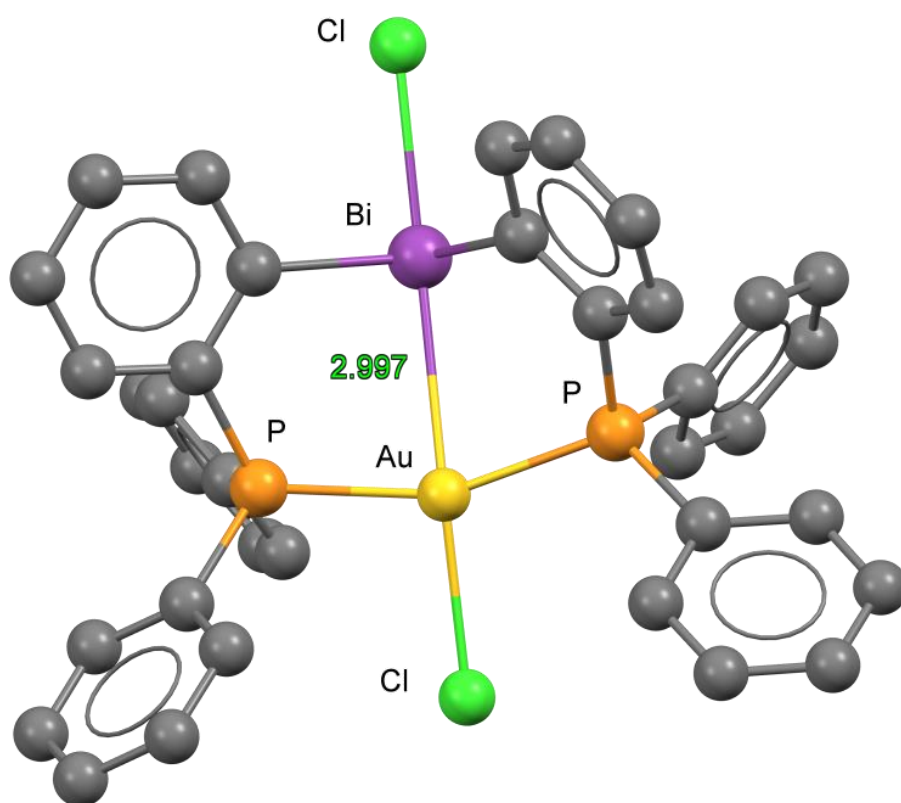

Figure 23 View of the structure of [AuCl{BiCl(C_6H_4-2-PPh_2)$_2$}]. Redrawn from reference 48.

4. Miscellaneous complexes

We have in general restricted this review to complexes of neutral, trivalent Sb and Bi ligands. However, these distinctions become difficult to maintain when considering complexes of transition metals with no organic substituents at Sb or Bi, in which bonding type and oxidation states are not always easily assigned.

The neutral [Cp(CO)$_2$Fe(SbBr$_2$·PMe$_3$)] is formed when [Cp(CO)$_2$Fe(SbBr$_2$)] is reacted with PMe$_3$,[49] in contrast to the behaviour of the analogous dialkylstibide complex, [Cp(CO)$_2$Fe(SbMe$_2$)], which undergoes displacement of CO ligands at Fe.[50] [Cp(CO)(L)Fe(SbBr$_2$·PMe$_3$)] (L = PMe$_3$, MeCN) can subsequently be formed in the presence of an excess of L (Figure 24). These compounds can be considered as metallostibines, with the difference in Lewis acidity at Sb dictating the difference in reactivity. The authors state that these compounds "provide the first evidence that trivalent

compounds of group 5B elements with σ-bonded transition-metal ligands are able to function not only as excellent electron donors but also as acceptors". This assumes an antimony oxidation state of Sb(III) and a formal iron oxidation state of Fe(0), which it should be noted is at odds with the higher electronegativity of Sb in comparison to Fe, which would tend to infer oxidation states Fe(II) and Sb(I). In reality, formal oxidation states are of very little use in elucidating the nature of the bonding in these unusual species, about which little is known.
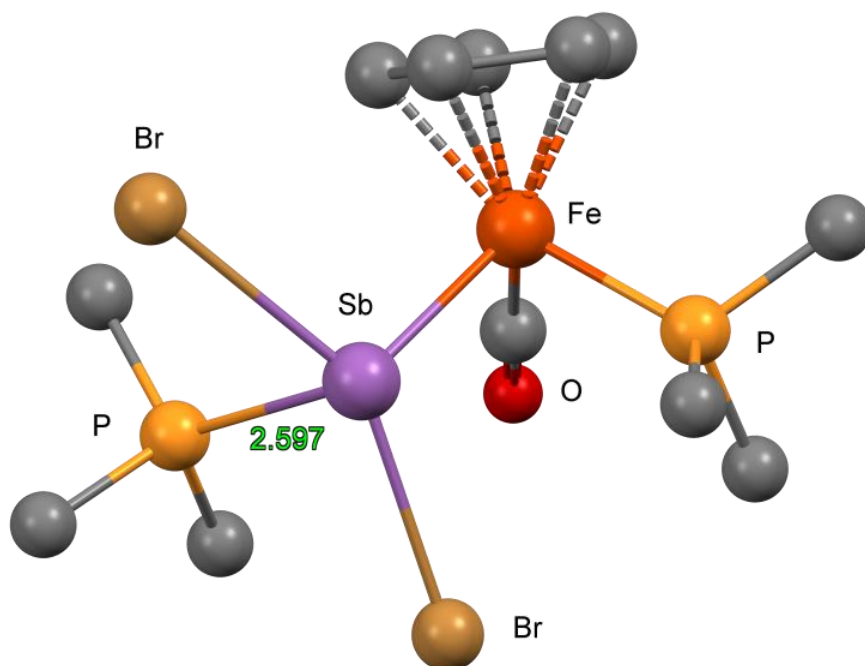

Figure 24 View of the structure of [Cp(CO)(PMe₃)Fe(SbBr₂·PMe₃)]. Redrawn from reference 49.

Bi(III) halides have been shown to form adducts with low-valent metal carbonyl species. These include the structurally characterised $[MoCp(CO)_3(BiCl_3)]_2^{2-}$, $[FeCp(CO)_2(BiCl_3)]_2^{2-}$ (Figure 25) and $[Fe(CO)_4(Bi_2Cl_6)]^{2-}$ ions.[51,52,53] The first two examples consist of a near planar Bi_2Cl_6 unit with one transition metal bonded to each Bi centre, whereas in the latter example a bent Bi_2Cl_6 unit is bridged by a single $Fe(CO)_4$ fragment. In these examples, we should consider the Bi(III) chlorides acting as a Lewis acid towards the transition metal centre, forming short M–Bi interaction (2.62 to 2.95 Å) in which the electron-rich transition metal is the donor. The Lewis acidity of the Bi centre is further satisfied by interactions with Cl substituents from neighbouring Bi atoms, giving dimers in which the Bi–Sb$_{bridging}$ distances are only slightly asymmetric.
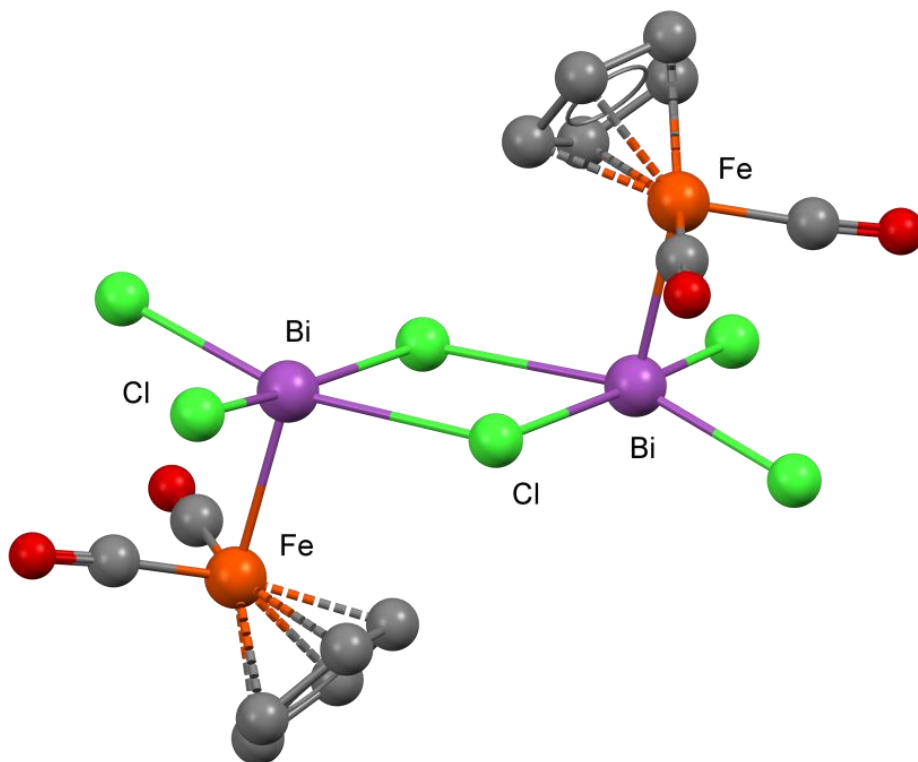
Figure 25 View of the structure of $[FeCp(CO)_2(BiCl_3)]_2^{2-}$. Redrawn from reference 52.

5. Conclusions and Outlook

The occurrence of 'hypervalent' interactions between transition metal coordinated Sb/Bi atoms and adjacent neutral or anionic donor groups is a quite recent phenomenon that as emerged mainly over the last 10 years or so; examples of this type of behaviour with the lighter Group 15 elements (P and As) are much rarer. The strength of the interactions are very variable in different systems, from long-range weak interactions falling just within the sum of the Van der Waals radii, through to much shorter contacts, with bond lengths similar to those in covalent compounds.

Evidence for 'hypervalency' has mainly come from X-ray crystallographic analyses to-date, although in certain cases spectroscopic data (mainly from $\nu(CO)$ and/or $\delta\{^{13}C\}$) provides supporting evidence for the occurrence of these interactions in the solid state and even in solution. This suggests that judicious choice of co-ligands may allow identification of 'hypervalency' even in those systems for which crystallographic analyses are not forthcoming. These types of interactions are increasingly associated with highly unusual reactivities (for example, acceleration of catalytic reactions, or reversal of bond polarity) and applications (such as enantiomeric separations, and in the development of new F^- sensors). As the field develops, it is expected that other new reaction

chemistry and applications utilising the 'hypervalent' interactions will emerge and become established.

DFT calculations have been applied sporadically within this chemistry to probe specific types of behaviour. Although DFT calculations on low symmetry, heavy atom systems are challenging, more in depth theoretical calculations would seem to be extremely timely to order to try to establish a unifying model for the bonding in these unusual complexes and to provide a description of the electronic environment. Such calculations may also shed valuable new insights into other phenomena that are prevalent in the chemistry of the heavier Group 15 elements. One example of such may be the occurrence of bridging or semi-bridging stibines (e.g. Sb^{i}Pr$_3$) between two transition metal centres, identified in the elegant studies from Werner and co-workers.[54,55] It is notable that while the lighter PR$_3$ and AsR$_3$ analogues may be also prepared, these are obtained by substitution of the initially formed μ-SbR$_3$ ligands, suggesting the importance of the Rh−Sb−Rh unit. Further calculations on the μ-SbR$_3$ complexes may determine whether it would be appropriate to also consider this as containing a SbR$_3$ as a delocalised donor/acceptor system.

Acknowledgements

6. References

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