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Coordination chemistry of stibine and bismuthine ligands

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ABSTRACT

The synthesis of the common monodentate and bidentate stibines and bismuthines, and of multidentates containing one or more antimony or bismuth donor are briefly reviewed. The detailed coordination chemistries of SbH_3, trialkyl- and triaryl-stibines and -bismuthines are described, followed by a treatment of distibine complexes and complexes of multidentates containing antimony (and rarely bismuth) in combination with other group 15 or 16 donors. The available X-ray structural data, antimony-121 Mössbauer results, and UV-visible data on these complexes are compiled. Throughout the article comparisons are drawn with complexes of lighter group 15 donor ligands and the considerable differences between stibine ligands and the more familiar phosphines and arsines are highlighted.

ABBREVIATIONS

R	alkyl or aryl group unless further qualified
X	halogen
Cp	cyclopentadienyl, C_5H_5-
Cy	cyclohexyl, $C_6H_{11}-$
bipy	2,2′-bipyridyl
THF	tetrahydrofuran
sacsacH	dithioacetylacetone

$DMGH_2$	dimethylglyoxime
acacH	acetylacetone
diglyme	diethyleneglycoldimethylether

1. INTRODUCTION

Transition metal complexes of tertiary phosphine ligands remain one of the most intensively studied areas of coordination chemistry, and there is a large literature on tertiary arsine complexes [1–3]. In contrast, the coordination chemistries of the heavier group 15 analogues, stibines and bismuthines, have received limited attention. In part, this reflects their significantly weaker coordinating ability, studies being often confined to soft metals in low oxidation states, and, particularly in the case of bismuthines, to the very weak C—Bi bonds which break easily in the presence of metal centres. In contrast to phosphines, the heavier ligands lack an NMR probe analogous to the ^{31}P nucleus. All naturally occurring antimony and bismuth nuclei have nuclear spins and reasonable sensitivities (^{121}Sb $I = 5/2$, 57.3%, $D_c = 5.3 \times 10^2$; ^{123}Sb $I = 7/2$, 42.7%, $D_c = 1.13 \times 10^2$; ^{209}Bi $I = 9/2$, 100%, $D_c = 8.2 \times 10^2$) but unfortunately these are associated with substantial quadrupole moments, which result in unobservably broad resonances unless in cubic symmetry environments [4], and thus no resonances have been observed in their coordination complexes. The fast quadrupolar relaxation also prevents observation of 1-bond coupling constants between Sb or Bi and other NMR active nuclei.

Commercially available ligands are limited to Ph_3Sb, $^nBu_3Sb$, and Ph_3Bi, and to ultra-pure (and correspondingly highly expensive) "electronic grade" Me_3Sb.

Previous major reviews of stibine and bismuthine complexes are listed in Table 1, and, as can be seen, most have treated the chemistry along with those of their lighter analogues. Inevitably, this has resulted in a fragmented account of R_3Sb or R_3Bi chemistry, and the aim of the present review is to provide a coherent account of the heavy donor chemistry.

TABLE 1

Reviews of stibine or bismuthine complexes

Authors	Topic(s)	Ref.
G. Booth	P, As, Sb ligand complexes	8
K.K. Chow, W. Levason and C.A. McAuliffe	Monodentate P, As, Sb ligand complexes	2
W. Levason and C.A. McAuliffe	P, As, Sb, ligand complexes	3
W. Levason and C.A. McAuliffe	Organostibine complexes	9
L.D. Freedman and G.O. Doak	Organobismuth compounds	10
M. Dub	Organo As, Sb, Bi compounds	11
C.A. McAuliffe	P, As, Sb, and Bi ligands	12

An attempt has been made to provide a complete coverage of the coordination chemistry of ligands containing neutral antimony or bismuth donor groups, including that of multidentates containing one such group in combination with N, P, As, etc. donors. Compounds containing R_2SbSbR_2 or R_2Sb^- or RSb^{2-} fragments have been excluded. A brief treatment of the synthesis of the ligands is included, to provide lead references to the more important types. Comprehensive coverage of the synthesis of organoantimony and organobismuth compounds is provided by the appropriate Gmelin [5,6] and Houben-Weyl [7] volumes.

2. STIBINE LIGANDS

2.1 *Tertiary stibines*

Symmetrical tertiary stibines, R_3Sb, are usually made from $SbCl_3$ and the appropriate Grignard reagent in ether solution [5,7,13–17], although RLi or R_3Al have sometimes been used. Trimethylstibine azeotropes with Et_2O and cannot be isolated by distillation, instead the ether solution is treated with Br_2 to precipitate Me_3SbBr_2, and this is subsequently reduced with zinc [13]. The reaction of $SbCl_3$ with Grignards containing bulky R groups may produce mixtures of R_3Sb and $R_{3-x}SbCl_x$, and in these cases the reactions are usually conducted with excess Grignard under prolonged reflux [16,18–20]. Mixed phenylalkylstibines $Ph_{3-x}R_xSb$ (R = alkyl) are made from Ph_2SbCl or $PhSbCl_2$ and RMgX, the halostibines being prepared by comproportionation of $SbCl_3$ and Ph_3Sb in CH_2Cl_2 [21–23]. Cleavage of a phenyl group from Ph_3Sb with Li in tetrahydrofuran or, better, Na/liquid ammonia gives $SbPh_2^-$ anions*, which can be alkylated with RX to RPh_2Sb [24–26]. Similar cleavage of $R_2R'Sb$ followed by alkylation with R″X yields asymmetric stibines, although sometimes mixtures ($R_2R''Sb$ and RR′R″Sb) result from competitive cleavage of R and R′ [27,28]. In contrast to $P(alkyl)_3$, $Sb(alkyl)_3$ are readily cleaved by Na/liquid ammonia, and the resultant SbR_2^- can be similarly alkylated [29].

Trialkyl- and alkylaryl-stibines are air-sensitive liquids, with characteristic odours, which must be handled under dinitrogen. The lower trialkylstibines may inflame spontaneously in air. Triarylstibines are air-stable solids.

2.2 *Distibines*

Distibinomethanes, $R_2SbCH_2SbR_2$ (R = Me or Ph) are readily made from $NaSbR_2$ and CH_2Cl_2 in liquid ammonia [30,31]. The methyl ligand is a pyrophoric oil, the phenyl compound an air-stable solid. Examples with other R groups are

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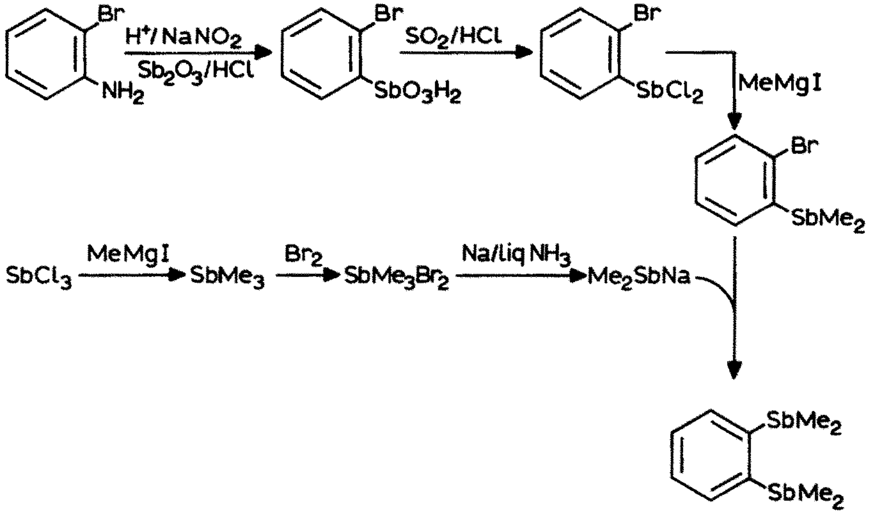
* The anion is usually used in situ, but it has been isolated as its $Li(12\text{-crown-}4)_2^+$ salt, and structurally characterised [26].

known, including $PhMeSbCH_2SbPhMe$ [27,29], but these have been little studied. All attempts to prepare the dimethylene-backboned ligands $R_2SbCH_2CH_2SbR_2$ with a variety of R groups have failed, the only products are R_4Sb_2 and $CH_2{=}CH_2$ [16,24,32–34]. In contrast, the trimethylene-backboned ligands $Ph_2Sb(CH_2)_3SbPh_2$ [27] and $Me_2Sb(CH_2)_3SbMe_2$ [35,36] are obtained in good yields from R_2Sb^- and $Cl(CH_2)_3Cl$. The preparation of longer-backboned α,ω-distibinoalkanes, $R_2Sb(CH_2)_zSbR_2$ ($R = Me$, Et, Ph, ^{t}Bu, c-C_6H_{11}; $z = 4$–6) have been described [16,24,32,33,36].

The reaction of stibide anions, SbR_2^- ($R = Me$ or Ph) with either *cis*- or *trans*-$ClCH{\equiv}CHCl$, gave only R_4Sb_2 (and presumably $HC{\equiv}CH$) [25,37], but R_2SbH are reported to add to $R_2SbC{\equiv}CH$ to give *trans*-$R_2SbCH{=}CHSbR_2$ [38]. Acetylenic distibines, $R_2SbC{\equiv}SbR_2$ ($R = Me$, Et, Ph, etc.) are made from R_2SbX and $NaC{\equiv}CH$ or $XMgC{\equiv}CMgX$ [39]. Low yields of *p*-$C_6H_4(SbPh_2)_2$ are obtained straightforwardly from *p*-$C_6H_4Li_2$ and Ph_2SbCl [40], but the syntheses of the much more useful *o*-phenylenebis(stibines) are considerably more difficult. The direct reaction of $SbMe_2^-$ with *o*-$C_6H_4Cl_2$ (carried out in liquid ammonia due to the thermal instability of $SbMe_2^-$) gives only trace amounts of *o*-$C_6H_4(SbMe_2)_2$ [41], and even with *o*-C_6H_4BrI the yield was only ca. 9% [42]. Better yields (ca. 20–30%) can be obtained by the route shown in Scheme 1, although the procedure is lengthy [43]. A similar route using *o*-$C_6H_4Br(SbPh_2)$ and $NaSbPh_2$ in liquid ammonia produces *o*-$C_6H_4(SbPh_2)_2$ (25%) [37].



Scheme 1.

In marked contrast to the large number of polydentate phosphines and arsines known [1,3,12], there are few reports of attempts to prepare polydentate stibines [9]. Multidentate ligands are usually obtained by multi-step routes involving sequential introduction of the donor atoms. Carbon–antimony bonds are easily broken by nucleophiles such as RLi or RMgX [9,36,37,43], and even to make distibines it is necessary to choose the reaction conditions carefully. Only one successful preparation of a tridentate stibine has appeared, in which the tripodal $MeC(CH_2SbPh_2)_3$ was formed from the reaction of $MeC(CH_2Br)_3$ and $NaSbPh_2$ in liquid ammonia [44].

2.3 Mixed-donor ligands

A considerable number of organoantimony compounds containing a second potential donor group drawn from groups 15 or 16 are known [6], but in relatively few cases have their coordination chemistries been examined in any detail. Scheme 2 shows representative synthetic routes, and Table 2 lists some examples. The syntheses are inevitably multi-stage, although overall yields are often quite good; certainly it is often easier to obtain $o\text{-}C_6H_4(SbR_2)ER_n$ (ER_n represents, for example, SMe, NMe_2, PPh_2) than to make the corresponding distibine. Incorporation of one antimony into bi- or tridentate ligands is straightforward, but relatively few polydentates containing two or more antimony centres have been prepared (Table 2).

3. BISMUTHINE LIGANDS

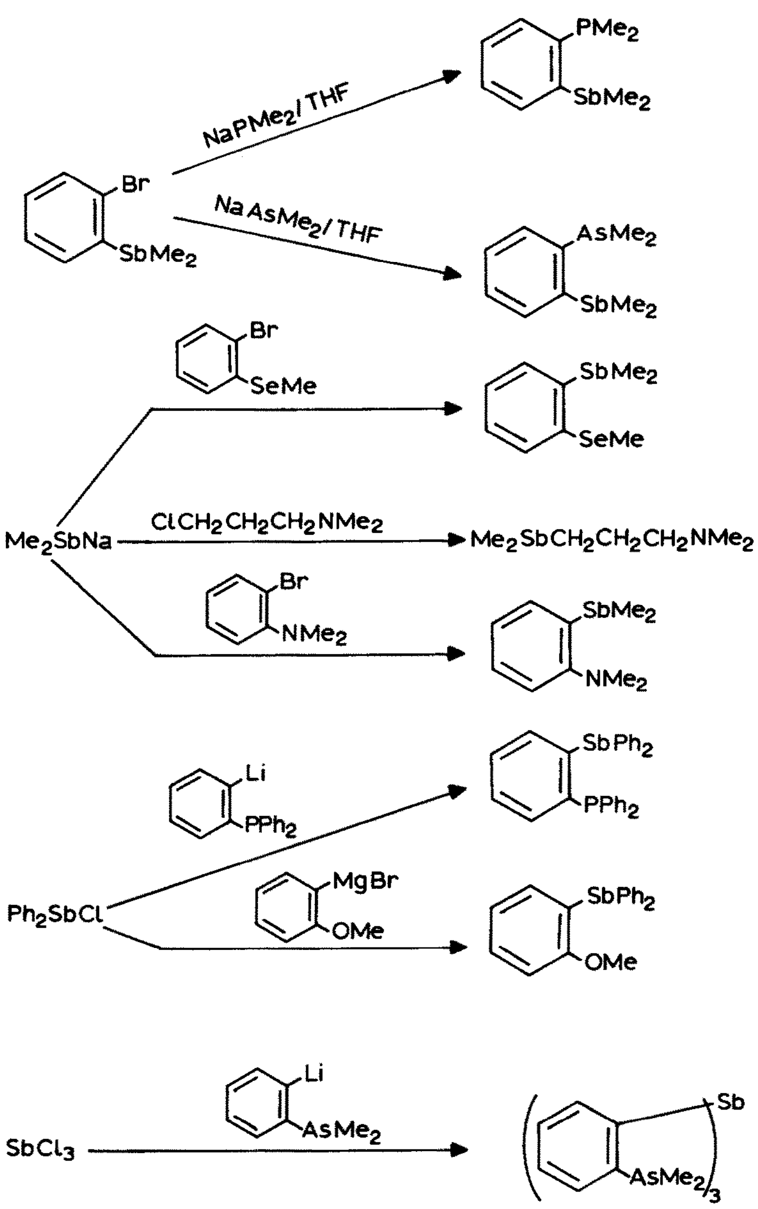
Symmetrical tertiary bismuthines, R_3Bi, are usually made by reaction of $BiCl_3$ with RMgBr in ether [60–64]. Whilst triarylbismuthines are waxy, air-stable solids, trialkylbismuthines are air-sensitive, sometimes pyrophoric liquids. Early attempts to prepare mixed alkylbismuthines $R_2R'Bi$ were unsuccessful, but $Me_2R'Bi$ ($R' = Et$, ^nPr, ^nBu, etc.) have recently been obtained by reaction of Me_2BiNa and R'X in liquid ammonia [65]. They are thermolabile, scrambling at room temperature in a few days. Mixed arylalkylbismuthines, $Me_2(aryl)Bi$, can be obtained from Me_2BiBr, Li, and aryl halides in tetrahydrofuran at low temperatures [65], and $Ph_2R'Bi$ ($R' = Me$, Et, ^nBu, etc.) from Ph_2BiBr and R'Li in diethyl ether [66].

Dichloromethane reacts with Ph_2BiNa in liquid ammonia to form $Ph_2BiCH_2BiPh_2$, a colourless air-sensitive crystalline solid [67]. The reactions of Me_2BiNa with XCH_2CH_2X lead only to Me_4Bi_2 and ethylene, analogous to the corresponding reactions with antimony, but with $Br(CH_2)_nBr$ ($n = 3$, 4, 5), the $Me_2Bi(CH_2)_nBiMe_2$ are formed. Only for $n = 5$ was a pure product isolated; for $n = 3$ the dibismuthine is mixed with Me_4Bi_2, and for $n = 4$ the impurity is the cyclic $Me\overline{Bi(C}H_2)_4$ [68].

Several mixed-donor bismuthines are known, including $Ph_{3-n}Bi(o\text{-}C_6H_4OMe)_n$, $Ph_{3-n}Bi(o\text{-}C_6H_4SMe)_n$, and $Ph_{3-n}Bi(o\text{-}C_6H_4NMe_2)_n$ ($n = 1$–3) [53], $o\text{-}C_6H_4(PPh_2)(BiPh_2)$ [69], $o\text{-}C_6H_4(AsPh_2)(BiPh_2)$ [69], $o\text{-}C_6H_4(SbPh_2)(BiPh_2)$ [53], $Bi(o\text{-}C_6H_4AsMe_2)_3$, and $Bi(CH_2CH_2CH_2AsMe_2)_3$ [70].

4. MONODENTATE STIBINE COMPLEXES

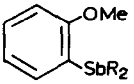
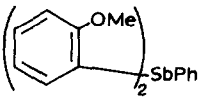
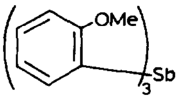
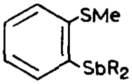
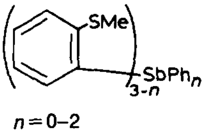
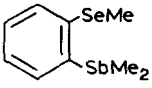
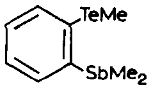
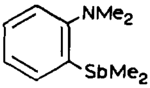
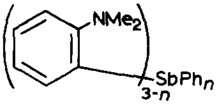
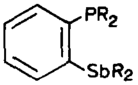
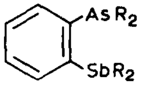
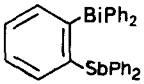
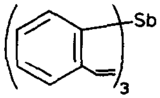
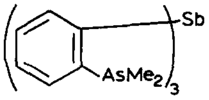
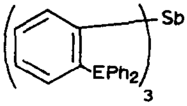
The overwhelming majority of reported coordination complexes of monodentate stibines contain Ph_3Sb. Trialkylstibine and phenylalkylstibine ($Ph_{3-n}R_nSb$)



Scheme 2.

complexes are much less common, perhaps a reflection of the air-sensitivity of the free ligands and correspondingly increased difficulties in handling, coupled with commercial unavailability. A few complexes of stibine (SbH_3) have been prepared, but no reports of complexes of primary ($RSbH_2$) or secondary (R_2SbH) stibines were found.

TABLE 2

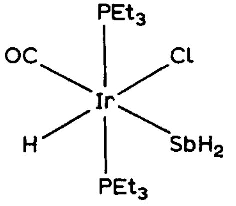
 R=Me [43,45] R=Ph [46]	 [46]	 [17,46]
 R=Me [43] R=Ph [46]	 $n=0–2$ [46]	 [47]
 [48]	$MeS(CH_2)_3SbMe_2$ $S\{(CH_2)_3SbPh_2\}_2$ [46]	 [43,45]
 $n=0–2$ [45,49]	$Me_2N(CH_2)_3SbR_2$ $N\{(CH_2)_3SbR_2\}_3$ R=Me, Ph [49]	$MeN(CH_2CH_2SbR_2)_2$ R=Me, Ph [49]
 R=Me [43] R=Ph [50]	 R=Me [43,51] R=Ph [50]	$Ph_2AsCH_2SbPh_2$ [52]
 [53]	 [54]	 [55,56]
 E = P, As [57]	$Sb\{(CH_2)_3AsMe_2\}_3$ [58]	$R_2Sb(CH_2)_3E(CH_2)_2E(CH_2)_3SbR_2$ E = NMe, S R = Ph, Me [59] $Me_2Sb(CH_2)_2O(CH_2)_2O(CH_2)_2SbMe_2$ [59]

The patent literature contains numerous reports of catalytic systems containing stibines. These reports have only been included in the present review when discrete complexes are described, those patents or articles merely stating the constituents of the "soup" are excluded. It is likely that in mixtures of main group halides or high valent early transition metal halides and R_3Sb, the stibines may function as sources of transferable R groups to the metal, rather than as ligands.

4.1 Complexes of SbH_3

Complexes with SbH_3 present as a ligand are only known for the chromium sub-group. The complex $Cr(CO)_5(SbH_3)$ was initially identified by mass spectrometry [71]. Subsequently, the three complexes $M(CO)_5(SbH_3)$ (M = Cr, Mo, W) were isolated from the reaction of SbH_3 with $M(CO)_5(NCCH{=}CHCN)$ in benzene at low temperature [72]. The labile yellow complexes were identified by IR, ^1H NMR spectroscopies and by mass spectrometry. The thermal stability of $M(CO)_5(L)$ complexes (M = Cr, Mo, W) decreased with L in the order $NH_3 > PH_3 > AsH_3 > SbH_3$.

The reaction of SbH_3 with *trans*-$[Ir(CO)X(PEt_3)_2]$ (X = Cl, Br) at 180 K in toluene [73] and CD_2Cl_2 [74] produced two isomers, **1** and **2**, with the SbH_3 cleaving in the oxidative addition reaction. Isomer **1** predominated at 180 K, but isomerisation occurred with increasing temperature and a 1 : 1 ratio of the isomers was present at room temperature. The complexes were identified by ^{31}P and ^1H NMR spectroscopies but were not isolated.



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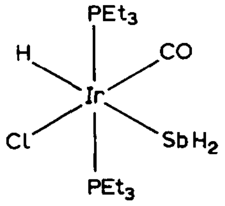


2

The homo-epitaxial growth of InSb by MOCVD has been carried out using the reaction of $InEt_3$ with SbH_3 [75].

4.2 Trialkylstibine and alkylarylstibine complexes

4.2.1 Groups 3–5

No complexes with groups 3 or 4 have been reported, and for group 5 only a few vanadium complexes have been identified. The first report of a vanadium complex was an ESR study of the 1 : 1 adduct formed between $VOCl_2$ and Sb^nBu_3 in toluene [76]. The complex, which was not isolated, was identified as $VOCl_2(Sb^nBu_3)$, in contrast to the arsine and phosphine compounds $VOCl_2(ER_3)_2$.

Subsequent reports of vanadium trialkylstibine complexes have centred on ^{51}V NMR studies with the stibine complexes being compared to complexes formed with a wide range of other ligands. The complexes $[Et_4N][V(CO)_5(SbR_3)]$ and $[(\eta^5\text{-}Cp)V(CO)_3(SbR_3)]$ (R = Et, OEt) were formed by photo-induced displacement of CO from $[Et_4N][V(CO)_6]$ and $[(\eta^5\text{-}Cp)V(CO)_4]$, respectively, in tetrahydrofuran [77]. The overall ligand strength was deduced as $BiEt_3 < AsR_3 < PR_3 < SbR_3$, which suggests that the stibine is unusually strongly bound to the vanadium. Similarly, the π-acceptor strength of the stibines was ordered $SbEt_3 < SbPh_3 < Sb(OEt)_3$.

Complexes of the form $[V(THF)_{4-n}(NO)_2(SbEt_3)_n]Br$ ($n = 1, 2, 3$) were prepared from $[V(THF)_4(NO)_2]Br$ and $SbEt_3$ in THF and were studied by IR and ^{51}V NMR spectroscopies by Naeumann and Rehder [78,79]. The nitrosyl groups were assigned as being cis from the infrared spectra.

4.2.2 Group 6

Alkylstibine complexes of the chromium sub-group are all carbonyl-containing species with $M(CO)_5L$ compounds being the most widely studied. $Mo(CO)_{6-n}L_n$ ($n = 1, 2, 3$, $L = SbEt_3$; $n = 1, 2$, $L = SbClEt_2$) were first prepared by the photolysis of $Mo(CO)_6$ and the ligand. Tri-substituted compounds, $Mo(CO)_3L_3$, were better prepared from the reaction of $Mo(CO)_3(C_6H_3Me_3)$ and three equivalents of ligand [80]. Spectroscopic data include infrared studies of the carbonyl stretching frequencies, for $Mo(CO)_5L$ [80–82] and for $W(CO)_5(Sb^nBu_3)$ [83], and ^{13}C NMR spectroscopic studies of $M(CO)_5L$ (M = Cr, Mo; $L = SbMe_3$, $SbEt_3$, $SbBu_3$, $SbPhMe_2$, $SbPhEt_2$, $SbPh_2Me$, $SbPh_2Et$) [84]. The latter study concluded that changing the substituent on the antimony has a larger effect on the chemical shift of the CO group than changing the donor atom from P to As to Sb.

The compounds $M(CO)_5(Sb^tBu_3)$ (M = Cr, Mo, W) were prepared by Schumann and Breunig [18] and $M(CO)_5L$ (M = Cr, W, $L = SbMe_2Cp$; M = W, $L = Sb^tBu_2Cp$) by Jutzi and Kuhn [85] by photolysis of the corresponding hexacarbonyl in tetrahydrofuran in the presence of one equivalent of ligand. The more unusual $M(CO)_5L$ (M = Cr, Mo, W; $L = Sb(GeMe_3)_3$, $Sb(SnMe_3)_3$) were reported by Schumann et al. [86,87]. The complexes $M(CO)_5(Sb(SiMe_3)_3)$ (M = Cr, Mo, W) were prepared similarly in pentane [88] and these compounds are reported as being initiators for the polymerisation of tetrahydrofuran.

The oxidative addition of I_2 to $W(CO)_5(SbMe_3)$ in benzene solution gave the seven-coordinate $WI_2(CO)_4(SbMe_3)$ along with some $[WI_2(CO)_4]_2$ and $SbMe_3I_2$ [89]. The $WX_2(CO)_4(SbMe_3)$ (X = Cl, Br, I) were reported in a subsequent study [90], and were found to undergo further CO substitution in hydrocarbon solvents to give mixed-donor $WX_2(CO)_3(SbMe_3)L'$ ($L' = PMe_3$, $AsMe_3$, $SbMe_3$, $AsMe_2H$, $P(OMe)_3$, PPh_3, py or I) species.

Less common species such as the carbenes *cis-* and *trans-* $Cr(CO)_4[C(CH_3)(OCH_3)]L$ ($L = SbMe_3$, $SbEt_3$, $SbCy_3$) have been prepared photochemically from $Cr(CO)_5[C(CH_3)(OCH_3)]$ at room temperature [91]. The cyclopentadienyl species *cis*-$[Mo(CO)_2(Cp)Br\{Sb(CH_2Ph)_3\}]$ was prepared by heating $Mo(CO)_3(Cp)Br$ with $(PhCH_2)_3SbBr_2$ in benzene at 50°C [92]. More unusually, the complex *trans*-$[W(CO)_2(PMe_3)(Cp)(Sb^tBuMeCl)]I$ has been prepared by the reaction of *trans*-$[W(CO)_2(PMe_3)(Cp)(Sb^tBu)Cl]$ with methyl iodide [93]. Although not strictly an example of a trialkyl stibine, this complex is notable due to the unusual preparation of the stibine whilst coordinated to the metal centre.

4.2.3 Group 7

The only trialkylstibine examples from this group are found in the patent literature. Complexes of the form $RMn(CO)_{3-n}(SbR'_3)_n$ ($n = 1, 2$; R = Cp, etc.; R' = Cy, CH_2Ph, hexyl, mesityl) [94,95] and $Mn(CO)_3X(SbR_3)_2$ (X = F, Br, I; R = Me, Cy, hexyl) [94,96] have been described. Other compounds are the antimonite complexes $Mn(\eta^5\text{-}Cp)(CO)_2(Sb(OR)_3)$ (R = Et, Bu, Ph) which are made by UV irradiation of $Mn(\eta^5\text{-}Cp)(CO)_3$ in THF in the presence of one equivalent of ligand. The antimonites are reported as having approximately equal σ-donor/π-acceptor abilities to phosphites but are better σ-donors and worse π-acceptors than arsenites [97].

4.2.4 Group 8

The iron sub-group is represented by a greater number and range of compounds, mostly carbonyl and nitrosyl complexes.

Carbonyl complexes have been studied extensively with three X-ray structures having been reported. In $Fe(CO)_4(SbMe_3)$, the trimethylstibine was found in an axial site of the distorted trigonal bipyramid with $Fe{-}Sb = 2.49(02)$ Å [98]. The complex $Ru(CO)_4(SbMe_3)$ (Fig. 1) is isostructural with the iron complex with $Ru{-}Sb = 2.619(1)$ Å [99]. Axial–equatorial isomerisation was observed for $M(CO)_5L$ complexes by infrared spectroscopy and the tendency to give the less common equatorial isomer was found to be $Ru > Os \gg Fe$, $Sb > As > P$ and $Ph > Me$. The third X-ray crystal structure study was of $Fe(CO)_4(Sb^tBu_3)$ (Fig. 2) in which the stibine is also found in an axial position [100] with a rather longer Fe–Sb distance (2.547(1) Å) than in the $SbMe_3$ analogue. These complexes were prepared from the metal pentacarbonyl and one equivalent of ligand in hexane, in the absence of light [99]. However, the complexes $Fe(CO)_4(Sb(EMe_3)_3)$ (E = Si, Ge) were prepared from $Fe_2(CO)_9$ and the ligand in pentane under an argon atmosphere [101]. The complexes $Fe(CO)_3L_2$ and $Fe(CO)_4L$ were also formed as decomposition products from the trinuclear iron complexes $Fe_3(CO)_{11}(SbR_3)$ and $Fe_3(CO)_{10}(SbR_3)_2$ (R = Et, ^{n}Pr) [102], prepared from $Fe_3(CO)_{12}$. The stibine complexes fragment less than those with phosphines and arsines, but to an equal degree to phosphite clusters. However, stibines form the least stable complexes with stability decreasing $P(OR)_3 > PR_3 > AsR_3 > SbR_3$. A few mixed-ligand complexes have been reported, including $Fe(CO)_2\{P(OPh)_3\}_2(SbCy_3)$ [103], prepared by photolysis of *trans*-$Fe(CO)_3\{P(OPh)_3\}_2$ and subsequent reaction with $SbCy_3$.

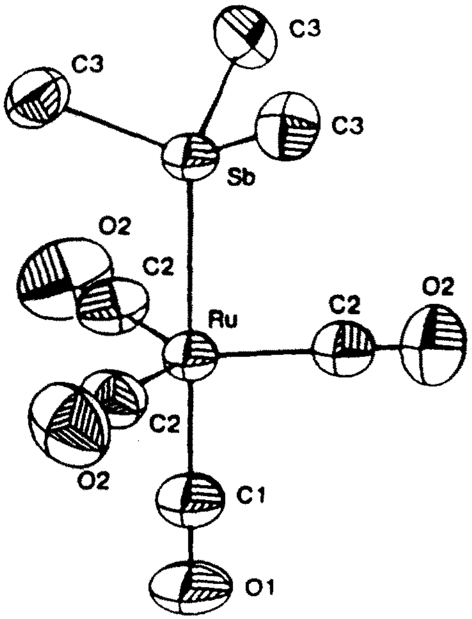


Fig. 1. Molecular structure of $Ru(CO)_4(SbMe_3)$. (From ref. 99 by permission of the American Chemical Society.)

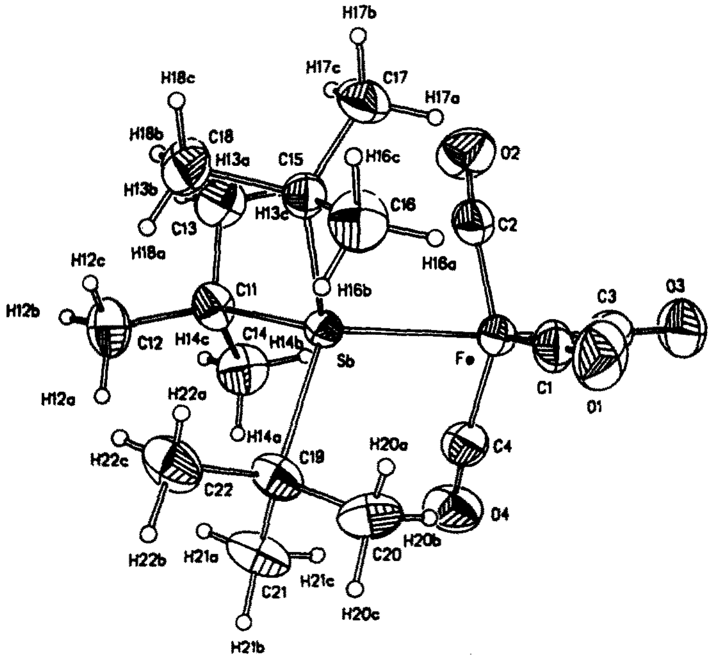
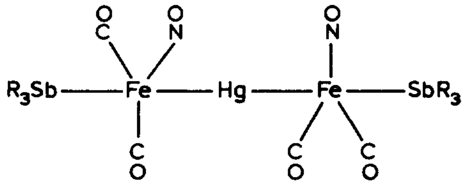


Fig. 2. Molecular structure of $Fe(CO)_4({}^tBu_3Sb)$. (From ref. 100 by permission of *Acta Crystallographica.*)

The complex $Fe(CO)_2(CS_2)\{P(OPh)_3\}(SbEt_3)$ was reported in a study of the reactions of $Fe(CO)_2(CS_2)\{P(OPh)_3\}_2$. Whereas phosphines were found to substitute both phosphite ligands, arsines substituted only one, and the reaction between the starting material and $SbEt_3$ did not completely substitute one phosphite ligand, the mixture still being in equilibrium after 24 h [104]. The complexes $[Fe(CO)_2(\eta^5\text{-}Cp)(SbR_3)]BF_4$ (R = Me, Et, ^{i}Pr) were prepared from $[Fe(CO)_2(\eta^5\text{-}Cp)(THF)]BF_4$ [105,106]. In a comparative study of ligand displacement in $[Fe(CO)_2(\eta^5\text{-}Cp)L]^+$ complexes where L was a variety of group 15 ligands, it was found that PMe_3 readily displaced other EMe_3 ligands, but $SbMe_3$ and $AsMe_3$ only substituted NMe_3 and $BiMe_3$. The reaction between the $SbMe_3$ complex and $AsMe_3$ gave an equilibrium between the two complexes with the arsine complex predominating [106]. The complex $[Fe(\eta^5\text{-}Cp)(CO)(PMe_3)(SbMe_3)]I$ was prepared in the reaction of $Fe(\eta^5\text{-}Cp)(CO)(PMe_3)(SbMe_2)$ and methyl iodide in benzene [107]. The ^{121}Sb and ^{57}Fe Mössbauer spectra of the complex $[Fe(CO)_2(\eta^5\text{-}Cp)(SbEt_3)]PF_6$ have been reported [105].



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The mixed-metal species $Hg\{Fe(CO)_2(NO)(SbR_3)\}_2$ (R = Et, ^{n}Bu) (3) have been prepared by reacting $Hg\{Fe(CO)_3(NO)\}_2$ with two equivalents of ligand in benzene in the dark. Interestingly, $SbEt_3$ was found to be markedly more reactive than triarylstibines, arsines and phosphines and even Sb^nBu_3. The reaction with Sb^nBu_3 gave poor yields and $Fe(Sb^nBu_3)(CO)(NO)_2$, $Fe(Sb^nBu_3)_2(NO)_2$ and *trans*-$Fe(Sb^nBu_3)_2(CO)_3$ were reported as side products though no further characterisation was included. The mixed-metal complexes were found to be unstable, especially in the presence of light, decomposing to $Fe(SbR_3)(CO)(NO)_2$ [108]. Two ESR studies have been reported for the complex $Fe(NO)_2(SbEt_3)Br$ [109,110].

The complex $Ru(CO)_2(SbEt_3)_2I_2$ has been prepared by Hieber and John from the polymeric $[Ru(CO)_2I_2]_n$ and triethylstibine in benzene, a reaction which also yielded some $Ru(CO)_2(SbEt_3)I_2$ [111]. The complex $Ru(CO)_2(SbMe_3)_2I_2$ was obtained by an unusual route, being isolated from a catalyst mixture of $Ru(acac)_3$, $SbPh_3$ and methyl iodide in methyl formate/hexane under a 50/50 H_2/CO atmosphere at 220°C [112].

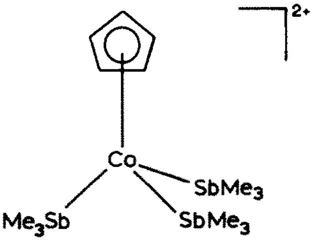
The orange-red nitrosyl complex $RuCl_3(NO)(SbEt_3)$ reported by Chatt and Shaw in 1966 [113] remains the only ruthenium trialkylstibine nitrosyl complex. It was prepared by boiling $RuCl_3(NO)\cdot 5H_2O$ with the ligand in 2-methoxyethanol.

4.2.5 Group 9

Trialkylstibine complexes of the cobalt sub-group have drawn little investigation, which is suprising considering the wealth of studies related to analogous phosphine complexes.

The dinuclear species $Co_2(IC{\equiv}CI)(CO)_5(SbEt_3)$ was prepared by treatment of $Co_2(IC{\equiv}CI)(CO)_6$ with $SbEt_3$ [114,115], whilst the ligand $Sb(C{\equiv}C{-}Ph)_3$ coordinates to the cobalt atoms via the C≡C rather than through the antimony atom in the complexes $\{Co_2(CO)_6(\eta^2\text{-}C{\equiv}C{-}Ph)\}_{3-n}(Ph{-}C{\equiv}C)_nSb$ [116].

The mixed-metal species $Hg\{Co(CO)_3(SbMe_3)\}_2$ were prepared from the reaction of $Hg[Co(CO)_4]_2$ with two equivalents of ligand [117]. The dimers $\{Co(CO)_3(R_3Sb)\}_2$ (R = Et or ^{i}Pr) were found to be carbonyl-bridged for R = ^{i}Pr, but with only terminal carbonyls for R = Et [117a]. The "piano-stool" complex $[(\eta^5\text{-}Cp)Co(SbMe_3)_3](BF_4)_2$ (**4**) was prepared from the analogous thioether complex $[(\eta^5\text{-}Cp)Co(SMe_2)_3]^{2+}$ [118].



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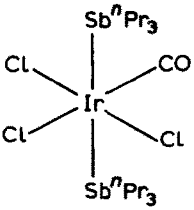
Two investigations into cobalt complexes with dimethylglyoximate anions and trialkylstibine as ligands have been published. The first describes the cobaloxime $Ph_3SnCo(DMG)(SbMe_3)$ [119]. The second study records the preparation of the compounds *trans*-$Co(DMGH)_2(Sb^nBu_3)X$ (X = Cl, CNS, CNSe), *trans*-$(Sb^nBu_3)Co(DMGH)_2{-}SeCN{-}Co(DMGH)_2SeCN$ from the reaction of CoX_2, dimethylglyoxime, Sb^nBu_3 and O_2. The products were studied by ^1H NMR and infrared spectroscopies [120].

The potentially bidentate ligands *o*-methoxyphenyldimethylstibine and *o*-methoxyphenyldiphenylstibine usually behave as monodentate stibine ligands with rhodium and iridium [121]; these compounds are dealt with in more detail in Sect. 7. No examples of rhodium trialkylstibine carbonyl complexes have been reported and only one such iridium complex. The $IrCl_3(CO)(Sb^nPr_3)_2$ was prepared by boiling together the ligand and chloroiridic acid in 2-methoxyethanol–hydrochloric acid. The yellow compound was identified as the isomer with *trans*-stibines and *mer*-chloride ligands (**5**) [122].

In contrast to most $Ir(ER_3)_2Cl_4$ complexes, which have a trans structure (including $ER_3 = SbPh_3$ q.v.), the complex with $SbMe_3$ has been identified as *cis*-$Ir(SbMe_3)_2Cl_4$ on the basis of its UV-visible and IR spectra [123,124]. The only other cis complex known is the pyridine complex, *cis*-$Ir(py)_2Cl_4$ [124].



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The nido-rhodacarborane, *nido*-9,9,9-$(SbMe_3)_3$-9,7,8-$RhC_2B_8H_{11}$, was prepared from the reaction of $RhCl(SbMe_3)_3$ with $NaC_2B_8H_{11}$ [125]. The starting material, $RhCl(SbMe_3)_3$, was prepared from $\{RhCl(C_2H_4)_2\}_2$ and the stibine. It was used in situ, and not further characterised.

4.2.6 Group 10

The first nickel carbonyl trialkylstibine compounds obtained were $Ni(CO)_{4-n}(SbEt_3)_n$ and $Ni(CO)_{4-n}(SbEt_2Cl)_n$ ($n = 1, 2$) [80]. The complexes were prepared by the reaction between $Ni(CO)_4$ and the ligand. The mixed stibine complex $Ni(CO)_2(SbEt_3)(SbEt_2Cl)$ was prepared by the reaction of $Ni(CO)_3(SbEt_3)$ with $SbEt_2Cl$, or conversely by reaction of $Ni(CO)_3(SbEt_2Cl)$ with $SbEt_3$ [80]. The complexes $Ni(CO)_3\{Sb(EMe_3)_3\}$ (E = Si, Ge, Sn) were characterised by ^1H NMR, IR and Raman spectroscopies [18]. The complexes $Ni(CO)_3(SbR_3)$ (R = Me, Et, Bu) have been studied by ^{13}C NMR spectroscopy and the effect of complexation upon the chemical shift of the stibine ligand carbon atoms was discussed [126].

Organometallic nickel complexes with trialkylstibines are limited to cyclopentadienyl derivatives. $[(\eta^5\text{-Cp})Ni(SbR_3)_2]^+$ (R = Me, ^{n}Bu) complexes were prepared by reaction of the stibine ligand with $[(\eta^5\text{-Cp})Ni(C_5H_6)]BF_4$. The $[(\eta^5\text{-Cp})Ni(SbR_3)_2]^+$ cations react with LiX (X = I, CN) to give species of the form $(\eta^5\text{-Cp})Ni(SbR_3)X$ (X = I, CN; R = Me, ^{n}Pr) [127]. The complexes $(\eta^5\text{-Cp})Ni(SbR_3)I$ (R = Me, ^{n}Bu) have also been prepared by reacting $Ni(\eta^5\text{-Cp})_2$ with the appropriate ligand and LiI [128].

Five-coordinate nickel(II) complexes have been reported containing trimethylstibine ligands, $NiX_2(SbMe_3)_3$ (X = Cl, Br, I, CN, $SbMe_3$) [129,130]. The complex $[Ni(SbMe_3)_5](BF_4)_2$ was prepared from $Ni(BF_4)_2$ and a large excess of $SbMe_3$. The complexes were assigned trans halogen/pseudo-halogen trigonal bipyramidal structures from their electronic spectra and the stability order $I > Br > SbMe_3 \gg CN > Cl$ was observed with the chloro and cyano complexes not being isolated as solids.

The trialkylstibine chemistry of the nickel sub-group is dominated by halogeno complexes of palladium and platinum. Complexes of the form $MCl_2(SbMe_3)_2$ (M = Pd, Pt), $[Pt(SbMe_3)_4][MCl_4]$ (M = Pt, Pd) and $[Pd(SbMe_3)_4]Cl_2$ were reported in 1925 [131], and further complexes of the form $PtX_2(SbEt_3)_2$ (X = Cl, Br, I, NO_2), $PdCl_2(SbEt_3)_2$, *cis*-$PtCl_2(SbR_3)_2$ (R = ^{n}Pr, ^{n}Bu) in 1936 [132].

The platinum(0) species, the very stable $Pt(Sb^{n}Bu_3)_4$, was prepared by reaction of the ligand with $Pt(COD)_2$. Little decomposition of the product was seen even in air in contrast to the arsine analogue which was found to be unstable in solution [133].

Trialkylstibine complexes $M(SbR_3)_2X_2$ ($M = Pt$ or Pd; $R = Me$, Et, ^{n}Pr, ^{n}Bu; $X = Cl$, Br, I, NO_2) have usually been prepared by reaction of the ligand with the appropriate MCl_4^{2-} (with added X^- where $X \neq Cl$) as yellow or orange-red crystalline solids [131,132,134–143]. The stereochemistry of these species were first investigated by Chatt in 1951 with a study of $PtCl_2(Sb^{n}Pr_3)_2$. The complex as prepared by reaction of the ligand with K_2PtCl_4 formed as a mixture of isomers but only the cis isomer was isolated. All attempts to isolate the trans isomer resulted in rapid isomerisation to give the solid yellow cis isomer [134]. The isomerisation of *cis*-$PtCl_2(SbEt_3)_2$ in benzene was studied further and the solution of the complex was found to be 34.4% the cis isomer at 25°C. In contrast, the analogous PEt_3 complex was found to include 7.5% of the cis isomer and the $AsEt_3$ analogue only 0.57% [135]. This greater tendency for the stibine complex to form the cis isomer is due to the entropy of isomerisation difference found between the $SbEt_3$ and PEt_3 compounds. The isomerisation of the analogous palladium species, $PdCl_2(SbR_3)_2$ ($R = Me$, Et, ^{n}Pr, ^{n}Bu, Ph) in benzene was investigated by measuring the dielectric constants of the solution at 25°C. Solutions of the complexes contained 3.5–40% of the cis isomer in labile equilibrium. The proportion is dependent upon the stibine substituents. Less cis isomer was reported to be present with the palladium complexes than with the corresponding platinum species but once again only the solid cis palladium complexes were isolated [136].

A further study of the platinum complexes determined the cis–trans equilibrium constants for a range of complexes $PtX_2(SbR_3)_2$. The investigation concluded that the equilibrium shifted to the trans side upon changing $X = Cl$ to $X = I$, $R = Ph$ to $R =$ alkyl groups and $R = Me$ to $R = {}^{n}Pr$. Increasing the length of the *n*-alkyl substituent beyond *n*-propyl had little effect upon the equilibrium. Varying the donor atom from Sb to P to As also shifted the equilibrium in favour of the trans isomer [137].

The isomers present in these complexes have been further probed in infrared and Raman spectroscopic studies of *cis*-$PtX_2(SbEt_3)_2$ ($X = Cl$, Br) [138], $PtX_2(Sb^{n}Pr_3)_2$ ($X = Cl$, Br) [139] and $MX_2(SbMe_3)_2$ ($M = Pt$, $X = Cl$, Br; $M = Pd$, $X = Cl$) [140].

An extensive UV-visible investigation of a range of complexes including $[MX_3(SbMe_3)]^-$ ($M = Pt$, $X = Br$; $M = Pd$, $X = Cl$, Br), *cis*-$PtCl_2(SbEt_3)_2$, *cis*-$MCl_2(SbMe_3)_2$, and *trans*-$MI_2(SbMe_3)_2$ ($M = Pt$, Pd) produced the spectrochemical series [144] $Cl < R_2Te < R_2Se \sim R_3Sb < R_2S \sim H_2O < R_3As \sim NH_3 < R_3P < (RO)_3P$.

These complexes have also been studied by ^{195}Pt NMR spectroscopy and in particular the effect of the halide ligands upon the ^{195}Pt chemical shifts. The following complexes were studied: *trans*-$Pt(SbMe_3)_2XY$ ($X = Y = I$; $X = I$, $Y = Cl$ or Br), *cis*-$Pt(SbMe_3)_2XY$ (X = Y = Cl or Br or I; X = Br, Y = Cl; X = I, Y = Cl or Br), $[PtX(SbMe_3)_3]^+$ (X = Cl, Br, I) and $[Pt(SbMe_3)XYZ]^-$ (X, Y, Z are varied to give 16 mixed-halide species). The mixed-halide species were prepared in situ by mixing solutions of the single-halide species but were not isolated [142].

A kinetic study of the trans-effect of various ligands upon the exchange reactions of the diethylamine compound *trans*-$PtCl_2(SbEt_3)\{[^{14}C]NHEt_2\}$ has also been reported [145] and the order of decreasing trans-effect was given as $Et_3Sb > Ph_3Sb > Me_3P > Et_3P > {}^nPr_3P > Ph_3P > Et_3As > Ph_3As \gg {}^nPr_2S$.

The thiocyanato complexes $[Pt(NCS)_3(SbMe_3)]^-$ [146] and *cis*- and *trans*-$Pt(NCS)_2(SbMe_3)_2$ [147] have been studied by Anderson and Goodfellow by ^1H NMR spectroscopy to determine the isomers present; in most cases, both *S*CN and *N*CS ligands were present in solution. The complexes *cis*- and *trans*-$Pt(NCS)_2(SbMe_3)_2$ were also studied by IR and Raman spectroscopies [147].

The bulky $SbCy_3$ forms only *trans*-$M(SbCy_3)_2X_2$ (M = Pd, X = Br, I, NO_2; M = Pt, X = Cl, Br, I, NO_2), and there is no evidence for cis isomers with this ligand [140].

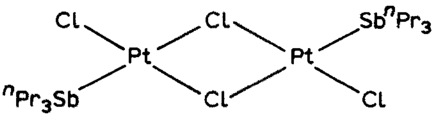
The ligands $SbPhMe_2$ and $SbPh_2Me$ were used to prepare a range of yellow-orange platinum complexes, *cis*-$Pt(SbPh_2Me)_2X_2$, *cis*-$Pt(SbPhMe_2)_2X_2$ (X = Cl, Br, I), $Pt(SbPhMe_2)_4Cl_2$ and the purple five-coordinate species $PtI_2(SbPh_2Me)_3$ and $PtI_2(SbPhMe_2)_3$ by reaction of ligand with K_2PtCl_4; subsequent metathesis with LiX was used to prepare the bromides and iodides. The five-coordinate complexes were prepared by using a 3 : 1 ratio of ligand to Pt instead of the more usual 2 : 1 ratio of L : Pt. These five-coordinate species were also found to dissociate in chloroform but in different ways depending on the ligand. $PtI_2(SbPh_2Me)_3$ dissociates losing a stibine ligand giving $Pt(SbPh_2Me)_2I_2$ and free ligand while $PtI_2(SbPhMe_2)_3$ lost an iodide ligand to give $[Pt(SbPhMe_2)_3I]I$, consistent with the smaller steric hindrance of $SbPhMe_2$ compared with $SbPh_2Me$ [23].

The other species with four stibine ligands was $[Pt(SbPhMe_2)_4]_2(ClO_4)_2$, prepared from $Pt(SbPhMe_2)_2Cl_2$ by treatment with $AgClO_4$ in the presence of excess ligand [148] and this is suggested as an alternative assignment to the complex previously reported as $[Pt(SbPhMe_2)_4Cl_2]$ [23]. The possibility of the five-coordinate complex $[Pt(SbPhMe_2)_4Cl]^+$ being prepared upon treatment of $[Pt(SbPhMe_2)_4]_2(ClO_4)_2$ with $[Ph_3PCH_2Cl]^+Cl^-$ was also reported.

A range of the aforementioned $M(SbR_3)_2X_2$ complexes and the $PtI_2(SbR_2R')_n$ (R′ = Ph, Me; R = Ph, Me; $n = 2, 3$) species were also studied by ^{121}Sb Mössbauer spectroscopy [149].

The novel complexes *cis*-$PtCl_2\{Sb(CH{=}CH_2)_3\}_2$, in which the ligand binds only through antimony, have been prepared by reacting K_2PtCl_4 with the ligand in deoxygenated water [141].

Many chloro-bridged binuclear species have been reported, the first being $Pt_2Cl_4(Sb^nPr_3)_2$ (6) which was prepared by reaction of $Pt_2Cl_4(C_2H_4)_2$ with Sb^nPr_3. Only the trans isomer was formed. This binuclear species reacted with 2,2′-bipyridyl



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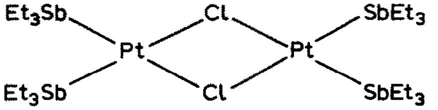
to give $PtCl_2(Sb^nPr_3)_2$ and $PtCl_2$(bipy) [150]. The complexes $Pt_2Cl_4(SbR_3)_2$ (R = Me, Et, ^{n}Pr) were prepared similarly from $Pt_2Cl_4(C_3H_6)_2$ [151] and the compound $Pt_2Cl_4(SbEt_3)_2$ was prepared from Na_2PtCl_4 [152]. Further examples of such binuclear species have been prepared by reaction of Sb^tBu_3 with $PtCl_2$, Na_2PdCl_4, $PdCl_2$(COD) and $MCl_2(C_6H_5CN)_2$ (M = Pd, Pt) in benzene. All starting materials give complexes of the form $M_2Cl_4(Sb^tBu_3)_2$ (M = Pd, Pt) [153].



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The unusual chloro-bridged complex $[Pt_2Cl_2(SbEt_3)_4](BF_4)_2$ (7) was prepared by reacting *cis*-$PtCl_2(SbEt_3)_2$ with BF_3 [154]. These binuclear species react with CO when stirred in chloroform under a CO atmosphere to give $[PtCl(CO)(SbEt_3)_2]BF_4$. The dimer $Pt_2Cl_4(Sb^nPr_3)_2$ reacts with pyridine to give *trans*-$PtCl_2(py)(Sb^nPr_3)$ [155].

Platinum(IV) complexes *cis*-$Pt(SbMe_3)_2X_4$ (X = Cl, Br) were prepared by halogen oxidation of a suspension of the platinum(II) complexes, *cis*-$Pt(SbMe_3)_2X_2$ in CCl_4 [156]. However, attempted halogen oxidation of $[Pd(SbMe_3)X_3]^-$ (X = Cl, Br) species resulted in decomposition [157].

4.2.7 Groups 11 and 12

Very few examples of trialkylstibine complexes formed with members of the copper sub-group have been reported. The first mention of such a complex was of $AuCl(SbEt_3)$ in 1857 [158]. The next report was of $Au(C{\equiv}CPh)(SbEt_3)$ in 1962, prepared from reaction of phenylethynyl gold or $Au(PhC{\equiv}C)(NH_2C_8H_{17})$ with $SbEt_3$ [159]. The complex was reported to decompose rapidly in air and even under nitrogen.

The complex $[Ag(Sb^tBu_3)_2]^+$ has been reported in solution during thermodynamic studies of the reaction of $AgClO_4$ with Sb^tBu_3 in pyridine solution. It was also believed that a mono-substituted complex was formed but neither compound was isolated [160]. $[Ag(Sb^tBu_3)_2]^+$ in pyridine solution was investigated by large-angle X-ray scattering [161], and was identified as having a tetrahedral configuration with the two remaining positions occupied by loosely coordinated pyridine molecules. The Ag—Sb distance was 2.69(2) Å and the Sb—Ag—Sb angle as 110°.

The only examples of copper complexes formed with trialkylstibines are $[Cu(SbR_3)_4]BF_4$ (R = Me, Et) species. These copper(I) compounds were prepared by reaction of the ligand with $[Cu(MeCN)_4]BF_4$ in acetonitrile, and slowly decomposed in air [162]. The complexes were characterised by ^1H and, unusually, ^{63}Cu NMR spectroscopies.

A range of mercury complexes are formed by reacting HgX_2 salts with $SbPh_2Me$ in methanol, or acetone, to give the halogen-bridged $\{HgX_2(SbPh_2Me)\}_2$ (X = Cl, Br, I) [163].

4.2.8 Other complexes

A few examples of trialkylstibine compounds with main group elements have also been reported. The 1 : 1 adduct formed, $BH_3 \cdot SbMe_3$, melted at −35°C and then decomposed, in contrast to NMe_3, PMe_3 and $AsMe_3$ analogues which were all stable at room temperature [164]. The reaction between $SbMe_3$ and BX_3 (X = Br, I) also leads to 1 : 1 adducts which decompose at room temperature. ^1H and ^{11}B NMR data led the authors to believe that $SbMe_3BI_3$ existed, at least partially, as the ionic species $[Me_3SbI]^+BI_4^-$ in chloroform solution [165]. Two studies of the reaction between $SbMe_3$ and BX_3 (X = F, Cl, Br, H) have been reported [166,167]. Again, 1 : 1 adducts were formed and these were studied by gas-phase calorimetry [166] and by ^1H NMR, IR and Raman spectroscopies and mass spectrometry [167]. No reaction was seen between $SbMe_3$ and BMe_3 [166]. In an investigation of the reactions of $SbMe_{3-n}(CF_3)_n$, it was reported that BH_3 forms a 1 : 1 adduct with $SbMe_3$ [168].

The equimolar reaction of $AlCl_3$ with $SbEt_3$ gave $SbEt_3 \cdot AlCl_3$ as a yellowish-green liquid, while a large excess of stibine in the reaction led to the formation of yellow-brown crystals formulated as $SbEt_3 \cdot SbEt_2Cl \cdot AlCl_3$ [169]. The adducts $SbEt_3 \cdot AlEt_2Cl$ and $SbEt_3 \cdot AlEtCl_2$ were also prepared. The compound $AlMe_3 \cdot SbMe_3$ has been mentioned in an NQR investigation of the indium compound $InMe_3 \cdot SbMe_3$. The product, prepared by direct reaction between $SbMe_3$ and $InMe_3$, was investigated by ^{115}In, ^{121}Sb and ^{123}Sb NQR studies [170]. Similar 1 : 1 adducts between MMe_3 (M = Al, Ga), or MMe_2 (M = Zn, Cd) and $SbMe_3$ have been reported [171,172]. The gallium compound $GaMe_3 \cdot SbMe_3$ is an unstable liquid at room temperature [172]. Further mention has been made of the gallium species $GaMe_3 \cdot SbEt_3$ [173,174] and of the exothermic reaction upon mixing $SbEt_3$ with $GaEt_3$ or with $GaPr_3$ [175].

4.3 Triarylstibine complexes

The number of complexes of triphenylstibine reported exceeds those of all other antimony donor ligands. In major part this is a reflection that this air-stable ligand is readily available commercially. Whilst a number of detailed studies of Ph_3Sb complexes in their own right have appeared, often a single complex appears as a token stibine in papers dealing primarily with arsine or phosphine complexes. Despite the large number of reports of Ph_3Sb complexes, coverage is far from complete, with most work concentrated on the carbonyls of groups 6 and 8 and class B metal halide complexes.

4.3.1 Groups 3–5

No complexes of the lanthanides or actinides have been isolated, hardly surprising in view of the paucity of phosphine complexes of these elements [1]. However, the formation in benzonitrile solution of complexes of Eu^{3+} with Ph_3Sb and Ph_3As has recently been established by an ion-exchange technique [176,177].

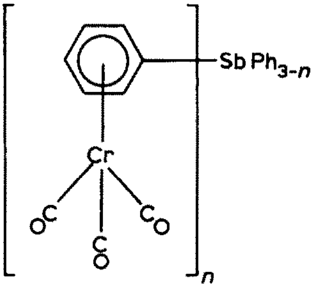
More surprising is the very limited number of reports concerning groups 4 or 5, although the patent literature contains several old claims for the use of $TiCl_4$ or $TiCl_3 + SbR_3$ as components of olefin polymerisation catalysts. The reaction of $TiCl_4$ with $SbPh_3$ in benzene was said [178] to give a deep violet coloured solution which rapidly deposited a black gum. However, another report [179] describes the product as the deep red solid $TiCl_4(Ph_3Sb)_2$. There appears to be no other mention of attempts to prepare group 4 complexes, although Zr and Hf analogues should be obtainable.

Photolysis of a mixture of $[Et_4N][V(CO)_6]$ and Ph_3Sb in tetrahydrofuran forms the golden $[Et_4N][V(CO)_5(Ph_3Sb)]$, and a similar reaction using $(\eta^5\text{-Cp})V(CO)_4$ afforded orange-yellow $(\eta^5\text{-Cp})V(CO)_3(Ph_3Sb)$ [77,180–184]. Direct reaction of $V(CO)_6$ with Ph_3Sb at room temperature was reported [185] to give the pyrophoric, paramagnetic $V(CO)_4(Ph_3Sb)_2$. Photolysis of $(\eta^5\text{-Cp})Nb(CO)_4$ and Ph_3Sb produced $(\eta^5\text{-Cp})Nb(CO)_3(Ph_3Sb)$ [186]. Niobium pentachloride reacted with Ph_3Sb in a 1 : 1 molar ratio in hexane to form brown $NbCl_5(Ph_3Sb)$, whilst a 1 : 2 ratio in benzene gave blue $NbCl_5(Ph_3Sb)_2$ [187]. Both complexes were characterised only by analysis and would be worth further study.

4.3.2 Group 6

Complexes derived from group 6 carbonyls have been much studied. Direct reaction of $M(CO)_6$ (M = Cr, Mo, W) with Ph_3Sb in various organic solvents under reflux or under UV irradiation, lead mainly to $M(CO)_5(Ph_3Sb)$ and *cis*-$M(CO)_4(Ph_3Sb)_2$, which are air-stable yellow or fawn solids [80,188–190]. More specific routes to *cis*-$M(CO)_4(Ph_3Sb)_2$ include the $NaBH_4$-catalysed reaction of $M(CO)_6$ with Ph_3Sb [191], and displacement of the other ligands from $M(CO)_4L_2$ (L = piperidine, NH_3, L_2 = 2,2′-bipyridyl, cyclooctadiene, etc.) [192–195]. More highly substituted complexes have been reported infrequently. *Fac*-$M(CO)_3(Ph_3Sb)_3$ are best made from $(C_7H_8)M(CO)_3$ and the ligand [196], and *fac*-$Cr(CO)_3(Ph_3Sb)_3$ is formed (along with the mono- and di-substituted complexes) from Ph_3Sb and $Cr(CO)_3(NH_3)_3$ [195]. Very poor yields of *cis*- and *trans*-$Mo(CO)_2(Ph_3Sb)_4$ have been reported among the products of the reaction of $Mo(CO)_6$ with the ligand at high temperatures [190], but have not been characterised in detail. Complexes of type $Cr(CO)_5(R_3Sb)$ have been made with a range of triarylstibines ($R = 4\text{-}FC_6H_4$, $3\text{-}FC_6H_4$, $4\text{-}ClC_6H_4$, $3\text{-}ClC_6H_4$) [197].

In contrast to the $Cr(CO)_{6-n}(Ph_3Sb)_n$ formed directly from $Cr(CO)_3(NH_3)_3$ and the ligand, in the presence of BF_3 or H_3BO_3, the products are



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$\{(CO)_3Cr(\eta^6\text{-}Ph)\}_nSbPh_{3-n}$ ($n = 1$–3) (**8**) [195]. η^6-coordination of phenylphosphines to group 6 carbonyl fragments is known and has been confirmed by X-ray crystallographic studies [1], but the report that all three phenyl rings on one ligand can coordinate to different $M(CO)_3$ moieties is unusual, and an X-ray crystal structure would be useful confirmation.

The $M(CO)_5L$ and $M(CO)_4L_2$-type complexes are among the most thoroughly spectroscopically characterised complexes, and many studies have included the Ph_3Sb complexes among other group 15 ligand types. Typical studies are of the vibrational [72,82,83,198–201], ^{13}C NMR [84,202,203], and mass [204] spectra. Perhaps surprisingly, only one complex has been studied crystallographically, $Cr(CO)_5(Ph_3Sb)$ [205], for which Cr—Sb is reported as 2.6170(3) Å. The kinetics and mechanism of carbonyl and ligand substitution in these 18e complexes have also been investigated [193,194,206–209].

Many substituted carbonyl complexes which contain other ligands in addition to Ph_3Sb have been prepared (Table 3).

Seven coordinate carbonyl halide complexes $M(CO)_3(Ph_3Sb)_2X_2$ (M = Mo, W; X = Cl, Br, I) were made by reaction of $M(CO)_4X_2$ with Ph_3Sb, or sometimes by sequential addition of X_2 and Ph_3Sb to $M(CO)_6$ in chlorocarbon solvents at low temperatures [232–235]. The molybdenum complexes are generally less stable than those of tungsten, especially for X = I. The treatment of $Mo(CO)_3(Ph_3Sb)_2X_2$ (X = Cl or Br) with Et_4NX or of $[Mo(CO)_4X_3]^-$ with Ph_3Sb generated the anions $[Mo(CO)_3(Ph_3Sb)X_3]^-$, which seem to exist in isomeric forms [236]. The reaction of the neutral molybdenum complexes with sodium dithiocarbamates forms red-brown, air-sensitive $Mo(CO)_2(Ph_3Sb)(dtc)_2$ (dtc = dimethyl-, diethyl-, or pyrrolidyl-dithiocarbamate) [237]. The six-coordinate $MoX_2(CO)_3(Ph_3Sb)$ (X = Cl, Br or I) are made by treatment of $M(CO)_5(Ph_3Sb)$ with X_2 in hexane [238]. The acetonitrile complexes $MI_2(CO)_3(MeCN)_2$ easily lose MeCN on reaction with two equivalents

TABLE 3

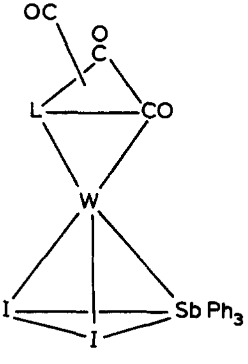
Mixed ligand complexes of group 6 carbonyls

Complex type	M	L	Ref.
$M(CO)_4(Ph_3Sb)L$	Mo	PPh_3	210
	W	P^iPr_3	211
	Cr	=CMe(OMe)	91
	Cr, Mo, W	$Ph_2PCSNR'R''$	212
	Mo	$\frac{1}{2}$(o-Phenylenebis-(picolinaldimine))	213
$M(CO)_3(Ph_3Sb)L$	Mo	2,7-Me_2-1,8-naphthyridine	214
	Mo	Pyridine-2-aldehyde-2′-pyridylhydrazone	215
	Mo	1,10-phenanthroline	216
	Mo	$Ph_2PCH_2CH_2PPh_2$	217,218
$M(CO)_2(Ph_3Sb)L$	Cr	Phenanthrene	219
	Cr	$C_6H_4CO_2Me$	220
$M(CO)_3Br(Ph_3Sb)L$	Cr, W	≡CPh	221,222
$[M(CO)_2(Ph_3Sb)L]^+$	W, Mo	C_7H_7	223,224
$[M(CO)_2(Ph_3Sb)L]$	Mo	C_7H_8	223
$[M(CO)_3(Ph_3Sb)L]^+$	W	C_7H_9	225
$M(C_5H_5)(CO)_2(Ph_3Sb)X$	Mo, W	Cl, Br, I	226–228
	Mo	$SnMe_3$	229
$M(C_5H_5)(CO)(Ph_3Sb)_2X$	Mo	Cl, I	226
$[M(C_5H_5)(CO)_2(Ph_3Sb)_2]^+$	Mo	–	230,231

of Ph_3Sb to produce brown $MI_2(CO)_3(Ph_3Sb)_2$ (M = Mo or W) [239]. However, on reaction with one equivalent of Ph_3Sb, the mixed-ligand complexes $MI_2(CO)_3(Ph_3Sb)(MeCN)$ form [240], and on treatment with L′ these are converted into a range of $MI_2(CO)_3(Ph_3Sb)L'$: L′ = PPh_3, PPh_2Cy, $PPhCy_2$, $AsPh_3$ [241,242], py, 2-Mepy, 4-Mepy, 2-ClPy [243,244], $P(OPh)_3$ [245], $OPPh_3$, $SPPh_3$ [246], $SC(NH_2)_2$, $SC(NMe_2)_2$ [247]. Generally, the complexes are brown or orange solids which show three ν(C—O) stretching vibrations and two ^{13}C carbonyl NMR resonances consistent with capped octahedral structures (9) [242].

If the $MI_2(CO)_3(MeCN)(Ph_3Sb)$ are treated with $Ph_2P(CH_2)_nPPh_2$, then dinuclear diphosphine bridged complexes, $\{MI_2(CO)_3Ph_3Sb\}_2(\mu$-diphosphine) are formed [248]. However, with 2,2′-bipyridyl, 1,10-phenanthroline or 1,2-phenylenediamine, the products are ionic with the bidentate chelating to the metal, $[MI(CO)_3(bidentate)(Ph_3Sb)]I$ [249]. The latter type of complex (as Br or I salts) is also formed by cautious halogenation of $Mo(CO)_3(bidentate)(Ph_3Sb)$ [250]. The molybdenum acetonitrile complex $MoI_2(CO)_3(Ph_3Sb)(MeCN)$ is unstable, and in the absence of added L′, loses MeCN and dimerises via iodide bridges $\{MI(CO)_3(Ph_3Sb)\}_2(\mu\text{-}I)_2$ [239].

The reaction of $MI_2(CO)_3(MeCN)_2$ with Ph_3Sb and N^nBu_4X in CH_2Cl_2



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gave $[N^nBu_4][MI_2X(CO)_3(Ph_3Sb)]$ [242,251]. An X-ray structural study of the related $[PPh_2CyH][WI_3(CO)_3(Ph_3Sb)]$, produced by decomposition of $WI_2(CO)_3(Ph_3Sb)(PPh_2Cy)$ in CH_2Cl_2, revealed the capped octahedral geometry shown in Fig. 3. Here the uncapped face is composed of three iodides, and the capped face $(CO)_2(Ph_3Sb)$ with a capping CO group, and the structure persists in solution on the basis of the ^{13}C NMR spectrum.

The $MI_2(CO)_3(Ph_3Sb)(MeCN)$ react with NaS_2CNR_2 ($R = Me$, Et, CH_2Ph) in a 1 : 1 ratio to form brown or black $MI(CO)_3(Ph_3Sb)(S_2CNR_2)$ [252,253]. Excess dithiocarbamate displaces the Ph_3Sb in most cases, although the seven-coordinate

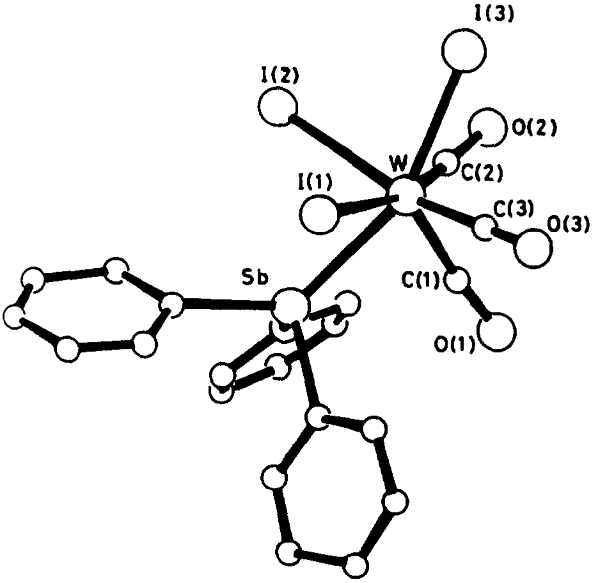


Fig. 3. Molecular structure of the anion $[W(CO)_3I_3(Ph_3Sb)]^-$. (From ref. 242 by permission of the Royal Society of Chemistry.)

mixed complexes $Mo(CO)_2(Ph_3Sb)(S_2CNR_2)\{S_2CN(CH_2Ph)_2\}$ are formed by the dibenzyldithiocarbamate anion. The air-sensitive complexes $M(CO)_2(Ph_3Sb)\{S_2CN(CH_2Ph)_2\}_2$ can also be made [253]. Other examples with sulphur ligands are $MI(CO)_3(Ph_3Sb)(S_2CNC_4H_8)$ [254], and $MI(CO)_3(Ph_3Sb)(S_2COEt)$ [255]. There are also mono- and di-nuclear trichlorostannate(II) complexes $MoCl(SnCl_3)(CO)_3(Ph_3Sb)(Ph_3P)$ and $\{Mo(SnCl_3)(CO)_3(Ph_3Sb)\}_2(\mu\text{-}Cl)_2$ [256].

Simple nitrosyl halides are restricted to Mo and W. The reaction of $M(CO)_3(Ph_3Sb)_2X_2$ (M = Mo or W; X = Cl or Br) with NO gave green $M(NO)_2(Ph_3Sb)_2X_2$, which exist as isomeric mixtures in which the NO groups are cis, but the X and Ph_3Sb either cis or trans [257]. The cleavage of $\{(\eta^5\text{-}Cp)W(NO)I_2\}_2$ with Ph_3Sb gave $(\eta^5\text{-}Cp)W(NO)I_2(Ph_3Sb)$ which is thought to be seven-coordinate (4 : 3) with the four monodentates occupying the square base plane [258]. Sodium amalgam reduction of $\{(\eta^5\text{-}Cp)M(NO)I_n\}_2$ (M = Cr, Mo or W) in tetrahydrofuran in the presence of Ph_3Sb afforded $(\eta^5\text{-}Cp)M(NO)(Ph_3Sb)_2$ [259]. The green cationic $[(\eta^5\text{-}Cp)M(NO)_2(Ph_3Sb)]PF_6$ (M = Mo or W) resulted from reaction of the ligand with $[(\eta^5\text{-}Cp)M(NO)_2(CO)]PF_6$ [260].

There appear to be no reports of molybdenum or tungsten halide complexes of arylstibines.

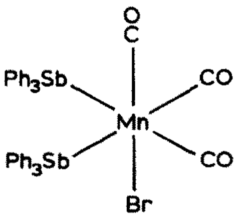
4.3.3 Group 7

As in group 6, the majority of Ph_3Sb complexes are substituted carbonyl derivatives, and only for rhenium have any halide complexes been obtained.

The reaction of $Mn_2(CO)_{10}$ with Ph_3Sb was reported to give yellow $Mn(CO)_4(Ph_3Sb)$ [261]. Reports of similar phosphine complexes have not been confirmed [262], and it seems likely that the isolated complex was, like the phosphines, dimeric $\{Mn(CO)_4(Ph_3Sb)\}_2$. The aryls $RMn(CO)_5$ (R = Ph or C_6F_5) substituted a carbonyl group on reaction with Ph_3Sb to form *cis*-$RMn(CO)_4(Ph_3Sb)$ [263,264], but $MeMn(CO)_5$ gave the acyl *cis*-$MeCOMn(CO)_4(Ph_3Sb)$ [264,265].

Irradiation of $(\eta^5\text{-}Cp)Mn(CO)_3$ and Ph_3Sb in tetrahydrofuran gave $(\eta^5\text{-}Cp)Mn(CO)_2(Ph_3Sb)$, but in ethanol the product was $(\eta^5\text{-}Cp)Mn(CO)(Ph_3Sb)_2$ [266]. Only the monosubstituted $(\eta^5\text{-}MeC_5H_4)Mn(CO)_2(Ph_3Sb)$ has been obtained with the methylcyclopentadienyl analogue [267,268], and the $(\eta^5\text{-indenyl})Mn(CO)_3$ behaved similarly [269]. Monosubstitution of a carbonyl group occurred on reaction of $(Ph_3M')Mn(CO)_5$ (M′ = Ge or Sn) with Ph_3Sb, and the M′—Mn bond was retained [270–272]. Monosubstitution also occurred with $HMn(CO)_5$, and the product $HMn(CO)_4(Ph_3Sb)$ lost hydrogen on heating to give the orange dimer $\{Mn(CO)_4(Ph_3Sb)_2\}_2$ [273]. The bimetallic (2,2′-bipyridyl)$Zn\{Mn(CO)_4(Ph_3Sb)\}_2$ was formed from $HMn(CO)_4(Ph_3Sb)$ and Et_2Zn(2,2′-bipyridyl) [273].

The reaction of $Mn(CO)_5X$ (X = Cl, Br or I) with one equivalent of Ph_3Sb gave *cis*-$Mn(CO)_4X(Ph_3Sb)$ [274,275], and the bromide has also been made from $[Et_4N][Mn(CO)_4Br_2]$ [276]. Under more forcing conditions and with two equivalents of Ph_3Sb, the products were *fac*-$Mn(CO)_3X(Ph_3Sb)_2$ (**10**) [275,277–279], which



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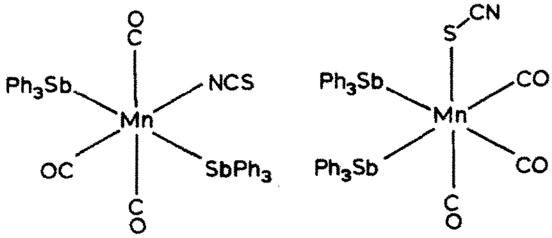
contrasts with the formation of mer isomers with most phosphines. However, the *mer*-$Mn(CO)_3(Ph_3Sb)_2Br$ has been formed on prolonged reflux of the fac complex in $CHCl_3$ [275]. The mixed-ligand $Mn(CO)_3(Ph_3Sb)\{P(O^nBu)_3\}Br$ has also been described [280]. Whereas $Mn(CO)_4L(CNS)$ complexes are isothiocyanato derivatives where L are N or P donor ligands, the Ph_3Sb complex is the thiocyanato *cis*-$Mn(CO)_4(Ph_3Sb)(SCN)$ [281,282]. Disubstitution, however, formed *cis*-$Mn(CO)_3(Ph_3Sb)_2(SCN)$ and *trans*-$Mn(CO)_3(Ph_3Sb)_2(NCS)$ (**11**), the mode of coordination of the CNS group seemingly controlled both by steric and electronic effects.



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The pentacarbonyl cation $[Mn(CO)_5(Ph_3Sb)]^+$ was formed by treatment of $Mn(CO)_5Br$ with $AgClO_4$, followed by displacement of the perchlorato ligand with Ph_3Sb [283].

In mixed complexes containing CO and CS, CO and NO or CO, CS and NO ligands, the CO is preferentially substituted by Ph_3Sb, as demonstrated by the formation of orange $(\eta^5\text{-Cp})Mn(CO)(CS)(Ph_3Sb)$ from $(\eta^5\text{-Cp})Mn(CO)_2(CS)$ [284], of $[(\eta^5\text{-Cp})Mn(CO)(NO)(Ph_3Sb)]PF_6$ from $[(\eta^5\text{-Cp})Mn(CO)_2(NO)]PF_6$ [285], and of brown $[(\eta^5\text{-Cp})Mn(CS)(NO)(Ph_3Sb)]SbF_6$ from $[(\eta^5\text{-Cp})Mn(CO)(CS)(NO)]SbF_6$ [286].

Dark green $Mn(NO)_3(Ph_3Sb)$ was made from $Mn(NO)_3(CO)$ and Ph_3Sb, or by treatment of $Mn(CO)_4(Ph_3Sb)I$ with NO [287,288]. The brown $Mn(NO)_2(Ph_3Sb)_2I$ is made similarly from $Mn(CO)_3(Ph_3Sb)_2I$ and NO [288].

Only one Ph_3Sb complex of technetium is known, the colourless octahedral $Tc(CO)_3(Ph_3Sb)_2Cl$ made from $Tc(CO)_5Cl$ and the ligand [289].

The carbonyl stibine complexes of rhenium are generally similar to those of manganese, but have been less thoroughly studied. The compounds *cis*-$Re(CO)_4X(Ph_3Sb)$ (X = Cl, Br or I) were made by reaction of the appropriate dimer $\{Re(CO)_4X\}_2$ with Ph_3Sb [290,291]. Under more forcing conditions, disubstituted products have been prepared, for example *fac*-$Re(CO)_3X(Ph_3Sb)_2$ (X = Br or I) [291,292], and a rare example of a carbonyl fluoride, white $Re(CO)_3F(Ph_3Sb)_2$, was made by reaction of the corresponding bromide with $AgHF_2$ in CH_2Cl_2 under anhydrous conditions [292]. Related complexes are $Re(CO)_3(Ph_3Sb)(S_2PEt_2)$ [293], and $(Ph_3M')Re(CO)_4(Ph_3Sb)$ (M′ = Ge or Sn) [294].

The reaction of $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}PPh_2)$ with Ph_3Sb gave $Re_2(CO)_7(\mu\text{-}PPh_2)(\mu\text{-}SbPh_2)(Ph_3Sb)$ [295] (Fig. 4) but no other properties have been described.

Treatment of $ReCl_3(NO)_2$ with excess Ph_3Sb in CH_2Cl_2 produced green crystals of $ReCl_2(NO)_2(Ph_3Sb)_2$ [296]. The study (Fig. 5) established that the Ph_3Sb groups were mutually trans, and NO trans to Cl.

No stibine complexes have been reported with the manganese halides, but examples with Re(III) and Re(IV) are known. The royal blue $ReCl_4(Ph_3Sb)_2$ was made by heating $ReCl_4(MeCN)_2$ with Ph_3Sb in the absence of a solvent, or by oxidation of $ReCl_3(MeCN)(Ph_3Sb)_2$ with CCl_4 [297]. The latter complex was obtained from $[Me_4N][ReCl_4(MeCN)_2]$ and the ligand [297]. The green Re(V) com-

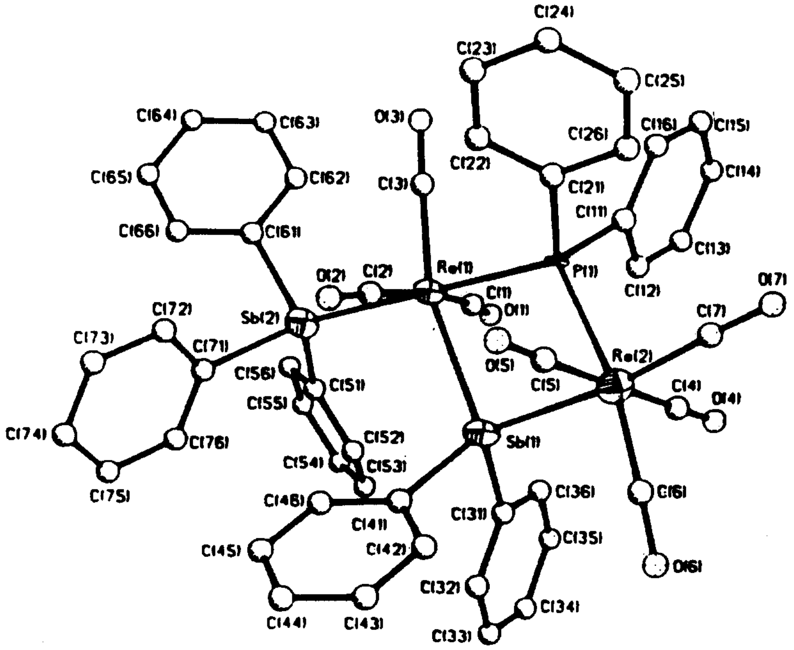


Fig. 4. Molecular structure of $Re_2(CO)_7(\mu\text{-}PPh_2)(\mu\text{-}SbPh_2)SbPh_3)$. (From ref. 295 by permission of *Acta Crystallographica*.)

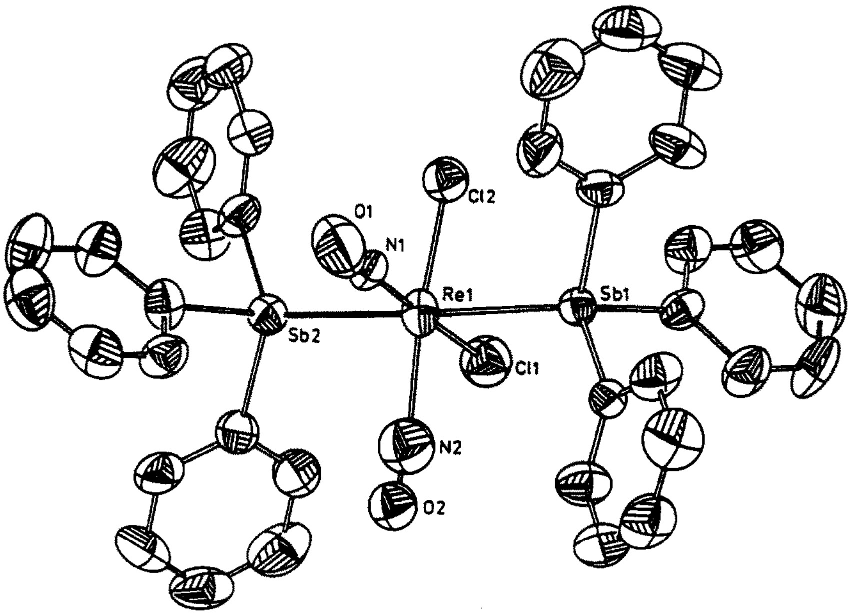


Fig. 5. Molecular structure of $ReCl_2(NO)_2(Ph_3Sb)_2$. (From ref. 296 by permission of *Zeitschrift für Anorganische und Allgemeine Chemie.*)

plexes $ReOX_3(Ph_3Sb)_2$ (X = Cl or Br) were made by prolonged reflux of perrhenic acid, Ph_3Sb and the appropriate HX, preferably in glacial acetic acid solution [298,299].

A second difference between the chemistries of manganese and rhenium is the formation of extensive series of polyhydrides by the latter. Sodium borohydride reduction of $ReOX_3(Ph_3Sb)_2$ produced red $Re_2H_8(Ph_3Sb)_4$, whilst the corresponding reduction of $Re_2Cl_6(PR_2Ph)_2$ and $Re_2Cl_5(PRPh_2)_3$ (R = Me or Et) in the presence of Ph_3Sb formed $Re_2H_8(PR_2Ph)_2(Ph_3Sb)_2$ and $Re_2H_8(PR_2Ph)_3(Ph_3Sb)$ respectively [299]. All have the $Re_2(\mu\text{-H})_4H_4L_4$ geometry with fluxional hydrides but with the L groups not exchanging on the NMR timescale. Subsequently [300], the $NaBH_4$ reduction of $[N^nBu_4]_2[Re_2Cl_8]$ in the presence of Ph_3Sb gave a mixture of $Re_2H_8(Ph_3Sb)_4$ and $Re_2H_6(Ph_3Sb)_5$, and with long reaction times (ca. five days) the latter can be obtained pure. The core geometry (Fig. 6) reveals the constitution to be $(Ph_3Sb)_3HRe(\mu\text{-H})_3Re(Ph_3Sb)_2H_2$. If a large excess of Ph_3Sb was present during the reduction of $ReOCl_3(Ph_3Sb)_2$ with $NaBH_4$, the product was the yellow mononuclear $ReH_5(Ph_3Sb)_3 \cdot 2H_2O$ [300].

Borohydride reduction of $ReCl_3\{MeC(CH_2PPh_2)_3\}$ in the presence of Ph_3Sb, or reaction of $ReH_5\{MeC(CH_2PPh_2)_3\}$ with Ph_3Sb gave yellow $ReH_3\{MeC(CH_2PPh_2)_3\}(Ph_3Sb)$, which can be protonated by $HBF_4 \cdot Et_2O$ to $[ReH_4\{MeC(CH_2PPh_2)_3\}(Ph_3Sb)]^+$, the reaction being reversed by Et_3N [301].

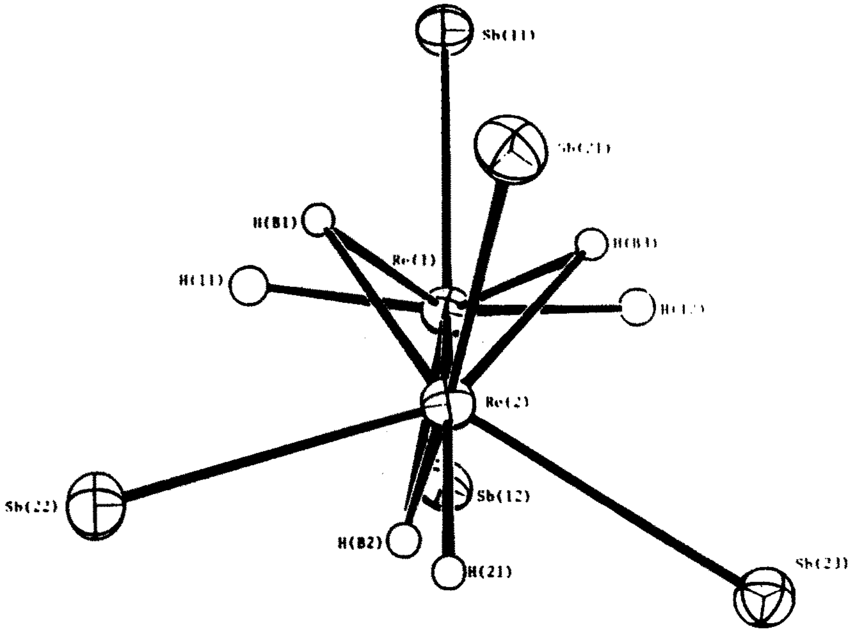


Fig. 6. Molecular structure of $Re_2H_6(Ph_3Sb)_5$. (From ref. 300 by permission of the American Chemical Society.)

4.3.4 Group 8

Iron stibine chemistry is again limited to substituted carbonyls, nitrosyls and organometallics. There are no complexes of iron halides, and indeed Ph_3Sb was chlorinated by $FeCl_3$ under reflux in $CHCl_3$ solution [302].

Heating together $Fe(CO)_5$ and the Ph_3Sb in a variety of organic solvents or photolysis formed mixtures of the yellow-brown $Fe(CO)_{5-n}(Ph_3Sb)_n$ ($n = 1$ or 2) [303–306]. Other workers [305–307] used the more reactive $Fe_3(CO)_{12}$ as the source of iron but still obtained mixtures which were separated by fractional crystallisation. More recently, a variety of catalysts, including $LiAlH_4$, $CoCl_2 \cdot nH_2O$, $\{(\eta^5\text{-}C_5H_4R)Fe(CO)_2\}_2$ and $[(\eta^5\text{-}Cp)_2Fe]^+$, have been employed to improve the yields and to maximise the amount of monosubstituted complex formed [307–309]. Photolysis of Ph_3Sb in an excess of neat $Fe(CO)_5$ has also been used [310,311]. The formation of $Fe(CO)_4(Ph_3Sb)$ alone or in addition to other products occurred on reaction of various organoiron compounds with Ph_3Sb (see, for example, refs. 312 and 313). A few mixed ligand complexes, such as $Fe(CO)_3(PPh_3)(Ph_3Sb)$ [304] and $Fe(CO)_3\{P(OPh)_3\}(L)$ ($L = Ph_3Sb$ or $(4\text{-}MeC_6H_4)_3Sb$) [104], have been described.

Many spectroscopic studies have been carried out on $Fe(CO)_{5-n}L_n$ complexes and these have included the Ph_3Sb complexes with $n = 1$ or 2; e.g. vibrational spectra [100,199,314] and ^{57}Fe and ^{121}Sb Mössbauer spectra [315,316]. Both $Fe(CO)_3(Ph_3Sb)_2$ and $Fe(CO)_4(Ph_3Sb)$ have trigonal bipyramidal geometries with

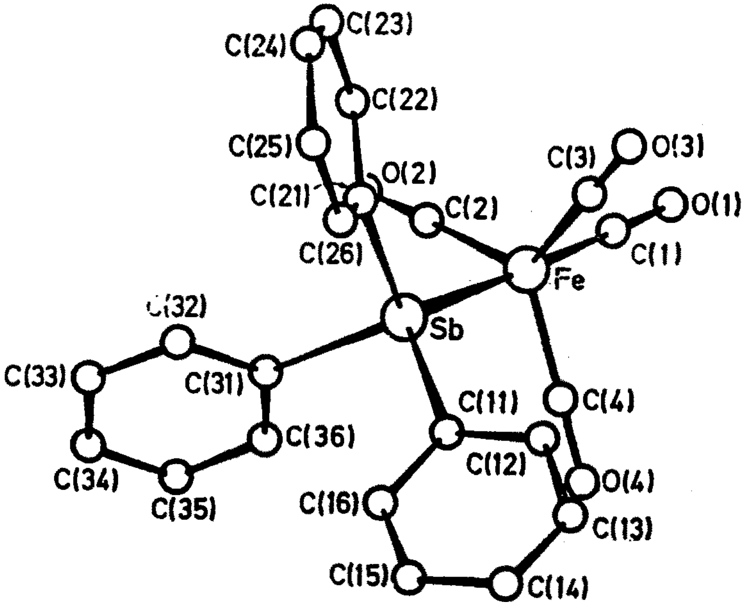


Fig. 7. Molecular structure of $Fe(CO)_4(SbPh_3)$. (From ref. 317 by permission of the Royal Society of Chemistry.)

axial stibines based upon these spectroscopic studies [100], and in the case of the latter, this has been confirmed by an X-ray study (Fig. 7) [317]. The electrochemical oxidation and reduction of $Fe(CO)_4(Ph_3Sb)$ and $Fe(CO)_3(Ph_3Sb)_2$ have been investigated [318,319].

The reaction of $Fe_3(CO)_{12}$ with Ph_3Sb often results in fragmentation to mononuclear products (see above), but under carefully controlled conditions green-black $Fe_3(CO)_{11}(Ph_3Sb)$ can be obtained [103,320], although in contrast to $(alkyl)_3Sb$, Ph_3Sb does not seem able to displace a second CO group. Irradiation of hexane solutions of $Fe_3(CO)_{12}$ containing Ph_3Sb gave, in addition to mononuclear products, red crystals identified [321] as $(Ph_3Sb)(CO)_3(Ph)Fe(Ph_2Sb)Fe(CO)_4$ (Fig. 8). Analogous complexes are not formed in the reactions with Ph_3P or Ph_3As, and this reflects the relative weakness of the C—Sb bonds.

Other stibine-substituted carbonyl clusters are the purple $Fe_3(H)_3(\mu^3\text{-COMe})(CO)_7(Ph_3Sb)$ formed by reaction of $Fe_3(H)(\mu^3\text{-COMe})(CO)_{10}$ and Ph_3Sb under dihydrogen (**13**) [322], $Fe_3H(CO)_{9-n}(SR)(Ph_3Sb)_n$ ($n = 1$–3) [323], and the phosphinidine bridged manganese–iron clusters $(\eta^5\text{-Cp})(CO)_2MnFe_2(CO)_5\text{-}(\mu^3\text{-PR})(Ph_3Sb)$ (R = Me, Et, or Ph) (**12**) [324]. The related cluster $(\eta^5\text{-Cp})\text{-}(CO)_2MnFe_2(CO)_6(\mu^3\text{-PPh})(Ph_3Sb)$ differs only by one carbonyl group (Fig. 9) [325]. Thiolate-bridged $\{Fe(CO)_3(SR)\}_2$ (R = Me, Et or Ph) substituted one

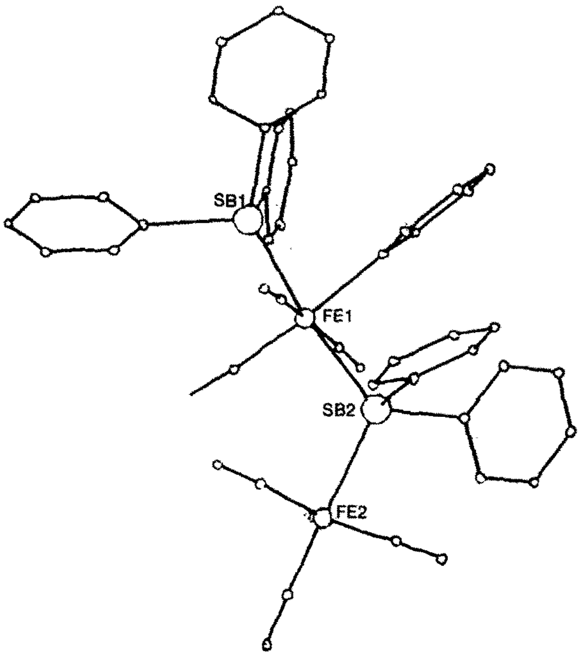
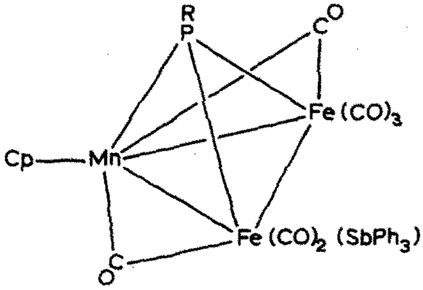


Fig. 8. Molecular structure of $(CO)_4Fe(\mu\text{-}SbPh_2)Fe(CO)_3Ph(Ph_3Sb)$. (From ref. 321 by permission of Elsevier Sequoia S.A.)



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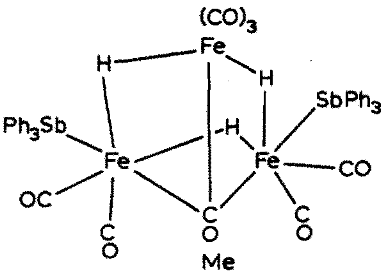
or two carbonyl groups on reaction with Ph_3Sb to form $Fe_2(CO)_{6-n}(SR)_2\text{-}(Ph_3Sb)_n$ ($n = 1$ or 2) [326,327].

The reaction of $H_2Fe(CO)_4$ with Ph_3Sb gave *fac*-$H_2Fe(CO)_3(Ph_3Sb)$ [328]. Carbonyl halide complexes $Fe(CO)_3I_2(Ph_3Sb)$ and $Fe(CO)_2X_2(Ph_3Sb)_2$ ($X = Cl$ or Br) are produced by substitution of one or two carbonyl groups from $Fe(CO)_4X_2$



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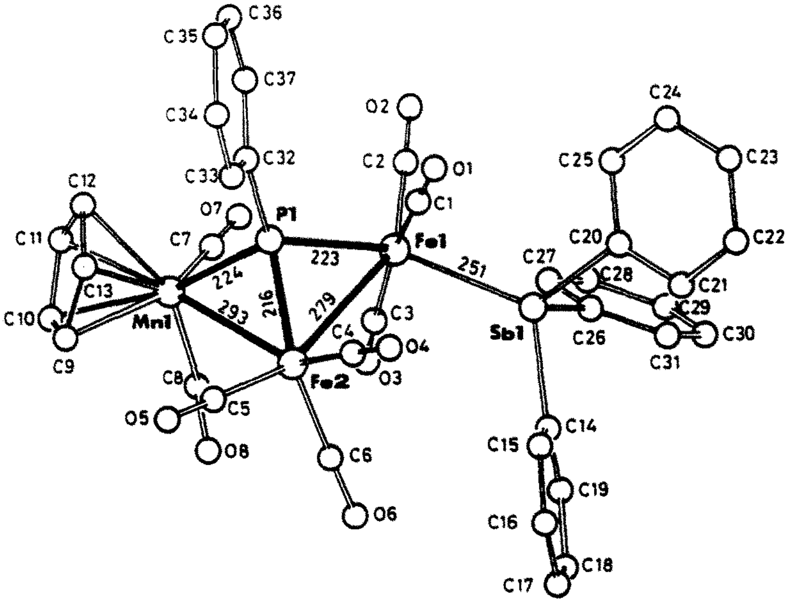


Fig. 9. Molecular structure of (η^5-Cp)Mn(CO)$_2$Fe$_2$(CO)$_6$(Ph$_3$Sb). (From ref. 325 by permission of *Acta Crystallographica.*)

[329–331]. However, reaction of Ph$_3$Sb with Fe(CO)$_2$(PPh$_3$)$_2$Br$_2$ brings about reduction to the five-coordinate Fe(0) complex, Fe(CO)$_2$(PPh$_3$)$_2$(Ph$_3$Sb) [332]. Mercury(II) halide adducts, (Ph$_3$Sb)$_2$(CO)$_3$FeHgX$_2$ (X = Cl or Br) formed by mixing HgX$_2$ with Fe(CO)$_3$(Ph$_3$Sb)$_2$ were suggested to contain an Fe$\rightarrow$Hg donor linkage [333].

A large number of organoiron carbonyl stibines have been described, the commonest organogroup being η^5-Cp. Only selected examples are discussed here, further examples are listed in Table 4. The [(η^5-Cp)Fe(CO)$_2$(Ph$_3$Sb)]$^+$ cation was first made by fusion of (η^5-Cp)Fe(CO)$_2$Cl with Ph$_3$Sb in a sealed tube [346]. When (η^5-Cp)Fe(CO)$_2$I and Ph$_3$Sb were reacted in refluxing toluene, a mixture of

TABLE 4

Organoiron, organoruthenium and organoosmium carbonyl and related complexes

Complex	Ref.
$(C_8H_8)Fe(CO)_2(Ph_3Sb)$	334
$(C_4F_8)Fe(CO)_3(Ph_3Sb)$	335
$(CH_2{=}CHC(Me){=}CH_2)Fe(CO)_2(Ph_3Sb)$	336
$(PhCH{=}CHCOR)Fe(CO)_3(Ph_3Sb)$	337
$(C_6H_4RCH{=}CHCHO)Fe(CO)_3(Ph_3Sb)$ ($R = 4\text{-}Me_2N$, 3-MeO, 4-MeO, 4-Cl, 4-Me)	338
$(PhCH{=}CHCH{=}NPh)Fe(CO)_2(Ph_3Sb)$	339
$[(C_7H_9)Fe(CO)_2(Ph_3Sb)][PF_6]$	340
$(C_{12}H_8N_2)Fe_2(CO)_5(Ph_3Sb)$	341
$\{(CF_3)_2C_2S_2\}Fe(CO)_2(Ph_3Sb)$	342
$\{(CF_3)_4C_4S_4\}Fe(Ph_3Sb)$	343
$[(C_9H_7)Fe(CO)_2(Ph_3Sb)]^+$	230
$(\eta^5\text{-}Cp)Fe(CO)(SCOR)(Ph_3Sb)$	344
$[C_4H_4Fe(CO)(NO)(Ph_3Sb)]PF_6$	345
$\{(CF_3)_2C_2S_2\}_2Ru(Ph_3Sb)_2$	342
$Ru(MeCOCHCOMe)_2(CO)(Ph_3Sb)$	369
$Ru_2(CO)_5(Ph_3Sb)\{C(Ph){=}C(Me)COC(Me){=}C(Ph)\}$	370
$[Ru(\eta^6\text{-}C_6H_6)(Ph_3Sb)_2Cl]^+$	371
$Ru(\eta^6\text{-}C_6Me_6)(Ph_3Sb)Cl_2$	372
$Ru(\eta^6\text{-}C_6Me_6)(Ph_3Sb)HCl$	372,373
$(C_7H_8)Ru(CO)(Ph_3Sb)Cl_2$	374
$(C_8H_8)RuHX(Ph_3Sb)_2$ ($X = Cl$, Br)	375
$Ru(2\text{-azopyridine})_2(Ph_3Sb)_2Cl_2$	376
mer-$Ru(CO)_3(SiCl_3)_2(Ph_3Sb)$	392
$(\eta^5\text{-}Cp)Ru(Ph_3Sb)_2X$ ($X = F$, Cl, Br, I, SCN, CN, $SnCl_3$)	393,396
$(\eta^5\text{-}Cp)Ru(Ph_3Sb)LX$ ($L = py$, 4-Mepy; X as above)	394
$[(\eta^5\text{-}Cp)Ru(L{-}L)(Ph_3Sb)]X$ ($L{-}L = 2,2'$-bipyridyl, 1,10-phenanthroline, X as above)	394–396
$(\eta^5\text{-}Cp)Ru(OCHS)(Ph_3Sb)L$ ($L = Ph_3P$, Ph_3Sb)	397
$(\eta^5\text{-}Cp)Ru(SCHS)(Ph_3Sb)L$ ($L = Ph_3P$, Ph_3Sb)	397
$(\eta^5\text{-}Cp)Ru(RCSNHCOR')(Ph_3Sb)Cl$	398
$[(\eta^5\text{-}Cp)Ru(Ph_3Sb)_2(C_6H_{10}N_2)]^+$	399
$[\{(\eta^5\text{-}Cp)Ru(Ph_3Sb)_2\}_2(\mu\text{-}C_6H_8N_4)]^{2+}$	399
$[\{(\eta^5\text{-}Cp)Ru(Ph_3Sb)_2\}_2(\mu\text{-phenylenebis(picolinaldimine)})]^{2+}$	400
$[(\eta^5\text{-}Cp)(Ph_3Sb)Ru(S_2CNCN)Ru(Ph_3Sb)_2(\eta^5\text{-}Cp)]$	401
$[(\eta^5\text{-}Cp)Ru(Ph_3Sb)(S_2CNCN)]$	401
$[(\eta^5\text{-}Cp)(Ph_3Sb)_2Ru(\mu\text{-}CN)Ru(Ph_3Sb)_2(\eta^5\text{-}Cp)]^+$	402
$[CN(2,2'\text{-bipyridyl})_2Ru(\mu\text{-}CN)Ru(Ph_3Sb)_2(\eta^5\text{-}Cp)]^+$	403
$[(\eta^5\text{-}Cp)(Ph_3Sb)_2Ru(\mu\text{-}NCC_6H_4CN)Ru(Ph_3Sb)_2(\eta^5\text{-}Cp)]^+$	404
$[(\eta^5\text{-}Cp)Ru(Ph_3Sb)(SnCl_3)L]$ ($L = AsPh_3$, PPh_3, py etc.)	405
$[(\eta^5\text{-}Cp)Ru(Ph_3Sb)(SnCl_3)(L{-}L)]SnCl_3$ ($L{-}L = 2,2'$-bipyridyl, 1,10-phenanthroline)	405
$(PhC{\equiv}CPh)Os_3(CO)_8(Ph_3Sb)$	424

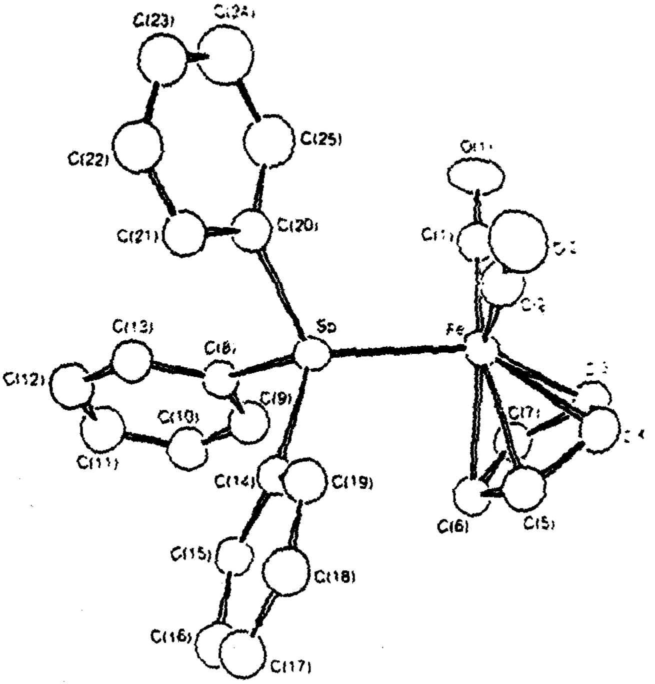


Fig. 10. Molecular structure of the cation *$[(\eta^5\text{-Cp})Fe(CO)_2(Ph_3Sb)]^+$*. (From ref. 350 by permission of *Acta Crystallographica*.)

$[(\eta^5\text{-Cp})Fe(CO)_2(Ph_3Sb)]I$ and $(\eta^5\text{-Cp})Fe(CO)(Ph_3Sb)I$ were formed [347], and the former was converted to the $[(\eta^5\text{-Cp})Fe(L{-}L)(Ph_3Sb)]I$ (L–L = 2,2′-bipyridyl or 1,10-phenanthroline) on treatment with L–L. Other preparations of the $[(\eta^5\text{-Cp})Fe(CO)_2(Ph_3Sb)]^+$ cation involved treatment of $\{(\eta^5\text{-Cp})Fe(CO)_2\}_2$ with Ag^+ in acetone, or with $[(\eta^5\text{-Cp})_2Fe]^+$, followed by addition of Ph_3Sb [106,107,348,349]. The structure of the PF_6^- salt is shown in Fig. 10 [350]. Related complexes include the chiral $[(\eta^5\text{-Cp})Fe(CO)(EMe_2)(Ph_3Sb)]^+$ (E = S, Se or Te) [351], $(\eta^5\text{-Cp})Fe(CO)(Ph_3Sb)(SnR_3)$ [352], $[(\eta^5\text{-Cp})Fe(CO)(CS)(Ph_3Sb)]^+$ [353], $(\eta^5\text{-Cp})Fe(CS)(Ph_3Sb)I$ [354], $[(\eta^5\text{-Cp})Fe(CNMe)_2(Ph_3Sb)]^+$ and $[(\eta^5\text{-Cp})Fe(CNMe)(Ph_3Sb)_2]^+$ [355], and $(\eta^5\text{-Cp})Fe(CO)Me(Ph_3Sb)$ [356].

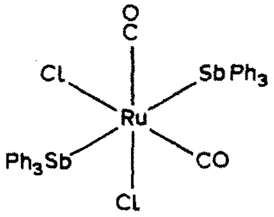
Triarylstibines (Ph_3Sb or $(4\text{-}MeC_6H_4)_3Sb$) displaced only one carbonyl group from $Fe(NO)_2(CO)_2$ to form $Fe(NO)_2(CO)(R_3Sb)$, which contrasts with Ph_3P or Ph_3As which can displace one or both carbonyls depending upon the conditions [287,328,357,358]. The paramagnetic (μ = ca. 1.9 B.M.) nitrosyl halides $Fe(NO)_2(R_3Sb)X$ (X = Br or I; R = Ph or $4\text{-}Me_2NC_6H_4$) are formed from $\{Fe(NO)_2X\}_2$ or $Fe(NO)_3X$ and R_3Sb, and have been the subject of detailed ESR studies [109,110,359]. Triphenylstibine also substituted one CO group on each iron centre in $Hg\{Fe(CO)_3(NO)\}_2$ to form $Hg\{Fe(CO)_2(NO)(Ph_3Sb)\}_2$, although this is unstable in solution, decomposing to $Fe(NO)_2(CO)(Ph_3Sb)$ [108,360].

The yellow diamagnetic $Na_3[Fe(CN)_5(Ph_3Sb)]$ was formed by displacing ammonia from $Na_3[Fe(CN)_5(NH_3)]$ and oxidation with bromine to the green complex $Na_2[Fe(CN)_5(Ph_3Sb)]$ ($\mu = 2.12$ B.M.). The IR and ^{57}Fe Mössbauer spectra, electrochemistry, and photoaquation of these complexes have been studied [361–367]. The yellow *p*-tolylisonitrile cation $[Fe(p\text{-}MeC_6H_4NC)_5(Ph_3Sb)]^{2+}$ was formed by displacing the perchlorate ligand from $[Fe(p\text{-}MeC_6H_4NC)_5(OClO_3)]^+$ [368].

The reaction of $Ru(CO)_5$ or $Ru_3(CO)_{12}$ with Ph_3Sb produced $Ru(CO)_4(Ph_3Sb)$ [99,314], in contrast to reactions with PR_3 which gave $Ru_3(CO)_9(PR_3)_3$. It appears that $Ru_3(CO)_{12}$ always fragments to mononuclear products on thermal or photochemical reaction with Ph_3Sb. The X-ray structure determination of $Ru(CO)_4(Ph_3Sb)$ showed that the stibine was in an equatorial site of a distorted trigonal bipyramid [377], which contrasts with the structure of the iron analogue where the stibine is axial (q.v.). In hexane solution, both axial and equatorial isomers are present [99]. The substitution of a second CO group in $Ru(CO)_4(Ph_3Sb)$ by Ph_3Sb is very slow and incomplete [378]. The monosubstituted $Ru_3(CO)_{11}(Ph_3Sb)$ was made from $Ru_3(CO)_{12}$ and Ph_3Sb using sodium diphenylketyl in tetrahydrofuran [379], and the kinetics of the reactions between $Ru_3(CO)_{12}$ and Ph_3Sb [380], and $Ru_3(CO)_{11}(Ph_3Sb)$ with Ph_3Sb in the presence of Me_3NO [381] have been investigated. Triphenylstibine substituted one or two carbonyl groups from $Ru_3(CO)_{11}(CN^tBu)$ to form $Ru_3(CO)_{11-n}(Ph_3Sb)_n(CN^tBu)$ ($n = 1$ or 2) [382]. Other stibine-substituted triruthenium clusters are $H_3Ru_3(\mu^3\text{-COMe})(CO)_7(Ph_3Sb)_2$ [322], and $Ru_3(\mu\text{-H})(\mu\text{-CNMe}_2)(CO)_9(Ph_3Sb)$ [383,384], which exist as mixtures of isomers in solution. The reaction of $Ru_3(\mu\text{-H})_3(\mu\text{-Bi})(CO)_9$ with Ph_3Sb and Me_3NO in CH_2Cl_2 led to mixtures of $Ru_3(\mu\text{-H})(\mu\text{-Bi})(CO)_{9-n}(Ph_3Sb)_n$ ($n = 1–3$), where the sequential substitution occurred at different ruthenium centres [385].

Carbonyl halides of type $Ru(CO)_2(Ph_3Sb)_2X_2$ and $Ru(CO)(Ph_3Sb)_3X_2$ (X = Cl or Br) were made by adding Ph_3Sb to a solution of $RuCl_3 \cdot nH_2O$ previously saturated with CO [386], by reaction of $Ru(Me_2SO)(Ph_3Sb)_3X_2$ with CO [387], and by reaction of $[R_4P][Ru(CO)Cl_3(C_7H_8)]$ with Ph_3Sb [374]. The iodide analogues $Ru(CO)_2(Ph_3Sb)_2I_2$ and $Ru(CO)(Ph_3Sb)_3I_2$ were formed from the stibine and $\{Ru(CO)_2I_2\}_n$ or $[Ru_2(CO)_4I_6]^{2-}$ [111,388,389]. There is some disagreement about the isomer(s) formed in these reactions, but it appears that $Ru(CO)_2(Ph_3Sb)_2Cl_2$ exists as (**14**), whilst the trisubstituted complexes have two forms (**15**). There is also an octahedral anion $[Ru(CO)(Ph_3Sb)_2Cl_3]^-$ [374], and reaction of $Ru(CO)_2(Ph_3Sb)_2X_2$ with CO and $AlCl_3$ gave the cations $[Ru(CO)_3(Ph_3Sb)_2X]^+$ (X = Cl, Br or I) [111]. Isonitrile complexes $Ru(CNC_6H_4Me\text{-}p)_2(Ph_3Sb)_2X_2$ and $Ru(CNEt)_2(Ph_3Sb)_2X_2$ (X = Cl or Br) have been described [390,391]. Treatment of $Ru(Ph_3Sb)_4X_2$ with CNEt in $CHCl_3$ gave trans isomers, which on boiling in 2-methoxyethanol isomerised to the cis form (**16**) [391].

There are a considerable number of stibine complexes based upon (η^5-Cp)Ru moieties (Table 4).



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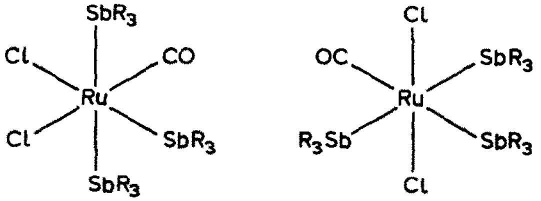

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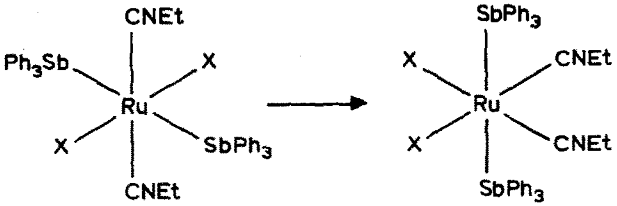

trans Cis

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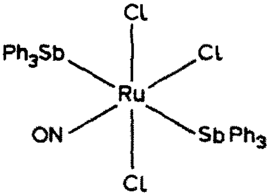
The yellow nitrosyl $Ru(NO)(Ph_3Sb)_2Cl_3$ was made from $K_2[Ru(NO)Cl_5]$ or $Ru(NO)Cl_3$ with Ph_3Sb, or from $RuCl_3 \cdot nH_2O$, Ph_3Sb and NOCl [406–412]. The



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structure appears to be mer-trans (**17**), although there is evidence that in CH_2Cl_2 solution photochemical isomerisation to a mer-cis form may occur [412]. Also reported are $Ru(NO)(Me_2SO)(Ph_3Sb)_2Cl_2$ [387], $Ru(NO)(Ph_3Sb)_2X_3$ ($X_3 = Cl_2Br$,

$ClBr_2$) [410], and the kinetics of Ph_3Sb substitution in $Ru(NO)(Ph_3Sb)_2Cl_3$ by phosphites [411]. Thionitrosyl complexes $Ru(NS)(Ph_3Sb)LCl_3$ [413,414] and a carbonyl sulphide derivative $Ru(COS)(Ph_3Sb)_2Cl_2$ [415] have been obtained.

The reaction of Ph_3Sb with $RuCl_3 \cdot nH_2O$ in alcohols has been variously reported to produce dark pink $Ru(Ph_3Sb)_3Cl_2$ or $Ru(Ph_3Sb)_4Cl_2$ [386,390,391,406,416], (both $Ru(PPh_3)_4Cl_2$ and $Ru(PPh_3)_3Cl_2$ are well established [417]). A reinvestigation confirmed the identity of *trans*-$Ru(Ph_3Sb)_4Cl_2$ by an X-ray study (Fig. 11), but found no evidence for the tris complex [416]. Corresponding claims for $Ru(Ph_3Sb)_nBr_2$ ($n = 3$ or 4) have been made [390,391,416]. A pink $Ru(Ph_3Sb)_3Cl_2$ has been claimed from the reaction of $RuCl_3 \cdot nH_2O$ reduced with Zn/Hg in ethanol and treated with Ph_3Sb [387], but a recent study suggested this was the impure tetrakis complex [416]. Nitric acid oxidation of *trans*-$Ru(Ph_3Sb)_4X_2$ in aqueous HBF_4 formed *trans*-$[Ru(Ph_3Sb)_4X_2]BF_4$ ($X = Cl$ or Br), and the Ru(II)–Ru(III) oxidation is electrochemically reversible [416]. A paramagnetic ($\mu = 2.02$ B.M./Ru) $\{Ru(CNS)_3(Ph_3Sb)_2\}_2$ has been reported [418].

Other Ru(II) complexes are $Ru(Ph_3Sb)_3Cl_2 \cdot HgCl_2$ and $Ru(Ph_3Sb)_3(GeEt_2Cl)Cl_2$ [419], $[Ru(NH_3)_5(Ph_3Sb)]^{2+}$ [420], and $[Ru(2,2'\text{-bipyridyl})_2(Ph_3Sb)Cl]^+$ [421,422].

The only example of Ru(VI) bonded to a stibine is the orange nitrido-complex $RuN(Ph_3Sb)_2Cl_3$, formed from $[RuNCl_4]^-$ and the ligand in boiling acetone [423].

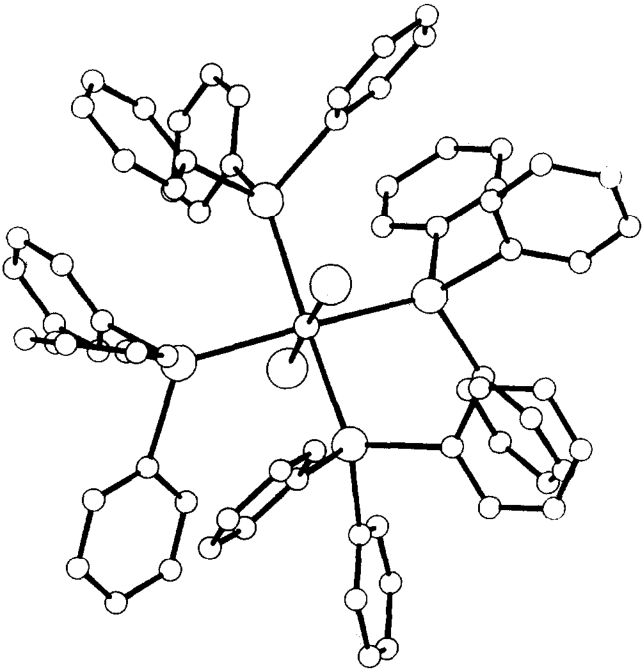


Fig. 11. Molecular structure of *trans*-$[Ru(Ph_3Sb)_4Cl_2]$. (From ref. 416.)

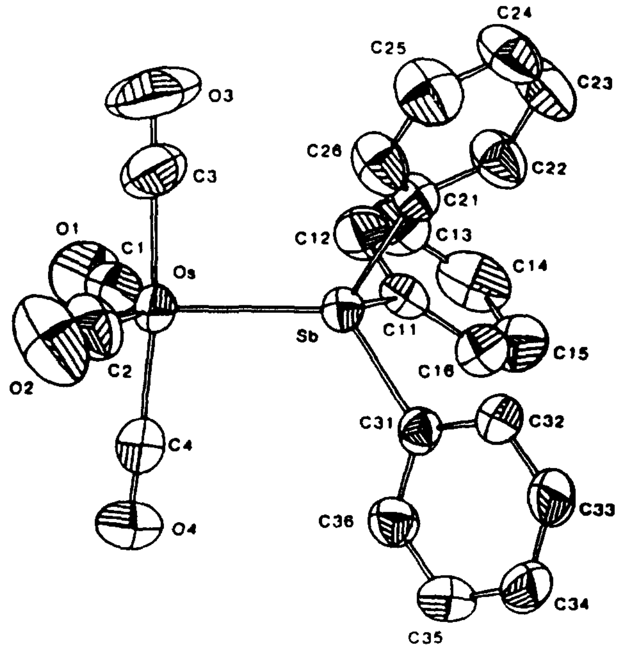
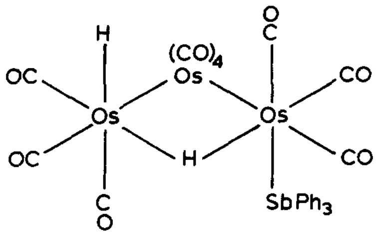


Fig. 12. Molecular structure of $Os(CO)_4(Ph_3Sb)$. (From ref. 314 by permission of the American Chemical Society.)

The yellow complex $Os(CO)_4(Ph_3Sb)$ was prepared by reaction of the ligand with $Os(CO)_5$ under 25 atm pressure of CO [314]. Like the ruthenium analogue, this complex has the Ph_3Sb occupying an equatorial site in a distorted trigonal bipyramid (Fig. 12), although both axially and equatorially substituted isomers are present in CH_2Cl_2 solution [99,314]. The monosubstituted cluster $Os_3(CO)_{11}(Ph_3Sb)$ has been prepared and studied in situ in $CHCl_3$, but does not appear to have been isolated [381]. Isolated larger clusters include the "spiked triangle" $Os_4(CO)_{15}(Ph_3Sb)$ [425], and $Os_6(CO)_{17}(Ph_3Sb)$ [426]. The latter, which has a bi-capped tetrahedral Os_6 core, was made from $Os_6(CO)_{18}$, Ph_3Sb and Me_3NO, and with further Me_3NO the hydrido-anion $[HOs_6(CO)_{16}(Ph_3Sb)]^-$ formed. The dihydride $H_2Os_3(CO)_{10}(Ph_3Sb)$ has structure (**18**) [427]. The grey-green $(\eta^5\text{-Cp})NiOs_3(\mu\text{-H})_3(CO)_7(Ph_3Sb)_2$ made from the parent nonacarbonyl, Me_3NO and Ph_3Sb, has the stibines bonded to two different osmium atoms [428].

Carbonylation of $Os(Ph_3Sb)_3Cl_3$ gave a mixture of green $Os(CO)(Ph_3Sb)_3Cl_2$, and two isomers of $Os(CO)_2(Ph_3Sb)_2Cl_2$ [429]. The yellow isomer has trans carbonyl groups and the white isomer cis carbonyls. The complexes *cis*-$Os(CO)_2(Ph_3Sb)_2X_2$ (X = Cl, Br or I) are formed from $Os(CO)_4X_2$ and Ph_3Sb in benzene [429–431]. The red nitrosyls $Os(NO)(Ph_3Sb)_2X_3$ (X = Cl, Br or I) were produced by reaction of NO with $Os(Ph_3Sb)_3Cl_3$ or from $[OsX_6]^{2-}$, Ph_3Sb and NO [429,432,433]. The structures are probably analogous to those of the ruthenium complexes (**17**).



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Osmium halide complexes are known in oxidation states II, III, IV and VI. The osmium(VI) complexes are the diamagnetic nitrides, $OsN(Ph_3Sb)_2X_3$ (X = Cl, Br or I) made from $[OsNX_4]^-$ and Ph_3Sb [423,434]. The iodide complex is notable since analogues with PPh_3, $AsPh_3$ or pyridine could not be obtained. In contrast, dioxoosmium(VI) complexes $OsO_2L_2X_2$ which are known with PR_3 and AsR_3 ligands, could not be isolated with Ph_3Sb [435]. The red *trans*-$Os(Ph_3Sb)_2Cl_4$ and purple *trans*-$Os(Ph_3Sb)_2Br_4$ were made by treatment of *mer*-$Os(Ph_3Sb)_3X_3$ with X_2 [436,437]. These are reduced by ascorbic acid to the brown Os(III) anions $[R_4N][Os(Ph_3Sb)_2X_4]$, although the chloro complex is unstable and decomposed to $Os(Ph_3Sb)_3Cl_3$ and $[OsCl_6]^{2-}$ in solution [436]. The green *mer*-$Os(Ph_3Sb)_3Cl_3$ and grey *mer*-$Os(Ph_3Sb)_3Br_3$ were made by refluxing $[OsX_6]^{2-}$ or OsO_4/HX with Ph_3Sb [429,438–440]. The report [437] of *fac*-$Os(Ph_3Sb)_3Br_3$ is probably in error, and the product is likely to be the mer isomer. The geometry of *mer*-$Os(Ph_3Sb)_3Br_3$ has been confirmed (X-ray) (Fig. 13) [441], and a detailed magnetic study of the chloride complex has been carried out [442]. Although the *mer*-$Os(Ph_3Sb)_3X_3$ gave reversible 1e oxidations in CH_2Cl_2 on the timescale of cyclic voltammetry, attempts to chemically oxidise these complexes to Os(IV) failed, in contrast to the ready isolation of *mer*-$[OsL_3X_3]^+$ ($L = PR_3$ or AsR_3) [439]. The yellow-brown *trans*-$Os(Ph_3Sb)_4X_2$ (X = Cl or Br) were prepared by $NaBH_4$ reduction of *mer*-$Os(Ph_3Sb)_3X_3$ in the presence of excess ligand [429,437,440,443]. The trans geometry (X = Cl) (X-ray) showed it to be isostructural with the ruthenium analogue [416]. Cyclic voltammetry studies revealed reversible 1e oxidations and further irreversible oxidation at highly positive potentials, and the green *trans*-$[Os(Ph_3Sb)_4X_2]BF_4$ were isolated by HNO_3 oxidation of the Os(II) complexes suspended in aqueous HBF_4 [443]. However, in contrast to many phosphine and arsine analogues, chemical oxidation to Os(IV) did not appear to be possible [443]. Other reported complexes are $Os(Ph_3Sb)_2(4\text{-}MeC_6H_4NC)Cl_2$ [444], $Os(Ph_3Sb)_4Cl_2 \cdot HgCl$ [419] and $Os(Ph_3Sb)_4Cl(SnCl_3)$ [419].

4.3.5 Group 9

Cobalt carbonyl, $Co_2(CO)_8$ reacted with Ph_3Sb in non-polar solvents below room temperature, to form $[Co(CO)_3(Ph_3Sb)_2][Co(CO)_4]$, but at higher temper-

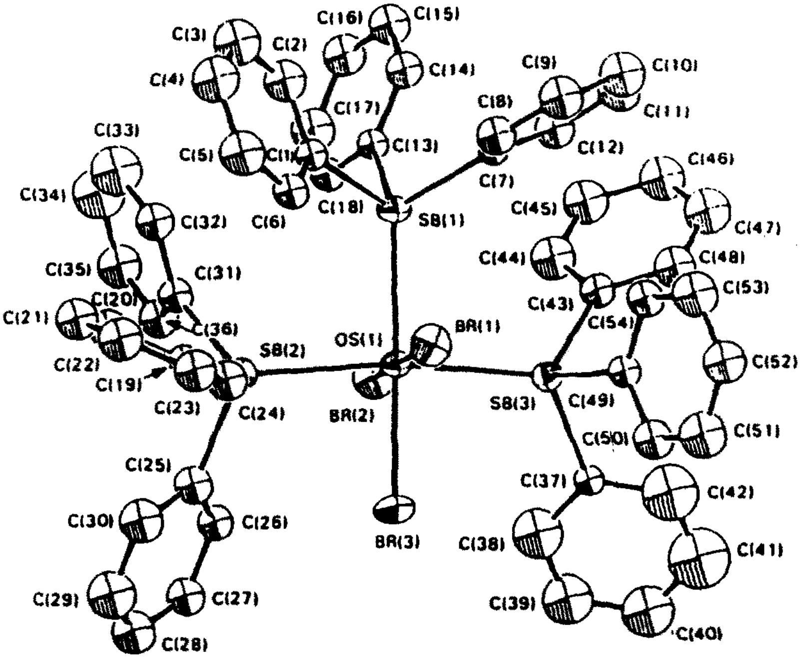
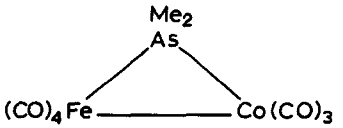


Fig. 13. Molecular structure of *mer*-$Os(SbPh_3)_3Br_3$. (From ref. 441 by permission of *Acta Crystallographica*.)

atures the product was the neutral dimer $\{Co(CO)_3(Ph_3Sb)\}_2$ [445]. A subsequent study [446] showed that the monosubstituted complex $Co_2(CO)_7(Ph_3Sb)$ could be obtained, but that it was unstable except under a CO atmosphere, disproportionating to the disubstituted complex and the parent carbonyl. Monosubstitution also occurred on treatment of $Co_4(CO)_{12}$ with Ph_3Sb, the reaction being reversed by passing CO through the solution [447]. The carbonyl cation *trans*-$[Co(CO)_3(Ph_3Sb)_2]BF_4$ has been made from $Co_2(CO)_8$, Ph_3Sb, and an oxidising agent such as the ferricenium cation [230]. Other cobalt carbonyl derivatives include $C_2F_5Co(CO)_3(Ph_3Sb)$ [448], $Hg\{Co(CO)_3(Ph_3Sb)\}_2$ [117,449], $Cl_2Sn\{Co(CO)_3(Ph_3Sb)\}_2$ [450], and $Tl\{Co(CO)_3(Ph_3Sb)\}_3$ which was formed when $Tl\{Co(CO)_4\}$ disproportionated to Tl(III) and thallium metal on treatment with the ligand [451]. Curiously, the bismuth analogue $Bi\{Co(CO)_4\}_3$ substituted only two carbonyl groups on reaction with Ph_3Sb to give $Bi\{Co(CO)_3(Ph_3Sb)\}_2\{Co(CO)_4\}$, whereas phosphines or arsines replace one CO group on each cobalt [452]. The mixed-metal dimer $(CO)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3$ (**19**) reacted with Ph_3Sb with cleavage of the M–M bond to form $(CO)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3(Ph_3Sb)$ [453].

Although several cobalt dinitrogen complexes are known, the only report of a stibine analogue is $Co(N_2)\{Sb(C_6H_3Me_2)_3\}_2$ [454]. The yellow hydride, $HCo(PF_3)_3(Ph_3Sb)$ was formed by reaction of $HCo(PF_3)_4$ and the ligand [455].



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Red $Co(CO)_2(NO)(L)$ ($L = Ph_3Sb$, $(p\text{-}MeC_6H_4)_3Sb$, $(p\text{-}ClC_6H_4)_3Sb$) and blue-black $Co(CO)(NO)(Ph_3Sb)_2$ were formed by substitution of carbonyl groups in $Co(CO)_3(NO)$ [357,456]. The X-ray study of $Co(CO)_2(NO)(Ph_3Sb)$ [457] revealed the expected distorted tetrahedral geometry about the cobalt centre (Fig. 14). The kinetics and equilibria in the reactions of $Co(CO)_3(NO)$ with Ph_3Sb, of $Co(CO)_2(NO)(Ph_3Sb)$ with CO, and of $Co(CO)_2(NO)(Ph_3Sb)$ with $Ph_2PCH_2CH_2\text{-}PPh_2$ have been studied [458–460]. The polarographic reduction of $Co(CO)_{3-n}\text{-}(NO)(Ph_3Sb)_n$ ($n = 1$, 2) have been reported [461]. The $Co(NO)_2(Ph_3Sb)Br$ was formed by cleavage of the dimeric $\{Co(NO)_2Br\}_2$ with Ph_3Sb [462], and the brown $Co(NO)_2(Ph_3Sb)SEt$ has been briefly described [463].

The dark-red square pyramidal cobalt(II) complex $Co(sacsac)_2(Ph_3Sb)$ (sacsac = dithioacetylacetonate), was obtained by reaction of $\{Co(sacsac)_2\}_2$ and Ph_3Sb [464]. Cobalt(III) complexes include $(\eta^5\text{-}Cp)Co(Ph_3Sb)I_2$

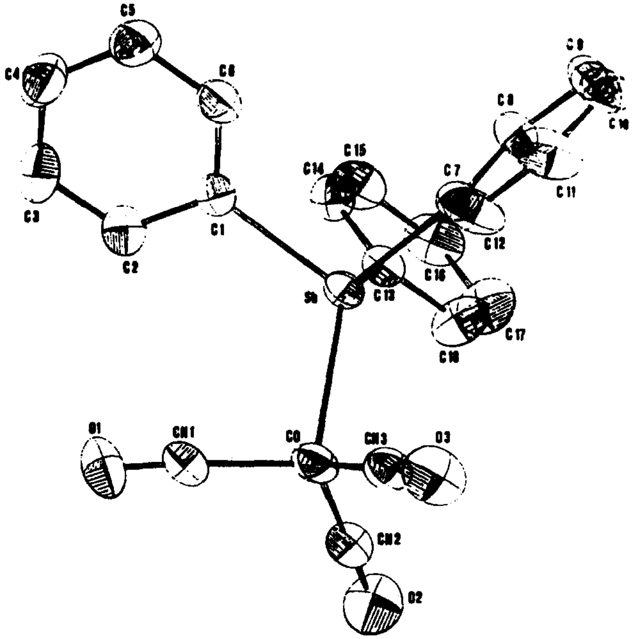


Fig. 14. Molecular structure of $Co(NO)(CO)_2(Ph_3Sb)$. (From ref. 457 by permission of *Acta Crystallographica.*)

and $[(\eta^5\text{-Cp})Co(S_2CNR_2)(Ph_3Sb)]^+$ [465]. Dithiolene adducts $[Co(Ph_3Sb)\{S_2C_2R_2\}_2]^{n-}$ ($n = 0$, 1; R = CF_3 or CN), which are probably square pyramidal have been described [342,446]. Dimethylglyoxime ($DMGH_2$) derivatives of both Co(II) and Co(III) have been intensively studied as cobaloxime models for vitamin B_{12}, and stibine complexes include the Co(II) $Co(DMGH)_2(Ph_3Sb)$ [467,468], and the Co(III) complexes $Co(DMGH)_2(Ph_3Sb)(SnPh_3)$ [469], *trans*-$Co(DMGH)_2Cl(Ph_3Sb)$ [125,470], $Co(DMGH)_2(N_3)(Ph_3Sb)$ [471], $[Co(DMGH)_2(Ph_3Sb)]^+$ [472], $Co(DMGH)_2(Ph_3Sb)O_2SR$ [473]. The X-ray structure of *trans*-$Co(DMG)_2Cl(Ph_3Sb)$ has been determined [470]. There is also a square pyramidal complex of benzoquinonediimine (L–L) $[Co(L{-}L)_2(Ph_3Sb)]ClO_4$ [474].

There are no known Ph_3Sb complexes of binary rhodium or iridium carbonyls, although there is a large and confused literature on carbonyl halides. A number of stibine derivatives of organorhodium and organoiridium complexes have been reported, usually in large compilations of group 15 complexes (see Table 5).

The reactions of $\{Rh(CO)_2Cl\}_2$ with PR_3 or AsR_3 usually produce yellow *trans*-$Rh(CO)Cl(ER_3)_2$ [1], but the corresponding reactions with triarylstibines were variously reported to yield pink, red-orange or purple materials which were formulated as $Rh(CO)Cl(R_3Sb)_n$ ($n = 2$, 3 or 4) or $Rh(CO)_2Cl(R_3Sb)_n$ ($n = 2$ or 3) [500,507–511]. A detailed reinvestigation by Garrou and Hartwell [479] showed that, for Ph_3Sb, the initial product on stepwise addition of Ph_3Sb to the carbonyl chloride was *cis*-$Rh(CO)_2Cl(Ph_3Sb)$ and when the amount of stibine increased, the equilibrium

$$Rh(CO)Cl(Ph_3Sb)_3 \rightleftharpoons Rh(CO)Cl(Ph_3Sb)_2 + Ph_3Sb$$

was present. When a large excess of stibine was present, the magenta five-coordinate $Rh(CO)Cl(Ph_3Sb)_3$ was isolated [479]. All attempts to isolate the yellow $Rh(CO)Cl(Ph_3Sb)_2$ in a pure state were unsuccessful [479]. For the bulky ligand $(o\text{-}MeC_6H_4)_3Sb$, only the yellow planar $Rh(CO)ClL_2$ complex was obtained, but for $(p\text{-}MeC_6H_4)_3Sb$, both the yellow bis- and orange-red tris(stibine) complex were isolated [479]. In dilute solution, the yellow complexes are monomeric, but the tris complexes are completely dissociated to the bis complex and free ligand, a result supported by their identical $\nu(CO)$ frequencies in solution in non-polar solvents. In an extension of this study, the reactions of $Rh_2Cl_2(CO)_x(C_2H_4)_{4-x}$ with R_3Sb in $CHCl_3$ were monitored in solution by IR spectroscopy [512], but although a number of new intermediates were observed, only $Rh(CO)Cl(R_3Sb)_n$ ($n = 2$ or 3) were isolated. Other studies have reported a range of $Rh(CO)X(Ph_3Sb)_2$ (X = Br, I, F, NO_2, CNS or CN) produced by methathesis from the chloride [513], isothiocyanate complexes $Rh(CO)(NCS)(R_3Sb)_2$ (R = Ph, $p\text{-}ClC_6H_4$) [514], and mixed ligand complexes $Rh(CO)XL(Ph_3Sb)$ (X = Cl or Br; L = PPh_3 or $AsPh_3$) [515]. It is also possible to isolate the red-brown five-coordinate $Rh(CO)Cl(PPh_3)(Ph_3Sb)_2$ [516], a further illustration of the tendency of stibines to promote the higher coordination number. A detailed study of the UV–visible spectrum of $Rh(CO)Cl(Ph_3Sb)_2$ has been reported

TABLE 5

Organorhodium and organoiridium complexes

Complex	Ref.
Rh(norbornadiene)$(Ph_3Sb)Cl$	475,476
Rh(cyclooctadiene)$(R_3Sb)_xCl$ (R = Ph, p-MeC_6H_4; $x = 1$ or 2 see text)	476,478–480
Rh(norbornadiene)$(SnCl_3)(Ph_3Sb)_2$	477
[Rh(norbornadiene)$_2(Ph_3Sb)]^+$	481
[Rh(norbornadiene)$L(Ph_3Sb)]^+$ (L = Me_2S, $(\overline{CH_2)_3S}$, $(\overline{CH_2)_4S}$, etc.)	482
$(\eta^5$-$Me_5Cp)Rh(CN^tBu)(Ph_3Sb)$	483
$Rh\{C_4(CF_3)_4\}(Ph_3Sb)_2Cl$	484
$Rh\{^tBuC(O)CHC(O)^tBu\}(CF_2{=}CFX)(Ph_3Sb)$ (X = F, Cl, Br, CF_3)	485
$Rh\{^tBuC(O)CHC(O)^tBu\}(CF_3C{\equiv}CCF_3)(Ph_3Sb)_2$	486,487
$Rh\{^tBuC(O)CHC(O)^tBu\}(CF_3C{=}CCF_3CCF_3{=}CCF_3)(Ph_3Sb)$	487
$Rh\{MeC(O)CHC(O)Me\}(CF_3C{\equiv}CCF_3)(Ph_3Sb)$	487
Rh(*trans*-1,3-pentadiene)$Cl(Ph_3Sb)_2$	488
Rh(acac)(CO)$(Ph_3Sb)_x$ ($x = 1$ or 2 see text)	479,489,490
Rh(8-hydroxyquinolato)(CO)(Ph_3Sb)	490
[Rh(LL)(CO)$(Ph_3Sb)_2]ClO_4$ (LL = 2,2′-biquinolyl or 2,9-Me_2-4,7-Ph_2-1,10-phenanthroline)	491,492
$Rh(MeCO)(CO)(Ph_3Sb)_3$	493
$Rh\{PhC(O)CHC(O)Ph\}Ph_2(Ph_3Sb)_2$	494
[Rh(tetrafluorobenzobarrelene)$(Ph_3Sb)_2]ClO_4$	495
Rh(σ-allyl)$ClBr(CO)(Ph_3Sb)_2$	496
[Rh(π-allyl)$X(CO)(Ph_3Sb)_2]^+$ (X = Cl or Br)	496
Rh(Schiff base)$L(Ph_3Sb)$ (L = CO or C_2H_4)	497,498
RhHX(Schiff base)$(Ph_3Sb)_2$	499
$[Rh(4\text{-}MeOC_6H_4NC)_2(Ph_3Sb)_2]ClO_4$	500
$Rh(DMGH)_2Cl(Ph_3Sb)$	501,502
$RhH(SiR_3)Cl(Ph_3Sb)_2$ (R = Cl or OEt)	503
$\{Rh(COS)Cl(Ph_3Sb)\}_2$	523
Ir(cyclooctadiene)$(Ph_3Sb)_2Cl$	476
Ir(cyclobutene)$Cl(Ph_3Sb)_2$	488
$[IrH_2$(cyclooctadiene)$L(Ph_3Sb)]ClO_4$ (L = Me_2S, Et_2S, $(\overline{CH_2)_4S}$, etc.)	504
Ir(tetrafluorobenzobarrelene)$X(Ph_3Sb)L$ (X = Cl, $SnCl_3$; Y = Ph_3Sb, PPh_3)	505
[Ir(tetrafluorobenzobarrelene)$_2(Ph_3Sb)]^+$	505
$IrHX(SiR_3)(Ph_3Sb)_2$	506

[517]. Other carbonyl derivatives are the red-brown $\{Rh(CO)(Ph_3Sb)(\mu\text{-}S_2PF_2)\}_2$ [518], the red $Rh(CO)(Ph_3Sb)_2I_3$ formed from $RhCl_3 \cdot 3H_2O$, NaI, CO and Ph_3Sb in ethanol [519], and some mixed complexes, including $Rh(CO)Cl_3(PPh_3)(Ph_3Sb)$ and $RhClIMe(CO)(PPh_3)(Ph_3Sb)$ [516].

The confusion surrounding the formulation of the reaction products obtained from $\{Rh(CO)_2Cl\}_2$ and R_3Sb, extends also to the nature of the stibine substitution products of $\{Rh(COD)Cl\}_2$ [476,478–480] and $Rh(acac)(CO)_2$ [479,489,490]. Reinvestigation [479] suggested that, in both cases, the products with Ph_3Sb, or $(p\text{-}MeC_6H_4)_3Sb$, were $Rh(COD)Cl(R_3Sb)_2$ and $Rh(acac)(CO)(R_3Sb)_2$, again demonstrating the preference of rhodium stibines to achieve higher coordination numbers than the phosphine or arsine analogues.

The carbonyl cation $[Rh(CO)_2(Ph_3Sb)_3]^+$ was made by reaction of $Rh(CO)Cl(Ph_3Sb)_x$ with CO and $AlCl_3$ [520], or from rhodium(I) perchlorate, CO and Ph_3Sb [521], and there are some mixed PPh_3/Ph_3Sb analogues [522]. The cation reacted with KOH in methanol to form $Rh(MeOCO)(CO)(Ph_3Sb)_3$, and this was converted into $RhHCl_2(CO)(Ph_3Sb)_2$ by HCl in diethyl ether at −60°C [520].

The red rhodium nitrosyl $Rh(NO)(Ph_3Sb)_3$ was formed from $\{Rh(NO)_2Cl\}_n$ and Ph_3Sb, but a second product, believed to be $Rh(NO)(Ph_3Sb)_2Cl_2$, was not isolated [524].

In marked contrast to the intensive studies of $Rh(Ph_3P)_3Cl$ [525], the deep purple $Rh(Ph_3Sb)_3Cl$ made from $\{Rh(C_2H_4)_2Cl\}_2$ and the ligand, is little known [526,527]. It is much less stable than the phosphine analogue, and although it adds HCl and H_2 in solution to give $RhHCl_2(Ph_3Sb)_3$ and $RhH_2Cl(Ph_3Sb)_3$, respectively, neither product has been isolated pure [526,528].

The reaction of $RhX_3 \cdot nH_2O$ with $(o\text{-}MeC_6H_4)_3Sb$ gave red-brown diamagnetic $RhX_2\{(o\text{-}MeC_6H_4)_3Sb\}$ ($X = Cl$ or Br), which are dimeric in solution, and tentatively formulated as halide bridged Rh(II) complexes [529]. An X-ray study would be most interesting, particularly since bulky phosphines produce mononuclear Rh(II) complexes with a $Rh(PR_3)_2X_2$ stoichiometry [1]. More familiar Rh(II) complexes are the dinuclear $Rh_2(L{-}L)_4Y_2$ type, one example of which is the light brown $Rh_2(\mu\text{-}MeCO_2)_4(Ph_3Sb)_2$ formed from $Rh_2(\mu\text{-}MeCO_2)_4$ and the ligand in methanol [530]. The long Rh–Sb bond of 2.732(4) Å (Fig. 15) suggests a strong trans influence of the Rh–Rh bond [530]. Complexes with related structures are the mixed-ligand complex $Rh_2(\mu\text{-}MeCO_2)_4(Ph_3Sb)\{P(OMe)_3\}$ [531], $Rh_2(\mu\text{-}PhCONH)_4(Ph_3Sb)_2$ [532], $Rh_2(\mu\text{-}MeCONH)_{4-n}(\mu\text{-}MeCO_2)_n(Ph_3Sb)_2$ (n = ca. 1) [533] and $Rh_2(\mu\text{-}MeCSO)_4(Ph_3Sb)_2$ [534]. Detailed spectroscopic studies, including resonance Raman investigations, have been carried out [531–536].

The reaction of $RhCl_3 \cdot 3H_2O$ with Ph_3Sb in ethanol under reflux gave orange *mer*-$RhCl_3(Ph_3Sb)_3$ [537,538]. The $RhXCl_2(Ph_3Sb)_3$ were prepared on reaction of this mer isomer with NaX ($X = Br$, I, SCN or $SnCl_3$), and surprisingly only one chlorine was replaced, even on prolonged reaction, presumably the chlorine trans to Ph_3Sb [537]. A reinvestigation of the reaction of $RhCl_3 \cdot 3H_2O$ with Ph_3Sb in

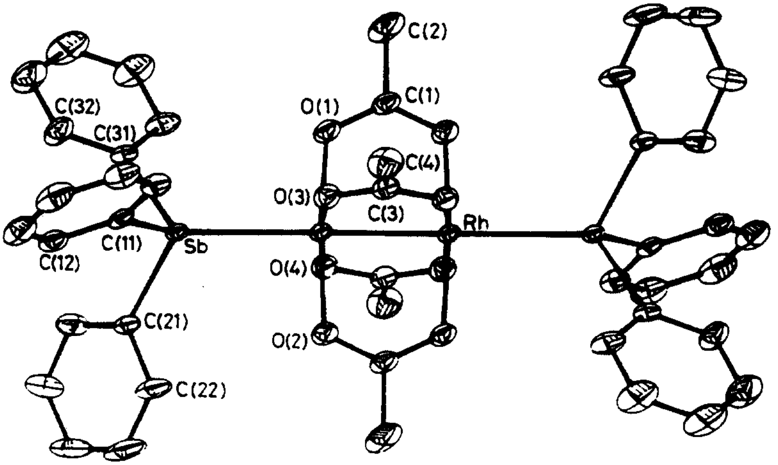


Fig. 15. Molecular structure of $Rh_2(\mu\text{-}MeCO_2)_4(Ph_3Sb)_2$. (From ref. 530 by permission of the Royal Society of Chemistry.)

boiling ethanol, identified *trans*-$RhCl_2(Ph)(Ph_3Sb)_3$ as a further product, and this was characterised by an X-ray study [539], (Fig. 16). On recrystallisation from MeCN, the latter complex was converted to $RhCl_2(Ph)(Ph_3Sb)_2(MeCN)$ (Fig. 17) [540].

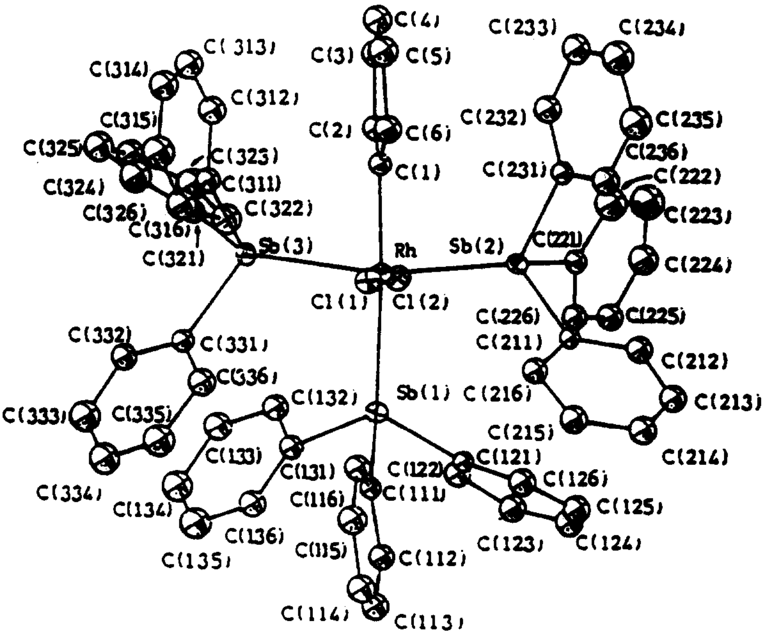


Fig. 16. Molecular structure of $RhCl_2(Ph)(Ph_3Sb)_3$. (From ref. 539 by permission of Elsevier Sequoia S.A.)

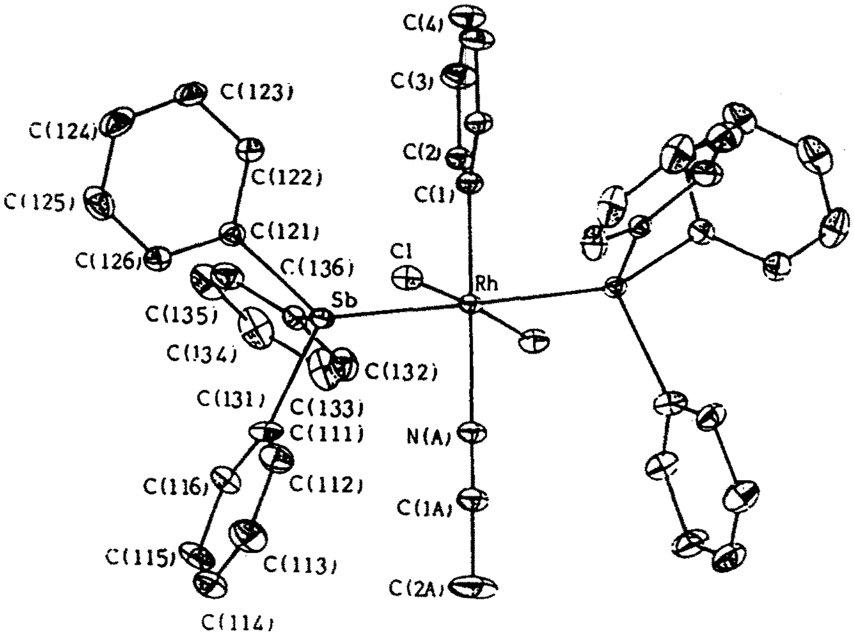
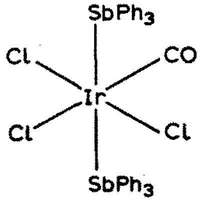


Fig. 17. Molecular structure of $RhCl_2(Ph)(Ph_3Sb)_2(MeCN)$. (From ref. 540 by permission of *Acta Crystallographica*.)

In contrast to rhodium, relatively little work has been reported on iridium carbonyl stibines. In contrast to phosphines and arsines, which form *trans*-$Ir(CO)Cl(ER_3)_2$, Ph_3Sb was reported to react with $Ir(CO)_2(p\text{-}H_2NC_6H_4Me)Cl$ to form the red $Ir(CO)Cl(Ph_3Sb)_3$ [541]. However, $Ir(CO)Br\{(p\text{-}ClC_6H_4)_3Sb\}_2$ has also been mentioned [542]. The carbonyl cations $[Ir(CO)_2(Ph_3Sb)_3]^+$ and $[Ir(CO)_2(PPh_3)_2(Ph_3Sb)]^+$ were made by analogous routes to the rhodium complexes [520,522]. The iridium(III) carbonyls $IrX_3(CO)(Ph_3Sb)_2$ ($X = Cl$ or Br) were obtained as yellow solids by passing CO through benzene solutions of $IrX_3(Ph_3Sb)_3$, and on the basis of the dipole moments, were assigned structure (**20**) [543,544]. The $IrHCl_2(CO)(Ph_3Sb)_2$ was formed from $Ir(EtCO_2)(CO)(Ph_3Sb)_3$ and HCl at low temperatures [520].



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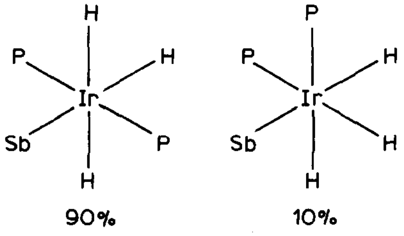
Iridium hydrides include $IrH_3(PEt_2Ph)_2(Ph_3Sb)$ formed as a mixture of isomers (**21**) by reaction of Ph_3Sb with $IrH_5(PEt_2Ph)_2$ [545]. The complex $[(\eta^5\text{-Cp})IrH_3(Ph_3Sb)]BF_4$ was made by reaction of $\{(\eta^5\text{-Cp})IrI_2\}_n$ with Ph_3Sb to form $(\eta^5\text{-Cp})Ir(Ph_3Sb)I_2$, followed by zinc reduction to $(\eta^5\text{-Cp})Ir(Ph_3Sb)H_2$, and finally protonation with HBF_4 [546].



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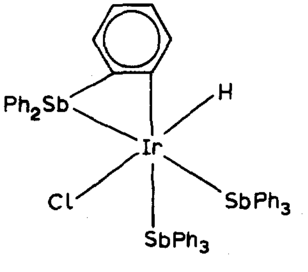
The red $IrCl(Ph_3Sb)_3$ was obtained from $Ir(cyclooctene)_2Cl$ and Ph_3Sb [547]. The product is very air-sensitive and ortho-metallated on heating in organic solvents



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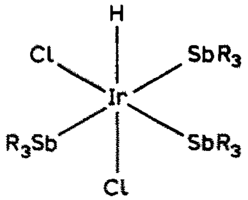
to form $IrHCl\{(o\text{-}C_6H_4)Ph_2Sb\}(Ph_3Sb)_2$ (**22**). A complex of an ortho-metallated phosphite, $Ir_2Cl_2(Ph_3Sb)_2\{P(OC_6H_3Me\text{-}o)_2(OC_6H_4Me\text{-}o)\}$ has also been characterised [548]. Addition of HCl to $IrCl(Ph_3Sb)_3$, heating $IrX_3 \cdot nH_2O$ with Ph_3Sb especially in the presence of base, or reaction of $IrX_3(Ph_3Sb)_3$ with $NaBH_4$ produced $IrHX_2(Ph_3Sb)_3$ ($X = Cl$, sometimes Br or I) [543,544,547,549–552]. It is unclear in many cases which isomer(s) were produced, although (**23**) appears to be the product formed in the first method. However, the mixed-ligand complex $IrHCl_2(PPh_3)_2(Ph_3Sb)$ was formulated as (**24**) [553].

The reactions of $IrX_3 \cdot nH_2O$ or of M_3IrX_6 ($X = Cl$ or Br; $M = Na$ or K) with Ph_3Sb in boiling alcohols produced a mixture of complexes including *mer*- and *fac*-$Ir(Ph_3Sb)_3X_3$, *trans*-$[Ir(Ph_3Sb)_2X_4]^-$, and $IrHX_2(Ph_3Sb)_3$, from which the individual components were separated by extraction with specific organic solvents or by chromatography [123,543,544]. The $[Ir(Ph_3Sb)_2X_4]^-$ anions have been obtained with a variety of cations, and on heating in alcohols or more slowly on standing in alcoholic solution formed $Ir(Ph_3Sb)_2X_3(ROH)$, from which the alcohol can be ex-



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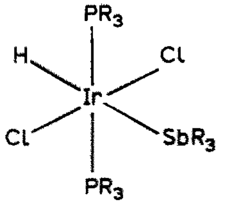

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changed for a range of other neutral ligands including NH_3, CO and pyridine. On heating the alcohol adducts in toluene, materials of composition $Ir(Ph_3Sb)_2X_3$ were produced which are probably dimeric with halide bridges [544]. Cyclic voltammetry showed that $[Ir(Ph_3Sb)_2Cl_4]^-$ underwent a reversible 1e oxidation, but that, for the bromide analogue, the process was reversible only at fast scan rates [123]. Chlorine oxidation of $Ir(Ph_3Sb)_3Cl$ or $[Ir(Ph_3Sb)_2Cl_4]^-$ produced the purple iridium(IV) complex *trans*-$Ir(Ph_3Sb)_2Cl_4$ (cf. the Me_3Sb complex which is cis), but bromination of $[Ir(Ph_3Sb)_2Br_4]^-$ caused decomposition [123]. The Ir(IV) complex is stable for some time in the solid state, although it decomposes more rapidly in solution. It is paramagnetic ($\mu = 1.6$ B.M.) and the Ir(III)/Ir(IV) redox potential is only ca. 0.04 V more positive than those of the phosphine and arsine analogues [123]. Attempts to obtain $[Ir(Ph_3Sb)Cl_5]^{2-/-}$ anions directly by substitution into $[IrCl_6]^{2-}$ were unsuccessful, but treatment of $[Ir(py)Cl_5]^{2-}$ with Ph_3Sb, followed by chlorine oxidation to Ir(IV), and removal of the pyridine by HCl/CH_2Cl_2 gave the purple $[NEt_4][Ir(Ph_3Sb)Cl_5]$ [554]. The Ir(III)/Ir(IV) redox potential is ca. 0.3 V less positive than that of the disubstituted analogue.

4.3.6 Group 10

Complexes of nickel with triarylstibines are mostly limited to oxidation states zero or +1, and in contrast to the complexes formed with Me_3Sb (q.v.), there was no reaction between anhydrous NiX_2 and Ph_3Sb even in non-polar solvents [555].

The reaction of triarylstibines with $Ni(CO)_4$ usually produced the $Ni(CO)_3(R_3Sb)$ (R = Ph, 4-FC_6H_4, 3-FC_6H_4, 4-ClC_6H_4, 3-ClC_6H_4, 4-MeC_6H_4) [80,84,126,556–558], although $Ni(CO)_2(Ph_3Sb)_2$ was also formed in this way

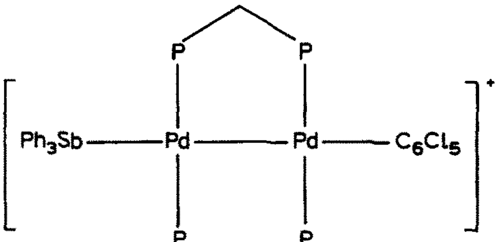
[80,557]. Further substitution does not seem to be possible although $Ni(R_3Sb)_4$ can be obtained in other ways. Related complexes are $Ni(CO)_2(PPh_3)(Ph_3Sb)$ [557] and the fluorophosphines $Ni(PF_3)_{4-n}(Ph_3Sb)_n$ ($n = 1$ or 2) [559]. The diamagnetic $Ni(NO)(Ph_3Sb)_2X$ (X = Br or I) were made from $\{Ni(NO)X\}_n$ and Ph_3Sb [560].

The yellow air-sensitive Ni(0) complexes, $Ni(R_3Sb)_4$ (R = Ph, p-MeC_6H_4, p-$MeOC_6H_4$) were formed by reaction of $K_4Ni(CN)_4$ with R_3Sb in liquid ammonia [561], by reduction of $Ni(acac)_2$ with $AlEt_3$ or $AlEt_2OEt$ in the presence of the stibine [562,563], by displacement of the diene from $Ni(COD)_2$ by R_3Sb [564], or by $NaBH_4$ reduction of a mixture of NiX_2 and Ph_3Sb [565]. The complexes decomposed slowly in solution depositing elemental nickel, but unlike the $Ni(PR_3)_4$ analogues, the ligand dissociation in solution was small.

Sodium borohydride reduction of NiX_2 (X = Cl, Br or I) in the presence of Ph_3Sb produced a range of Ni(I) complexes [566,567]. Depending upon the Ni : Ph_3Sb ratio used $Ni(Ph_3Sb)_3X$, $[Ni(Ph_3Sb)_4]BPh_4$, $[R_4N][Ni(Ph_3Sb)_2X_2]$ and unstable $\{Ni(Ph_3Sb)_2X\}_2$, were isolated. All are air-sensitive with magnetic moments of ca. 2.0–2.2 B.M. and with UV–visible spectra consistent with tetrahedral d^9 Ni(I) complexes. A number of Ph_3Sb derivatives of organonickel complexes have been briefly mentioned. These include $(\eta^5\text{-Cp})Ni(Ph_3Sb)X$ (X = Me or I) and $[(\eta^5\text{-Cp})Ni(Ph_3Sb)_2]^+$ [127,128]; $[Ni(\pi\text{-}C_3H_5)(Ph_3Sb)_2]PF_6$ [568]; $Ni(C_6F_5)_2(Ph_3Sb)_2$ [569,570]; $[Ni(C_6F_5)(Ph_3Sb)_2Br]$ [570]; $Ni(CH_2{=}CHCHO)_2(Ph_3Sb)_2$ and $Ni(PhCH{=}CHCN)_2(Ph_3Sb)_2$ [571].

In contrast to the chemistry of earlier platinum metals, carbonyl complexes of palladium and platinum are not widespread, and no stibine-substituted examples of zero-valent metals seem to have been reported. The cluster $(PPh_3)(Ph_3Sb)PtFe_2(CO)_8$ has the carbonyl groups on the iron and the ER_3 ligands on the platinum [572]. Pale yellow $Pd(R_3Sb)_4$ (R = Ph, p-MeC_6H_4, p-$MeOC_6H_4$) were made by $EtOAlEt_2$ reduction of $Pd(acac)_2$ in the presence of R_3Sb [563]. The $Pd(Ph_3Sb)_4$ has also been produced by displacement of the organic ligands from Pd(COD)(acac) [573] but early reports of $Pd(Ph_3Sb)_n$ ($n = 2$ or 3) [574] have not been confirmed. Mixed-ligand complexes such as $Pd(Ph_3P)_2(Ph_3Sb)_2$ [563,575], $Pd\{Ph_2(p\text{-}FC_6H_4)P\}_2(Ph_3Sb)_2$ [576], and $Pd(AsPh_3)_3(Ph_3Sb)$ [575], have been made by reaction of $Pd(ER_3)_4$ (E = P or As) or Pd(fumaronitrile)$(PPh_3)_2$ with Ph_3Sb. All attempts to make $Pt(Ph_3Sb)_4$ have failed, although $Pt(PPh_3)_2(Ph_3Sb)_2$ was made from $Pt(PPh_3)_3$ and Ph_3Sb [563], and $Pt\{{}^tBu(Me_3Si)NPN{}^tBu\}(Ph_3Sb)_2$ similarly from $Pt\{{}^tBu(Me_3Si)NPN{}^tBu\}_3$ [577]. The claimed [578] $Pt(Ph_3Sb)_n$ ($n = 2$ or 3) and $\{Pt(Ph_3Sb)_2\}_n(N_2)$ made by $NaBH_4$ reduction of $Pt(Ph_3Sb)_2Cl_2$ are incompletely characterised. The evidence presented does not rule out cyclometallated or fragmented ligands.

Palladium(I) complexes are rare, but include $Pd_2(Ph_3Sb)_2(CO)X_2$ (X = Cl, $MeCO_2$) [579], and the diphosphine bridged $[(Ph_3Sb)Pd(\mu\text{-}Ph_2PCH_2PPh_2)_2Pd(C_6Cl_5)]BPh_4$ (**25**) [580]. A Pd/Pt analogue of the latter, $[(Ph_3Sb)Pd(\mu\text{-}Ph_2PCH_2PPh_2)_2Pt(C_6F_5)]BPh_4$, is also known [581].



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Palladium halide triphenylstibine complexes $PdX_2(Ph_3Sb)_2$ (X = Cl, Br or I) have been prepared by reaction of the ligand with PdX_2 or PdX_4^{2-} [138,142,143,610]. The complex $PdCl_2(Ph_3Sb)_2$ has also been obtained by melting together $PdCl_2$ and the ligand [611]. The complexes have usually been assigned cis planar structures, although the iodide was considered to be weakly associated via I bridges in the solid state [136,143]. However, the ^{121}Sb Mössbauer data [149] suggested that the solid complexes were trans isomers, and this was subsequently confirmed for $PdI_2(Ph_3Sb)_2$ by an X-ray study [612] (Fig. 18). For the platinum analogues, the assignment of cis geometry is consistent with the vibrational and Mössbauer (^{121}Sb and ^{127}I) spectra [137,149,613]. Palladium complexes $Pd(R_3Sb)_2X_2$ (R = *p*-MeC_6H_4, *m*-MeC_6H_4, or *o*-MeC_6H_4) have been described [137,614]; the tris(*o*-tolyl)stibine complexes are trans isomers but the geometry of the others is less clear, although, like the Ph_3Sb,

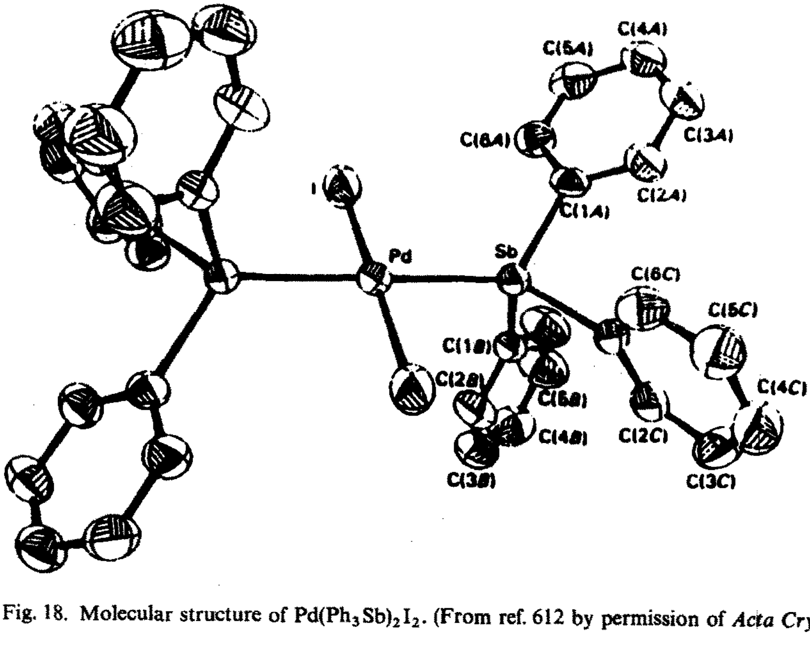


Fig. 18. Molecular structure of $Pd(Ph_3Sb)_2I_2$. (From ref. 612 by permission of *Acta Crystallographica*.)

they may be trans. Triphenylstibine has been investigated as a possible reagent for solvent extraction of palladium [615]. For the platinum complexes, the bulky tris(*o*-tolyl)stibine is likely to favour trans geometry, but the smaller ligands may produce cis isomers in the solid state. Halide-bridged $Pd_2X_4(R_3Sb)_2$ (X = Cl, Br or I; R = *o*-, *m*-, or *p*-MeC_6H_4) have been prepared [614], but are much less stable than the phosphine or arsine analogues. The complex $[Pt_2Cl_2(Ph_3Sb)_4][BF_4]_2$ was made from *cis*-$PtCl_2(Ph_3Sb)_2$ and $AgClO_4$, and the chlorine bridges were cleaved by CO to form *trans*-$[Pt(CO)Cl(Ph_3Sb)_2]BF_4$ [154].

Pseudo-halide complexes have attracted considerable attention, but whilst the linkage mode of the pseudo-halide has usually been established by vibrational spectroscopy, the geometric isomers present are not always clear. Examples include the isocyanates $M(Ph_3Sb)_2(NCO)_2$ prepared from the corresponding chlorocomplexes and AgNCO [616], and the nitro complexes $M(R_3Sb)_2(NO_2)_2$ (R = Ph, *o*-, *m*-, *p*-MeC_6H_4) which may have cis geometries except for those of the bulky (*o*-$MeC_6H_4)_3Sb$ [137,614,617]. Thiocyanate complexes have attracted most study [137,149,614,618–620], and with the exception of $Pt\{(o\text{-}MeC_6H_4)_3Sb\}_2(NCS)(SCN)$, all contain thiocyanato ligands in the solid state. In solution, complex solvent-dependent equilibria sometimes involving thiocyanate-bridged species are present [137].

A tetrakis(stibine) complex $[Pt(Ph_3Sb)_4](NO_3)_2$ has been made by treatment of a mixture of $Pt(Ph_3Sb)_2Cl_2$ and Ph_3Sb with $AgNO_3$, and appears to be five-coordinate in solution [621]. The palladium analogue $[Pd(Ph_3Sb)_4]^{2+}$ has been obtained from palladium perchlorate and the ligand in tetrahydrofuran [622], or from $Pd\{CF_3C(O)CHC(O)CCF_3\}_2$ and Ph_3Sb, followed by treatment with PF_6^- [623]. Palladium perchlorate and Ph_3Sb in MeCN were reported to form $[Pd(Ph_3Sb)_3](ClO_4)_2$ [622], but the possibility that the product was $[Pd(Ph_3Sb)_3(MeCN)](ClO_4)_2$ was not apparently considered.

A series of platinum diaryls $Pt(Ph_3Sb)_2R_2$ (R = Ph, *p*-MeC_6H_4, *m*-MeC_6H_4, *o*-MeC_6H_4) and $Pt(Ph_3Sb)_2Me_2$ have been prepared by displacement of COD from $Pt(COD)R_2$ by Ph_3Sb [624]. The cream products are rather less reactive than the phosphine analogues. Several series of Pd and Pt complexes of C_6F_5 or C_6Cl_5 have been obtained [625–631], including *cis*-$M(C_6X'_5)_2(Ph_3Sb)_2$, *cis*-$[Pt(C_6H_5)_2Cl(Ph_3Sb)]^-$, $[Pt(C_6X'_5)_3(Ph_3Sb)]^-$, $[Pt(C_6Cl_5)Cl_2(Ph_3Sb)]^-$, $[Pd(C_6X'_5)Br_2(Ph_3Sb)]^-$, and the halide-bridged $[Pd_2(\mu\text{-}X)_2(C_6X'_5)_2(Ph_3Sb)_2]$ (X = Cl or Br; X′ = F or Cl). Palladium and platinum have considerably less affinity for η-Cp ligands than other platinum metals, but $[Pd(\eta^5\text{-}Cp)(Ph_3Sb)_2]PF_6$ has been obtained from $[Pd(Me_2CO)_2(Ph_3Sb)_2][PF_6]_2$ and C_5H_6 [632]. The unstable blue complex has been characterised by a single-crystal X-ray study which revealed the "two-legged piano-stool" geometry (Fig. 19). Other complexes are listed in Table 6.

The appearance of black decomposition products in the reactions of Ph_3Sb with noble metals is a familiar observation to all workers in the area, but in very few cases have the reactions been explored. When Ph_3Sb was refluxed with

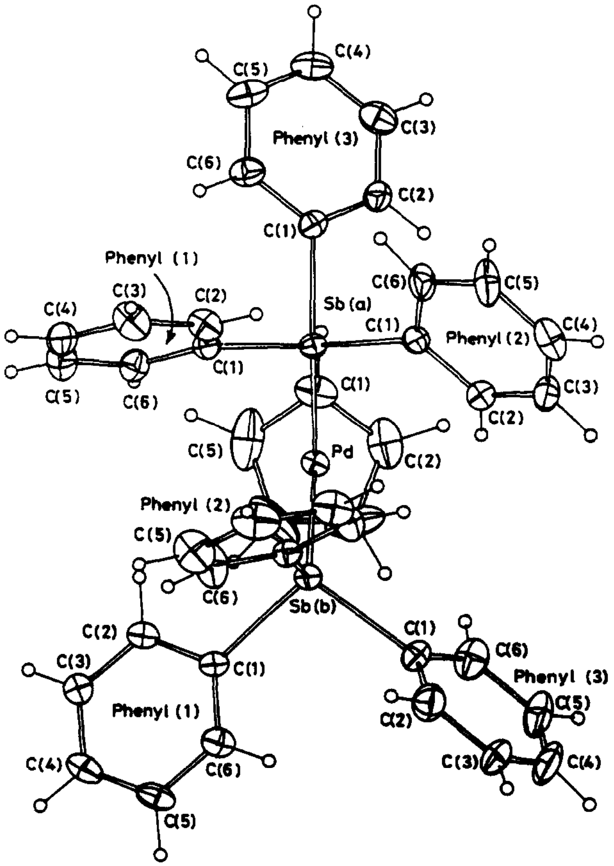


Fig. 19. Molecular structure of the cation $[Pd(\eta^5\text{-}Cp)(Ph_3Sb)_2]^+$. (From ref. 632 by permission of the Royal Society of Chemistry.)

$Pd(MeCO_2)_2$ in toluene, the organic products included phenyl acetate, biphenyl, and some benzene, all of which must originate from the stibine [633]. A more detailed study by Barton et al. [634] found that $Pd(MeCO_2)_2$ and Ph_3Sb reacted in $CHCl_3$ to form the dinculear complex shown in Fig. 20. Heating this complex in $CHCl_3$ to 60°C gave biphenyl (96%) along with a black deposit, presumably elemental Pd and Sb. At lower temperatures (45°C), a trinuclear complex (**26**) (Fig. 21) was formed which contained coordinated Ph groups.

4.3.7 Groups 11 and 12

The only copper(II) complex is the brown cluster $Cu_4OCl_6(Ph_3Sb)_2 \cdot Et_2O$, prepared by substitution of the methanol in $Cu_4OCl_6(MeOH)_4$ by Ph_3Sb in diethyl ether solution [635]. The product is less stable than the phosphine analogues and is very easily reduced to Cu(I).

TABLE 6

Palladium(II) and platinum(II) arylstibine complexes

Complex	Ref.
$[PtH(PEt_3)_2(Ph_3Sb)]ClO_4$	582
$[PtH(PCy_3)_2(Ph_3Sb)]PF_6$	583
$[PtH(PBz_3)_2(Ph_3Sb)]BPh_4$ (Bz = benzyl)	584
$[PtH(Ph_2PCH_2CH_2PPh_2)(Ph_3Sb)]^+$	585
$[PtH(PPh_3)_2(Ph_3Sb)]^+$	586
$[Pt(NH_3)_2(Ph_3Sb)Cl]^+$	587
cis-$Pt(PEt_3)(Ph_3Sb)Cl_2$	588
$[PtMe(L{-}L)(Ph_3Sb)]ClO_4$ ($L{-}L = Ph_2PN(R)PPh_2$, diop, chiraphos)	589
$[M(Ph_2PCH_2CH_2P(CHCOPh)Ph_2)(Ph_3Sb)Cl]^+$ (M = Pd or Pt)	590
$Pt(S_2PPh_2)_2(Ph_3Sb)$	591
$Pd(S_2CNR_2)Cl(Ph_3Sb)$	592
$Pd(SOCPh)_2(Ph_3Sb)_2$	593
$Pd\{2,4,6\text{-}(NO_2)_3{-}C_6H_2\}Cl(Ph_3Sb)_2$	594
$PtMe(Ph_2PCH_2CH_2PPh_2)(Ph_3Sb)$	595
cis-$Pt(CF_3)_2(Ph_3Sb)_2$	596
trans-$Pt(CF_3)(PMe_2Ph)(Ph_3Sb)$	597
$Pt(p\text{-}MeC_6H_4)Cl(PEt_3)(Ph_3Sb)$	598
$Pt(C_6H_4OCH_2)(Ph_3Sb)_2$	599
$PtPh_2(Ph_3Sb)_2$	599
$Pt(COMe)(PPh_3)I(Ph_3Sb)$	600
$Pt(acac)Cl(Ph_3Sb)$	601
$Pd(\pi\text{-}2\text{-}Me\text{-}allyl)Cl(Ph_3Sb)$	602
$Pd(\eta^3\text{-}H_2CC(Me)CHCH_2X)Cl(Ph_3Sb)$ (X = OMe or OCOMe)	603
$Pd(\eta^3\text{-}allyl)X(Ph_3Sb)$ (X = Cl or Br)	604
$Pd\{o\text{-}C_6H_4C(Me){=}NNPhH\}X(Ph_3Sb)$ (X = Cl or Br)	605
$Pt\{OC_6H_4CH{=}NCH_2CH_2O\}(Ph_3Sb)$	606
$Pt\{OC_6H_4CH{=}NC_6H_4O\}(Ph_3Sb)$	606
$Pt(^tBu_2PCMe_2CH_2)(SnCl_3)(Ph_3Sb)$	607
$[Pd(C_6F_5)(AsPh_3)_2(Ph_3Sb)]ClO_4$	608
$Pd_2(\mu\text{-}4,4'\text{-}bipyridyl)Cl_2(C_6Cl_5)_2(Ph_3Sb)_2$	609
$Pd(R_3Sb)LX_2$ ($R = o$-, m- or $p\text{-}MeC_6H_4$; L = py, NH_3 or PPh_3)	614

Copper(I) halide complexes have been prepared by reaction of Ph_3Sb with CuX_2 (X = Cl or Br) in ROH, with aqueous $KCuX_2$, with CuX (X = Cl, Br or I) in chlorocarbons, or even by melting together the ligand and CuCl [611,636,637]. Complexes of stoichiometry $CuCl(Ph_3Sb)_2$, $Cu_2X_2(Ph_3Sb)_3$ (X = Cl or I),

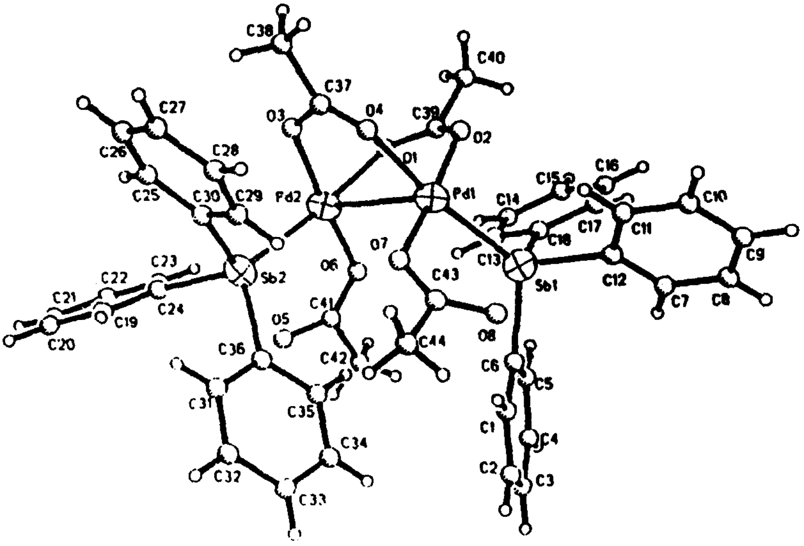
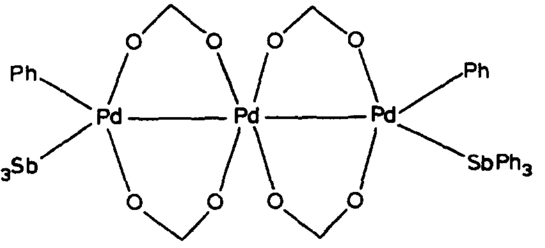


Fig. 20. Molecular structure of $Pd_2(MeCO_2)_4(Ph_3Sb)_2$. (From ref. 634 by permission of Pergamon Press Ltd.)



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$CuBr(Ph_3Sb)_2$, and $CuCl(Ph_3Sb)_3$ have been described. Complexes with 1 : 1 and (rarely) 1 : 2 Cu : L ratios have been reported with bulky stibines R_3Sb ($R = o$-MeC_6H_4, p-MeC_6H_4, 3,5-$Me_2C_6H_3$, 2,4-$Me_2C_6H_3$, and 2,5-$Me_2C_6H_3$) [638]. The structures of group 11 complexes are notoriously difficult to establish by spectroscopic studies and solution measurements often do not indicate the constitution of the solid due to the lability of the d^{10} metal centres. Unfortunately, only one X-ray study has been reported, of the complex $CuCl(Ph_3Sb)_3 \cdot CHCl_3$ [639], which revealed a distorted tetrahedral geometry (Fig. 22).

Other 1 : 3 complexes in which the anion appears to bond to the copper are $Cu(NO_3)(Ph_3Sb)_3$ [640,641] and $Cu(Ph_3Sb)_3(B_3H_8)$ [642].

The tetrakis(stibine) complexes $[Cu(Ph_3Sb)_4]Y$ ($Y = ClO_4$ or BF_4) were made from $[Cu(MeCN)_4]^+$ and the ligand, and the cation retained the tetrahedral structure in solution since it easily gave a ^{63}Cu NMR resonance [162,637,643]. A recent

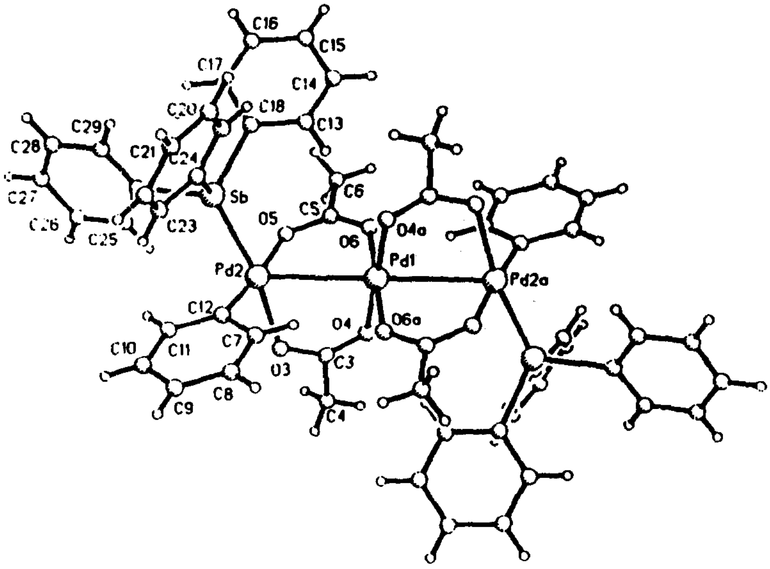


Fig. 21. Molecular structure of $Pd_3(MeCO_2)_4Ph_2(Ph_3Sb)_2$. (From ref. 634 by permission of Pergamon Press Ltd.)

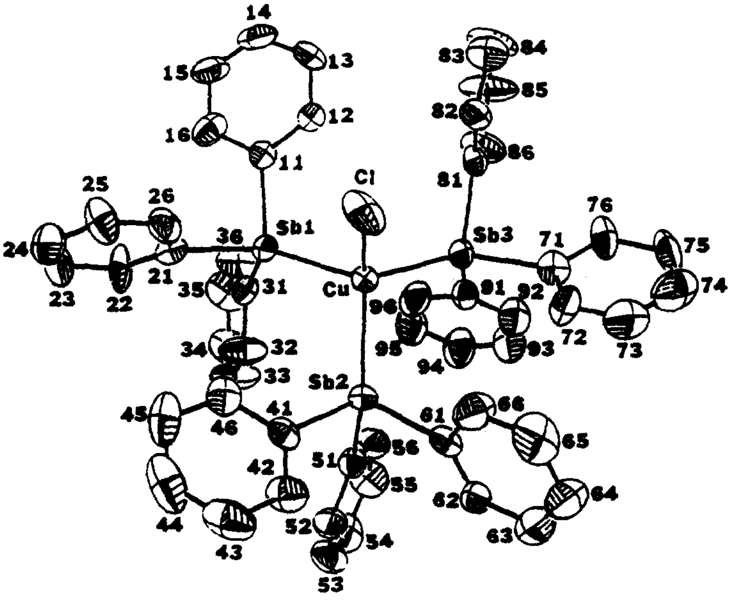


Fig. 22. Molecular structure of $CuCl(Ph_3Sb)_3$. (From ref. 639 by permission of Plenum Publishing Corporation.)

detailed study of $[Cu(R_3Sb)_4]Y$ ($Y = BF_4$ or ClO_4) used $(p\text{-}RC_6H_4)_3Sb$ with R groups that confer either electron donating (Me) or withdrawing (F) power [644]. Corresponding arsines also favoured the formation of complexes with Cu : L ratios of 1 : 4 but the phosphines usually preferred 1 : 3 stoichiometry. The structure of $[Cu\{(p\text{-}FC_6H_4)_3Sb\}_4]BF_4$ was determined and revealed the core to have a distorted (C_3) tetrahedral geometry (Fig. 23) [644].

Silver complexes of triarylstibines have not been much studied. Two papers report the formation of complexes in solution [645,646], but isolated complexes seem to be limited to $Ag(Ph_3Sb)_2(NCS)$ [647], $Ag(Ph_3Sb)$\{tris(pyrazolyl)borate\} [648], $Ag(Ph_3Sb)_3(MeCO_2)$ [649], $Ag\{(p\text{-}FC_6H_4)_3Sb\}_3Y$ and $[Ag(R_3Sb)_4]Y$ (R = Ph, $p\text{-}MeC_6H_4$; $Y = BF_4$, ClO_4) [644,650]. In the bimetallic anion $[PtAgCl_2(C_6Cl_5)_2(Ph_3Sb)]^-$, the stibine is coordinated to the silver [651].

The thermodynamics of the reaction of gold(I) perchlorate with Ph_3Sb in solution showed that the Au–Sb interaction was stronger than the Ag–Sb [652]. A kinetic study of the reaction of $[AuCl_4]^-$ with Ph_3Sb to form $AuCl(Ph_3Sb)$ and Ph_3SbCl_2 found no evidence for a Au(III)–stibine intermediate [653]. The $AuCl(Ph_3Sb)$ has been made from $[AuCl_4]^-$ and excess ligand [654], or by prior reduction of the gold to Au(I) with SO_2 followed by addition of Ph_3Sb [655]. Related 1 : 1 complexes $AuCl(R_3Sb)$ with $R = p\text{-}MeC_6H_4$, $m\text{-}MeC_6H_4$, $o\text{-}MeC_6H_4$, $2,4\text{-}Me_2C_6H_3$ and $2,5\text{-}Me_2C_6H_3$ have been reported, and metathesis with KI, LiBr or KNCS gave the corresponding $AuX(R_3Sb)$ [655,656]. Complexes with a 1 : 2 Au : L ratio are rarer but include $AuCl(Ph_3Sb)_2$ [657] and $AuBr\{(m\text{-}MeC_6H_4)_3Sb\}_2$ [655]. The reaction of $AuCl(Ph_3Sb)$ with $NaMn(CO)_5$

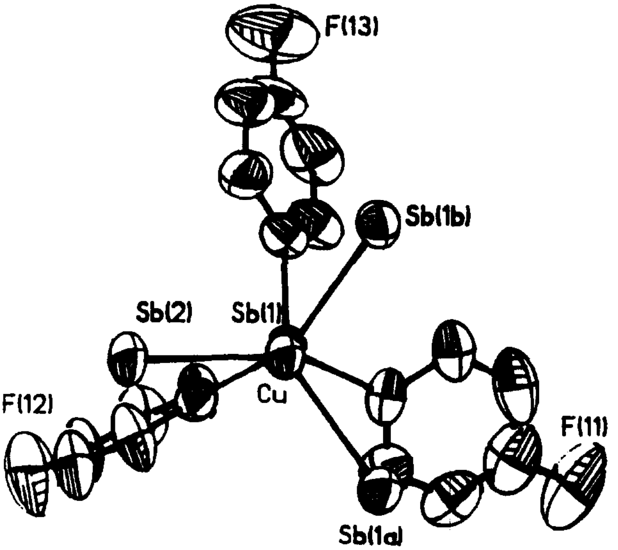


Fig. 23. Molecular structure of $[Cu\{(p\text{-}FC_6H_4)_3Sb\}_4]^+$. (From ref. 644 by permission of the American Chemical Society.)

afforded the metal–metal bonded $(Ph_3Sb)AuMn(CO)_5$ which is much less stable than the better known PPh_3 analogue [658,659].

The best-known Ph_3Sb complex of Au(I) is the white $[Au(Ph_3Sb)_4]ClO_4$, obtained by treatment of $[Au(tht)_4]ClO_4$ (tht = tetrahydrothiophene) with Ph_3Sb [660]; this complex has an almost exactly tetrahedral cation (Fig. 24) [661]. The same cation (as the $[AuR_2]^-$ salt) was formed by treatment of Au(tht)R (R = C_6F_5, C_6Cl_5, 4,4′-$C_6F_4C_6F_4H$, Ph, o-$C_6H_4NO_2$, 2,4,6-$C_6H_2(NO_2)_3$) with Ph_3Sb [662–667]. In the cases of o-$C_6H_4NO_2$, C_6Cl_5 and C_6F_5, the species behaved in solution as though they were in equilibrium with $AuR(Ph_3Sb)_2$. The X-ray structures of $[Au(Ph_3Sb)_4][AuPh_2]$ and $[Au(Ph_3Sb)_4][Au\{2,4,6\text{-}C_6H_2(NO_2)_3\}_2]$ have also been reported [662,663]. The ^{197}Au Mössbauer spectrum has been reported for $[Au(Ph_3Sb)_4][Au(C_6F_5)_2]$ [668].

No gold(III) halide complexes have been isolated since Au(III) is reduced to Au(I) by R_3Sb, but several organogold(III) adducts have been characterised. The unstable *cis*-$[Me_2Au(Ph_3Sb)_2][CF_3SO_3]$ was formed by reaction of Me_2AuI, Ph_3Sb and $AgCF_3SO_3$ in tetrahydrofuran [669]. White $Au(Ph_3Sb)(2,4,6\text{-}C_6F_3H_2)_3$ [670] and $Au(Ph_3Sb)(C_6F_5)_3$ [671] are also known.

No complexes with zinc or cadmium have been reported, and the data on mercury complexes are limited. Complexes of $HgCl_2(R_3Sb)$ stoichiometry (R = Ph, 2,4-$Me_2C_6H_3$, o-$MeOC_6H_4$, m-$MeOC_6H_4$, p-phenetyl, p-phenoxyphenyl) were reported many years ago [17,672]. Similar 1 : 1 complexes which were formulated as $(R_3Sb)XHg(\mu\text{-}X)_2HgX(R_3Sb)$ (R = Ph, o-MeC_6H_4, p-MeC_6H_5, m-MeC_6H_4,

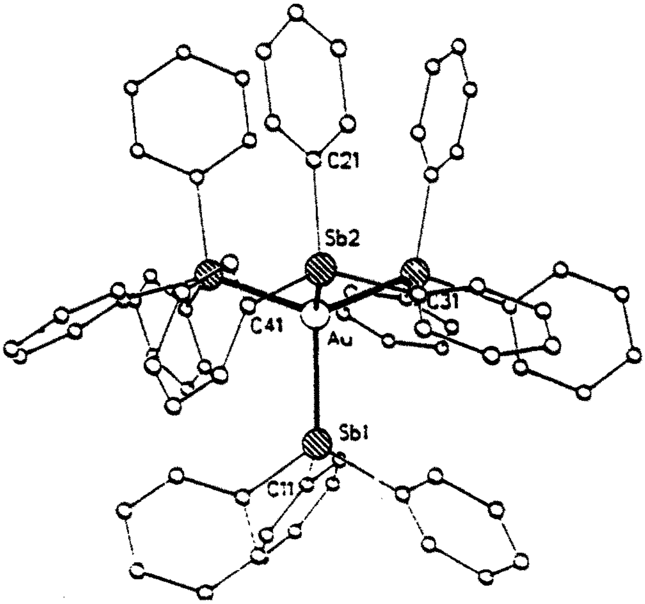
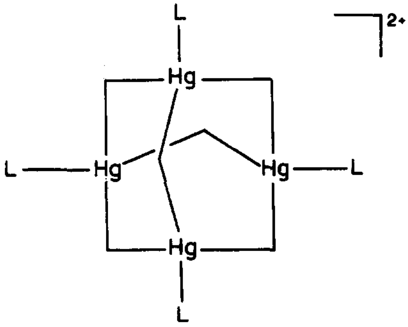


Fig. 24. Molecular structure of $[Au(Ph_3Sb)_4]^+$. (From ref. 661 by permission of *Acta Crystallographica*.)

2,4-$Me_2C_6H_3$, 2,5-$Me_2C_6H_3$, 3,4-$Me_2C_6H_3$; X = Cl, Br or I) have been obtained by mixing the constituents in benzene or ethanol [673–675]. Triphenylstibine was also said to form $HgX_2(Ph_3Sb)_2$-type complexes, which are presumably tetrahedral monomers [674], and the three tri(tolyl)stibines form materials of stoichiometry $(HgX_2)_3(R_3Sb)_2$ of uncertain structure [673]. Under reflux in benzene, $HgCl_2$ and $(o\text{-}MeC_6H_4)_3Sb$ formed Hg_2Cl_2 and Ph_3SbCl_2 [673]. Mercury(II) thiocyanate formed a 1 : 1 complex with Ph_3Sb, which is probably dimeric [676]. The reaction of $[Hg(PPh_3)_2][ClO_4]_2$, $Hg(SPh)_2$ and Ph_3Sb gave the cluster $[(\mu\text{-SPh})_6(HgPPh_3)_{4-n}(HgPh_3Sb)_n]^{2+}$ ($n = 0$–2), which had the structure (**27**) with an adamantane-like core [677]. The $[(\mu\text{-SPh})_6(HgPh_3Sb)_4]^{2+}$ has not been isolated.



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4.3.8 Other complexes

The chemistry of main group element adducts of Ph_3Sb is very limited. In a number of cases, including $SbCl_3$, $SbCl_5$, $TlCl_3$ and $BiCl_3$, the reaction led to scrambling of the substituents to form $Ph_{3-n}SbCl_n$ or to oxidation to Ph_3SbCl_2 [5]. Triorganotin(IV) chlorides R_3SnCl (R = Me, Et, Ph or ^{n}Bu) were reported to form 1 : 1 adducts on mixing the constituents in benzene, and were characterised by ^{119}Sn Mössbauer spectroscopy [678]. The reaction of $SnCl_4$ or $SnBr_4$ with Ph_3Sb in pentane gave unstable yellow solids, which on the basis of their Mössbauer spectra contained Sn(IV), but which on washing with pentane decomposed to white materials of composition $SnSbPh_3X_4$ [679]. Mössbauer spectroscopy indicated that the latter contained Sn(II) and hence were probably mixtures of SnX_2 and Ph_3SbX_2. This behaviour contrasts with the isolation of SnX_4L_2 adducts with several phosphine and arsine ligands [679]. The only complex of a group 13 metal seems to be $InMe_3(Ph_3Sb)$ reported in a patent [680].

5. BISMUTHINE COMPLEXES

The coordination chemistry of bismuthine ligands is extremely limited. This is a reflection of the limited commercial availability of bismuthine ligands (Sect. 2), the weakness of the Bi—C bond, and the poor donor ability of the Bi atom. Formation of bismuthine complexes is often inhibited by the tendency of the Bi—C bond to cleave upon reaction with a transition metal centre.

5.1 Groups 3–5

Bismuthine complexes have been reported for group 5 elements vanadium and niobium. The vanadium carbonyl complexes $[Et_4N][V(CO)_5(BiEt_3)]$, $(\eta^5\text{-}Cp)V(CO)_{4-n}(BiEt_3)_n$ ($n = 1$ or 2) were reported as the products of photo-induced carbonyl substitution from $[Et_4N][V(CO)_6]$ or $(\eta^5\text{-}Cp)V(CO)_4$ in THF. Interestingly, the disubstituted product *cis*-$(\eta^5\text{-}Cp)V(CO)_2(BiEt_3)_2$ was formed in addition to $(\eta^5\text{-}Cp)V(CO)_3(BiEt_3)$, in contrast to the reactions of phosphines, arsines and even stibines which form only the monosubstituted complex [77]. The reaction between $VOCl_2$ and Bi^nBu_3 is reported to fail [76].

Niobium pentachloride reacted with $BiPh_3$ to give orange $NbCl_5(BiPh_3)$ in CCl_4, *n*-hexane and cyclohexane, and red $NbCl_5(BiPh_3)_2$ in benzene [187]. Evidence for these products consists of elemental analysis only.

5.2 Group 6

As with the stibines, a relatively large number of studies have been reported for group 6 carbonyl species. Bismuthine compounds are often mentioned in large studies as one-off examples, though a few investigations have focussed on bismuthine complexes alone.

The complexes $M(CO)_{6-n}(BiR_3)_n$ (M = Cr, Mo, W, R = Ph, $^nBu_3$, $n = 1$; M = Mo, R = Et, $n = 1$ or 2) have been prepared as orange or yellow solids, and their IR spectra included in a study of carbonyl stretching frequencies [80,82,208,681,682]. The $W(CO)_5(BiPh_3)$ was prepared during a study of the displacement of the amine from $W(CO)_5(PhNH_2)$ by group 15 ligands, which concluded that the basicity of $BiPh_3$ was less than that of $SbPh_3$, and that this resulted in a weak W—Bi bond [208]. The unusual ligands $Bi\{M(CH_3)_3\}_3$ (M = C, Ge or Sn) have coordinated to group 6 elements in the complexes $M(CO)_5Bi\{M(CH_3)_3\}_3$ [62].

The X-ray crystal structure of $Cr(CO)_5(BiPh_3)$ [205] shows the Cr—Bi bond length to be 2.705(1) Å.

The carbene $Cr(CO)_5\{C(OCH_3)CH_3\}$ has been reacted both photochemically and thermally with BiR_3 (R = Me, Et, Cy) to give only $Cr(CO)_5(BiR_3)$ compounds. This is in contrast to the reactions observed for stibines and arsines where the products are *cis*- and *trans*-$Cr(CO)_4(ER_3)\{C(OCH_3)CH_3\}$ through loss of a carbonyl group [91].

The black compound $Mo(CO)_3(phen)(BiPh_3)$ was prepared from $Mo(CO)_4(phen)$ and $BiPh_3$ [216]. The range of compounds $MI_2(CO)_3(BiPh_3)_2$, $MI_2(CO)_3(NCMe)(BiPh_3)$, $MI_2(CO)_3\{P(OPh)_3\}(BiPh_3)$ (M = Mo or W),

$[Mo(\mu\text{-}I)I(CO)_3(BiPh_3)]_2$, $MoI_2(CO)_3(AsPh_3)(BiPh_3)$ and $[WI_2(CO)_3(PPh_3)(BiPh_3)]$ have been prepared by similar routes to the stibine analogues from $MI_2(CO)_3(MeCN)_2$ [683].

The cyclopentadienyl complex $[(\eta^5\text{-Cp})Mo(CO)_2(BiPh_3)_2]BF_4$ has been prepared from $[(\eta^5\text{-Cp})Mo(CO)_3]_2$ in *o*-dichlorobenzene, in the presence of both the ferricenium ion and light. ^{13}C NMR and IR data were reported for the complex, but attempts to record the ^{95}Mo NMR failed due to rapid decomposition and poor solubility of the compound [684].

In contrast to $SbPh_3$, which yielded *fac*-$Cr(CO)_3(SbPh_3)_3$ as well as mono- and di-substituted species on reaction with $Cr(CO)_3(NH_3)_3$, $BiPh_3$ was reported to coordinate to the chromium centre through the ligands' phenyl rings rather than through the bismuth atom, forming $\{Cr(CO)_3(Ph)\}_{3-n}BiPh_n$ ($n = 0$, 1 or 2) [195].

5.3 *Group 7*

The monosubstituted species $(\eta^5\text{-Cp})Mn(CO)_2(BiPh_3)$ has been prepared photochemically, but in contrast to the analogous reactions with stibines, phosphines and arsines no disubstituted complex was formed [266]. The complex $[(\eta^5\text{-Cp})Mn(CO)_2(NO)]PF_6$ did not react with $BiPh_3$ upon reflux in MeOH, in the absence of UV irradiation [285].

5.4 *Group 8*

The bismuthine chemistry with the iron sub-group is limited to carbonyl chemistry of iron. Iron(III) chloride reacted with $BiPh_3$ in refluxing $CHCl_3$ to give $BiCl_3$ and benzene [685]. Ironically, the first report of an iron bismuthine complex was of $Fe(CO)_4(BiPh_3)_2$, a 20e system, which has not been confirmed by more recent work [686]. Subsequently, the monosubstituted species $Fe(CO)_4(BiR_3)$, stable in inert atmospheres, were isolated from the reaction of $Fe_2(CO)_9$ with BiR_3 (R = Me, Pr, Bu) [682].

Other organometallic complexes of the form $[(\eta^5\text{-Cp})Fe(CO)_2(BiR_3)]^+$ {R = Me, ^{i}Pr, Ph} are products of the reaction between $[(\eta^5\text{-Cp})Fe(CO)_2(THF)]^+$ and the ligand [108,349]. Oddly, the $BiEt_3$ complex could not be isolated with the reaction yielding carbonyl free products. The X-ray crystal structure [106] of $[(\eta^5\text{-Cp})Fe(CO)_2(BiPh_3)]^+$ (Fig. 25) shows an Fe—Bi bond length of 2.570(1) Å.

5.5 *Group 9*

The only example of a cobalt bismuthine complex is the possibly square-pyramidal dark red $Co(sacsac)_2(BiPh_3)$, prepared by stirring $Co(sacsac)_2$ and $BiPh_3$ in dry, deoxygenated benzene [464].

The rhodium complex $\{(MeO)_3P\}Rh(O_2CCH_3)_4Rh(BiPh_3)$ has been prepared

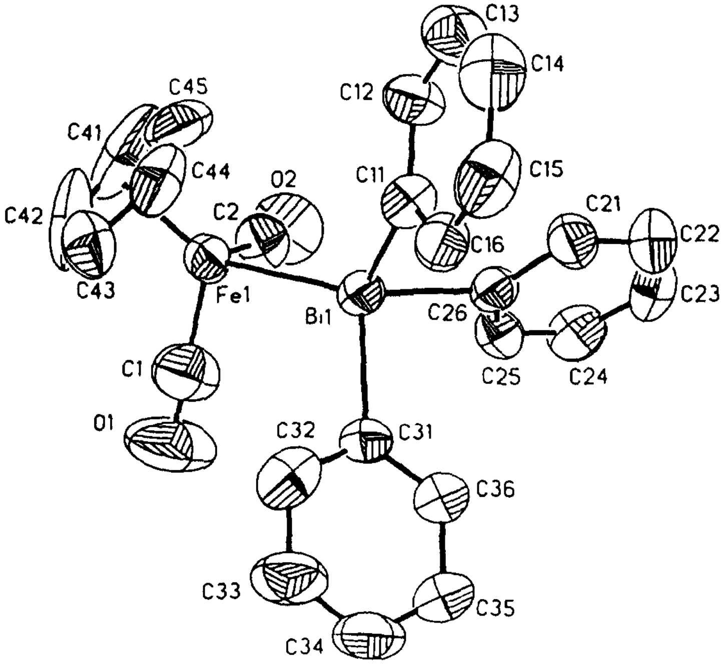


Fig. 25. Molecular structure of $[(\eta^5\text{-Cp})Fe(CO)_2(Ph_3Bi)]^+$. (From ref. 1086 by permission of Elsevier Sequoia S.A.)

by mixing $\{(MeO)_3P\}_2Rh_2(O_2CCH_3)_4$, $Rh_2(O_2CCH_3)_4$ and $BiPh_3$ in CD_2Cl_2 for an in situ NMR (^{31}P, ^1H, ^{13}C and ^{103}Rh) spectroscopic study of the trans effect of the bismuthine ligand [531].

The cation $[Rh(COD)(BiPh_3)]^+$ is a catalyst for the hydroformylation of 1-heptene [687]. There is a greater selectivity toward *n*-octanal formation with $[Rh(COD)(EPh_3)]^+$ (E = N, P, As) than for the $BiPh_3$ and $SbPh_3$ complexes.

The only iridium complex, $[Ir(PPh_3)_2(CO)(BiPh_3)]ClO_4$, was prepared by displacement of the perchlorato ligand from *trans*-$[Ir(OClO_3)(CO)(PPh_3)_2]$ with $BiPh_3$ [522].

5.6 Group 10

The chemistry of nickel bismuthine compounds is limited to carbonyl complexes of the form $Ni(CO)_3(BiR_3)$ (R = Me, Et, ^{n}Bu, Ph, CMe_3, $GeMe_3$, $SnMe_3$), prepared by reaction of $Ni(CO)_4$ with the ligand in a hydrocarbon [62,80,126].

No complexes of bismuthines with platinum or palladium have been reported. Attempts to prepare platinum dimers $Pt_2Cl_4(BiR_3)_2$, by reacting $[Pt(C_2H_4)Cl_2]_2$ with Bi^nPr_3 were unsuccessful, in contrast to the analogous stibine complexes [150]. $Pd(OAc)_2$ and $Ni(COD)_2$ convert $BiPh_3$ quantitatively to diphenyl and metallic bismuth [688]. Analogous reactions were observed with Bi(p-MeOC$_6$H$_4$)$_3$, Bi(p-tolyl)$_3$ and Bi(β-phenylethyl)$_3$, giving the appropriate diaryl compound. Similarly, BiPh$_3$ reacts with acid chlorides in the presence of a Pd(0) catalyst, to give phenyl ketones.

5.7 Groups 11 and 12

Neither CuCl or CuI reacted with BiPh$_3$ in CHCl$_3$ at room temperature [637], and a thermodynamic study of the interaction between BiPh$_3$ and Cu(ClO$_4$)$_2$ in DMSO concluded that no reaction occurred [689], both observations being in contrast to the reactions of SbPh$_3$. A further thermodynamic study of the interaction between BiPh$_3$ and AgClO$_4$ in DMSO concluded that only a monosubstituted species, [Ag(BiPh$_3$)]$^+$, was formed in solution. This contrasts with the reactions of PPh$_3$, AsPh$_3$ and SbPh$_3$, which form mono-, di- and tri-substituted complexes in solution and the tetrakis complexes [Ag(EPh$_3$)$_4$]$^+$ (E = P, As, Sb) can be isolated as solids [646]. The only isolated silver bismuthine complex is Ag(BiPh$_3$)ClO$_4$ [650]. It is likely that the bismuthine is η^6-C$_6$H$_5$ bonded to the silver. No gold complexes with bismuthine ligands have been isolated and [Au(MeCN)$_2$]$^+$ is reduced to metallic gold by BiPh$_3$ [653].

5.8 Other complexes

The pale green U(V) dimer [U$_2$Cl$_9$(BiPh$_3$)]Cl has been isolated [690] and studied by ESR spectroscopy. The analogous arsine complex was also prepared but oddly no stibine has been reported.

Complexes formed with main group elements are also limited, with only [Tl(BiPh$_3$)]$^+$ being identified in the mass spectrum of the products of the reaction between Tl(CF$_3$COCHCOCF$_3$) and BiPh$_3$ [691]. GaMe$_3$ does not react with BiMe$_3$, in contrast to the 1 : 1 adduct formed with SbMe$_3$ [172].

However, most commonly BiPh$_3$ reacts with main group and many transition metal chlorides to form BiPh$_2$Cl and other decomposition products, for example TlCl$_3$ [692,693], TiCl$_4$ [693], PCl$_3$, AsCl$_3$ and SbCl$_3$ [693,694], CuCl$_2\cdot$H$_2$O [694] and HgCl$_2$ [694].

6. DISTIBINE COMPLEXES

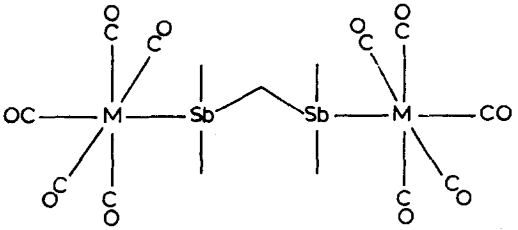
The coordination chemistry of distibine ligands has been investigated only in the last 20 years, and studies are limited to the work of a small number of research groups. The ligands used are of three types: distibinomethanes, R$_2$SbCH$_2$SbR$_2$, 1,3-distibinopropanes, R$_2$SbCH$_2$CH$_2$CH$_2$SbR$_2$, and 1,2-distibinobenzenes, o-C$_6$H$_4$(SbR$_2$)$_2$.

The distibinomethanes rarely chelate to metal centres, preferring to bond as monodentate or bridging bidentate ligands. This increasing reluctance to chelate continues the trend observed between $Ph_2PCH_2PPh_2$ and $Ph_2AsCH_2AsPh_2$, and is probably due to the increasing strain in the four-membered chelate ring as the donor atoms increase in size, and the effect will be reinforced by the reduced donor strength $P > As > Sb$. The distibinopropanes and *o*-distibinobenzenes usually chelate, like their analogues, with lighter donors.

6.1 Groups 3–6

Three vanadium carbonyl complexes of $Ph_2SbCH_2SbPh_2$ have been reported, all obtained as red oils [184]. Photolysis of (η^5-Cp)V(CO)$_4$ in THF in the presence of the ligand produced a mixture of (η^5-Cp)V(CO)$_3$($Ph_2SbCH_2SbPh_2$) and {(η^5-Cp)V(CO)$_3$}$_2$(μ-$Ph_2SbCH_2SbPh_2$), whilst a similar reaction using $[V(CO)_6]^-$ gave {V(CO)$_5$}$_2$(μ-$Ph_2SbCH_2SbPh_2$).

Group 6 carbonyl derivatives have been studied in some detail. On heating $M(CO)_6$ (M = Cr, Mo or W) with $Ph_2SbCH_2SbPh_2$, the products were the yellow $M(CO)_5(Ph_2SbCH_2SbPh_2)$ in which the distibine behaved as a monodentate ligand [695,696]. The chromium complex was also formed by reaction of $Cr(CO)_5CH_2S(O)Me$ with the ligand [697]. Very similar complexes were isolated with (p-MeC_6H_4)$_2$SbCH$_2$Sb(p-MeC_6H_4)$_2$ [696]. In contrast, $Me_2SbCH_2SbMe_2$ reacted with $Mo(CO)_6$ or $W(CO)_6$ to form the ligand-bridged dimers {M(CO)$_5$}$_2$(μ-$Me_2SbCH_2SbMe_2$) (**28**) [696]. Analogues are known with $Ph_2SbCH_2SbPh_2$, including both symmetrical species such as the chromium complex {Cr(CO)$_5$}$_2$(μ-$Ph_2SbCH_2SbPh_2$) and the mixed metal complexes $(CO)_5M(Ph_2SbCH_2SbPh_2)M'(CO)_5$ ($M \neq M'$ = Cr, Mo or W) made from $M(CO)_5(Ph_2SbCH_2SbPh_2)$ and $M'(CO)_5(THF)$ [698,700].



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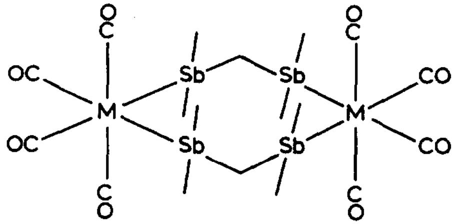
When bis(diphenylstibino)methane was heated with $M(CO)_6$ in methylcyclohexane for long periods, the products were *cis*-{M(CO)$_4$}$_2$(μ-$Ph_2SbCH_2SbPh_2$)$_2$ (**29**) [695]. These and the *p*-tolyl ligand analogues were better obtained from the ligand and $Cr(CO)_4(COD)$, $M(CO)_4$(norbornadiene) or $W(CO)_4$(diamine) [695,699]. In contrast, photolysis of mixtures of $M(CO)_6$ and the ligand in hexane for several days gave very poor yields of different products of stoichiometry $M(CO)_4(Ph_2SbCH_2SbPh_2)$ [695]. The molybdenum complex was monomeric in



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$CHCl_3$ and these complexes are rare examples of chelating bidentate behaviour by this ligand. For molybdenum alone, a tricarbonyl, $Mo(CO)_3(Ph_2SbCH_2SbPh_2)_2$, was formed by heating the dinuclear tetracarbonyl with more ligand, or better by displacement of the organic ligand from $Mo(CO)_3$(cycloheptatriene); this complex probably contains one monodentate and one chelating distibine [695].

In contrast, $Ph_2Sb(CH_2)_3SbPh_2$ and o-$C_6H_4(SbMe_2)_2$ behaved only as cis chelates in the white $M(CO)_4(L{-}L)$ complexes [42,699]. The reaction of $M(CO)_4X_2$ ($M = Mo$ or W; $X = Cl$, Br or I) with $Ph_2SbCH_2SbPh_2$, followed by recrystallisation of the mixture of products from CH_2Cl_2 saturated with CO, gave the yellow or orange $M(CO)_3(L{-}L)_2X_2$, except for the reaction with $Mo(CO)_4I_2$ which gave $Mo(CO)_3(L{-}L)I_2$ [701]. The former type are probably capped octahedral complexes with monodentate distibines, but the latter seems to contain a chelating distibine and be analogous to $Mo(CO)_3(Ph_2PCH_2CH_2PPh_2)Br_2$ which has been characterised by an X-ray study [702]. On heating the $M(CO)_3(Ph_2SbCH_2SbPh_2)_2X_2$ complexes in CH_2Cl_2, both CO and one ligand are lost to form the octahedral $M(CO)_2(Ph_2SbCH_2SbPh_2)X_2$ [701].

6.2 Groups 7 and 8

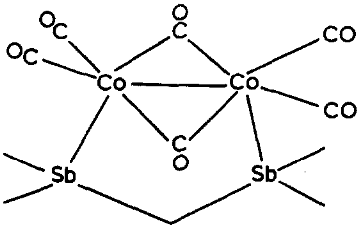
No complexes with group 7 metals have been isolated. Attempts to make manganese(II) complexes of o-$C_6H_4(SbMe_2)_2$ or $Me_2Sb(CH_2)_3SbMe_2$, even under rigorously anhydrous conditions, failed, although diarsine and arsine–stibine complexes are known (q.v.) [703].

Orange-red $Fe(CO)_4(Ph_2SbCH_2SbPh_2)$ was obtained by refluxing $Fe(CO)_5$ with the ligand, the IR spectrum suggesting the structure was an axially substituted trigonal bipyramid [696]. Bis(dimethylstibino)methane again behaved as a bridging ligand and formed the yellow complex $\{Fe(CO)_4\}_2(\mu\text{-}Me_2SbCH_2SbMe_2)$ where the antimony occupied axial positions bridging two trigonal bipyramidal iron centres [696]. No complexes with iron halides have been isolated, but $Ph_2SbCH_2SbPh_2$ and $Me_2Sb(CH_2)_3SbMe_2$ are chlorinated to form the appropriate $R_2Cl_2Sb(CH_2)_nSbR_2Cl_2$ on heating with $FeCl_3$ in CH_2Cl_2 [704]. A complex

$RuCl_3(NO)\{Ph_2Sb(CH_2)_3SbPh_2\}$ has been mentioned [705], but few details were given.

6.3 Group 9

Dicobalt octacarbonyl reacted with $R_2SbCH_2SbR_2$ (R = Me, Et, Ph, p-MeC_6H_4) to form the red $Co_2(CO)_6(R_2SbCH_2SbR_2)$, which were assigned structure (**30**) [706]. The distibines were easily displaced by $Ph_2PCH_2PPh_2$ or $Ph_2AsCH_2AsPh_2$, and treatment with RC≡CR replaced the bridging carbonyl groups to form $Co_2(CO)_4(RC{\equiv}CR)(R_2SbCH_2SbR_2)$ [706]. Cobalt(II) complexes have not been characterised, but air-oxidation of a mixture of CoX_2 (X = Cl, Br or I) and o-$C_6H_4(SbMe_2)_2$ in n-propanol containing HX gave yellow-green *trans*-$[Co\{o\text{-}C_6H_4(SbMe_2)_2\}_2Cl_2]Cl$ and red-brown *trans*-$[Co\{o\text{-}C_6H_4(SbMe_2)_2\}_2X_2]X$ (X = Br or I) [707]. Similar reactions with $Me_2Sb(CH_2)_3SbMe_2$ produced *trans*-$[Co\{Me_2Sb(CH_2)_3SbMe_2\}_2X_2]X$ (X = Br or I), but the chloride could not be isolated. The complexes decomposed slowly in solution, but were remarkably stable for stibine complexes of a high-oxidation state metal centre. The UV–visible spectra showed that the distibines produce a strong ligand field, although somewhat weaker than those of o-$C_6H_4(AsMe_2)_2$ or o-$C_6H_4(PMe_2)_2$. The complexes were also characterised by ^{59}Co NMR spectroscopy and by an X-ray study of *trans*-$[Co\{o\text{-}C_6H_4(SbMe_2)_2\}_2Cl_2]_2[CoCl_4]$. The latter is the only X-ray study of a distibine complex (Fig. 26) [707].



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Rhodium carbonyl chloride reacted with $Ph_2SbCH_2SbPh_2$ to produce red $\{Rh(CO)Cl(Ph_2SbCH_2SbPh_2)\}_2$, which is distibine-bridged [708]. Rhodium trichloride and $Ph_2SbCH_2SbPh_2$ gave poor yields of orange or brown $Rh(Ph_2SbCH_2SbPh_2)_2X_3$ (X = Cl, Br or I), which are monomeric non-electrolytes in solution [704]. The structures are not certainly established, but octahedral complexes with X_3Sb_3 donor sets seem most likely, and hence containing both mondentate and chelating distibine ligands. Iridium(III) halides reacted only very slowly with this ligand in refluxing ethanol to give impure materials of approximate composition $Ir(Ph_2SbCH_2SbPh_2)X_3$ [704]. Rhodium(III) complexes of 1,3-bis(diphenylstibino)propane are also of Rh : L–L 1 : 2 stoichiometry, but they were 1 : 1 electrolytes

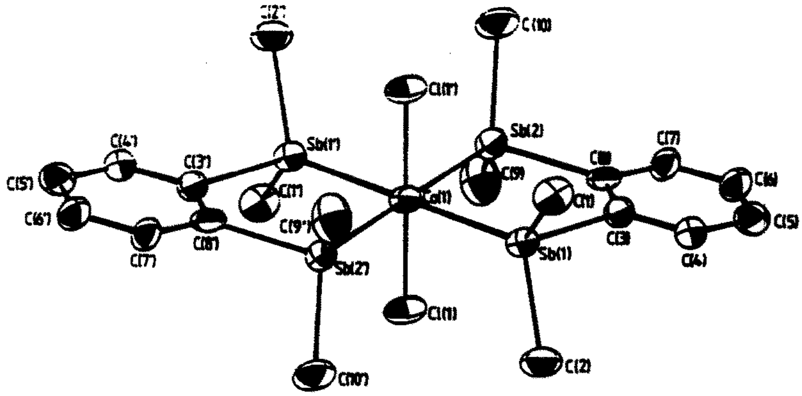
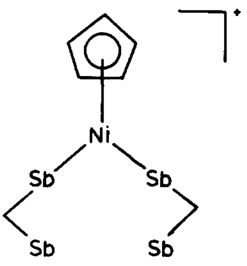


Fig. 26. Molecular structure of $[Co\{o\text{-}C_6H_4(SbMe_2)_2\}_2Cl_2]^+$. (From ref. 707 by permission of the American Chemical Society.)

in 1,2-dichloroethane solution, and are hence formulated as $[Rh(L{-}L)_2X_2]X$ ($X = Cl$, Br or I), and on the basis of their UV–visible spectra are cis isomers [709]. Iridium trichloride reacted with $Me_2Sb(CH_2)_3SbMe_2$, or $o\text{-}C_6H_4(SbPh_2)_2$, to form insoluble fawn solids $\{Ir(L{-}L)Cl_3\}_n$, which are probably chloride-bridged polymers [124].

6.4 Group 10

Red or purple diamagnetic square-pyramidal $[Ni\{o\text{-}C_6H_4(SbMe_2)_2\}_2X]X$ ($X = Cl$, Br or I) were isolated from reaction of the ligand with nickel halides [42,710]. Comparison of their UV–visible spectra with those of the related diarsine complexes, confirmed the weaker ligand field strength of the distibine. Purple square-pyramidal $[Ni(Me_2Sb(CH_2)_3SbMe_2)_2X]ClO_4$ ($X = Cl$, Br or I) were made from the constituents [35,711]. Interestingly, the nickel(II) perchlorate complex was not the expected square-planar $[Ni(L{-}L)_2]^{2+}$, but the purple five-coordinate $[Ni(Me_2Sb(CH_2)_3SbMe_2)_2(H_2O)][ClO_4]_2$, showing the tendency of antimony ligands to promote higher coordination numbers [35]. The formation of square-pyramidal complexes by the distibine contrasts with the complexes of 1,3-bis(dimethylarsino)propane, which are trigonal bipyramidal $[Ni(Me_2As(CH_2)_3AsMe_2)_2X]^+$ [35]. In contrast to the corresponding diphosphine and diarsine complexes, attempts to oxidise nickel(II) distibine complexes to nickel(III) caused decomposition, although bromination of $[Ni\{o\text{-}C_6H_4(SbMe_2)_2\}_2Br]Br$ in CH_2Cl_2 and immediate quenching to 77 K, gave a glass which exhibited an ESR spectrum characteristic of nickel(III) [710,712]. No nickel(II) complexes of phenyl-substituted distibines have been isolated, although anhydrous nickel iodide and $Ph_2Sb(CH_2)_3SbPh_2$, when refluxed together, gave a deep blue solution, which had a UV–visible spectrum consistent with a tetrahedral Ni(II) complex [50]. Nickel(II) complexes of both $Ph_2SbCH_2SbPh_2$ and $Ph_2Sb(CH_2)_3SbPh_2$ have been obtained with $(\eta^5\text{-}Cp)Ni$ moieties. The distibinopropane complex is $[(\eta^5\text{-Cp})\mathrm{Ni(Ph_2Sb(CH_2)_3SbPh_2)}]^+$ containing a chelating distibine, but with $\mathrm{Ph_2SbCH_2SbPh_2}$ the products were $[(\eta^5\text{-Cp})\mathrm{Ni(Ph_2SbCH_2SbPh_2)I}]$ or $[(\eta^5\text{-Cp})\mathrm{Ni(Ph_2SbCH_2SbPh_2)_2}]^+$ (**31**) [153].



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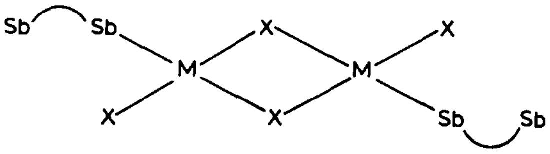
Bis(dimethylstibino)methane formed orange $\mathrm{M(Me_2SbCH_2SbMe_2)Cl_2}$ (M = Pd or Pt) with the appropriate $[\mathrm{MCl_4}]^{2-}$ [30,31]. It is unclear whether these are monomers or dimers. Bis(diphenylstibino)methane also formed yellow or orange 1 : 1 complexes with $[\mathrm{MX_4}]^{2-}$ (M = Pd or Pt; X = Cl, Br or I) [704], but these have molecular weights in $\mathrm{CHCl_3}$ solution corresponding to a dimeric formulation. The



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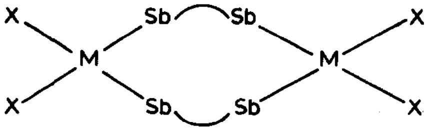
structures were tentatively proposed to be (**32**) on the basis of their far-IR spectra, although since strong ligands bands obscured some of this region, the identification of the ν(M–X) vibrations was incomplete. In view of subsequent work on the $\mathrm{Ph_2PCH_2PPh_2}$ and $\mathrm{Ph_2AsCH_2AsPh_2}$ complexes [713], it seems more



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likely that the complexes are ligand-bridged (**33**). Reaction of these $\{\mathrm{MX_2(Ph_2SbCH_2SbPh_2)}\}_2$-type complexes with more ligand in acetone, gave yellow $\mathrm{MX_2(Ph_2SbCH_2SbPh_2)_2}$ [704]. These complexes are monomeric non-electrolytes, and probably cis planar, although the iodides may have a higher coordination number. A series of diaryl complexes $Pt(Ph_2SbCH_2SbPh_2)(C_6H_4R)_2$ (R = Me, $CHMe_2$, CMe_3, Br, F, or CF_3) have been prepared from $Pt(COD)(C_6H_4R)_2$ and the ligand [714], and photolysed to $RC_6H_4C_6H_4R$. Although the complexes were formulated as monomers with a chelating distibine, no molecular weight data were reported and the mass spectra did not show parent ions, so that dinuclear complexes with bridging distibines were not certainly ruled out.

The behaviour of $Ph_2Sb(CH_2)_3SbPh_2$ or $Me_2Sb(CH_2)_3SbMe_2$ were straightforward in that only planar $M(L{-}L)X_2$ (M = Pd or Pt; X = Cl, Br or I) formed, even in the presence of excess ligand [35,709,711]. The thiocyanato complexes were also prepared, and were shown to have S-bonded ligands based upon the usual IR spectroscopic criteria.

o-Phenylenebis(dimethylstibine) formed 1 : 1 complexes $M\{o\text{-}C_6H_4(SbMe_2)_2\}X_2$ (M = Pd or Pt; X = Cl, Br, I or SCN) upon reaction with $[MCl_4]^{2-}$ (for $X \neq Cl$ in the presence of the appropriate NaX) [42], whereas $o\text{-}C_6H_4(EMe_2)_2$ (E = P or As) usually form 2 : 1 complexes in these reactions. The $o\text{-}C_6H_4(SbPh_2)_2$ formed exclusively 1 : 1 complexes with palladium(II) or platinum(II) halides, even when excess ligand was used, which suggests that the ligand cannot compete with X^- for coordination positions on the neutral metal centres [156,715]. However, with palladium(II) nitrate, the fawn complex $[Pd\{o\text{-}C_6H_4(SbPh_2)_2\}_2][NO_3]_2$ was formed, which seems to be planar in the solid state, but its conductivity in nitromethane indicated partial formation of $[Pd\{o\text{-}C_6H_4(SbPh_2)_2\}_2(NO_3)]^+$ in solution [715]. ^{195}Pt NMR spectra have been reported for platinum(II) complexes of $R_2Sb(CH_2)_3SbR_2$ (R = Me or Ph) [716]. Attempts to make palladium(IV) complexes with distibine ligands have failed [717] but platinum(IV) complexes $Pt(L{-}L)X_4$ (X = Cl or Br; L–L = $o\text{-}C_6H_4(SbPh_2)_2$, $Me_2Sb(CH_2)_3SbMe_2$ or $Ph_2Sb(CH_2)_3SbPh_2$) were made by addition of the appropriate halogen to suspensions of the corresponding platinum(II) complexes in CCl_4 [156]. The orange solids decompose in a few days at room temperature, and immediately on dissolution in $CHCl_3$ or Me_2SO with the formation of a mixture of the platinum(II) complex and oxidised ligand.

6.5 Groups 11 and 12

The $R_2Sb(CH_2)_3SbR_2$ (R = Ph or Me) reacted with $[Cu(MeCN)_4]BF_4$ to form the white $[Cu\{R_2Sb(CH_2)_3SbR_2\}_2]BF_4$ [162] which exhibited relatively sharp ^{63}Cu NMR resonances, indicating that they had an approximately regular tetrahedral geometry and did not undergo ligand dissociation. Copper(II) chloride was reduced to CuCl by $Ph_2SbCH_2SbPh_2$ [704]. Other complexes of unknown structure include the yellow $(AgI)_2(Ph_2SbCH_2SbPh_2)$ and $(HgI_2)_2(Ph_2SbCH_2SbPh_2)$ [704], and $[Au(PPh_3)(Ph_2SbCH_2SbPh_2)]Co(CO)_4$ [718]. There is a report of $[Au(PPh_3)(Ph_2SbCH_2CH_2SbPh_2)]Co(CO)_4$ [718], but this seems likely to be in error, since all attempts to prepare distibinoethane ligands have failed (see Sect. 2).

7. COMPLEXES OF MIXED DONOR LIGANDS

In this section, complexes of ligands containing other donor atoms in addition to antimony are considered. Considerably more mixed donor ligands containing antimony have been prepared (Sect. 2) than have been used as ligands thus far. In this section, the sub-classification is in terms of the hetero-donor group.

7.1 Carbon ligands

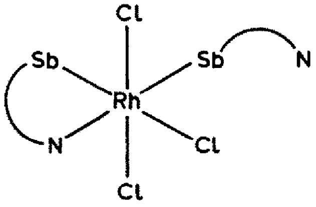
Phosphorus analogues of this group include olefin- and acetylenic-phosphines and cyclometallated phosphines. Cyclometallation in coordinated phosphines and arsines was thoroughly studied in the 1970s and 1980s and the essentials have been summarised elsewhere [719]. Factors important in promoting cyclometallation include bulky substituents on the ligand, the size of the chelate ring formed upon metallation, and the presence of a coordinatively unsaturated electron-rich metal. However, even ligands as small as PMe_3 may cyclometallate in appropriate systems. In contrast, very few cyclometallation reactions of stibines have been reported (ref. 547 contains one example), and none has been studied in detail or substantiated by an X-ray study. This absence is partially due to lack of effort, but in view of recent renewed interest in bulky stibines as precursors for MOCVD syntheses of III–V electronic materials, suitable ligands are now available. However, it may be that cyclometallation is much less favoured in stibine chemistry, where the larger antimony atom removes the organic substituents further from the metal centre. It is also likely that, with the weakness of the C–Sb bond, fission of this bond will compete with metallation of a C–H bond, particularly by nucleophilic metal centres.

Only one example of an olefin–stibine complex has been reported, the yellow $PtBr_2\{Sb(o\text{-}C_6H_4CH{=}CH_2)_3\}$ [54]. The complex had a square planar structure with the antimony, both bromines and one olefin coordinated to the platinum, and exchange between the coordinated and free olefin groups was fast on the NMR time scale. Bromination of the complex caused decomposition, whereas bromination of the olefin–phosphine analogue gave a Pt(IV) complex with bromine added to the "free" olefin groups.

Examples of triarylstibines bonded both through the antimony and η^6 via an aryl ring could also be placed in this category, but have been described in Sect. 4.3 (see, for example, ref. 195).

7.2 Nitrogen ligands

o-Dimethylaminophenyldimethylstibine, $o\text{-}C_6H_4(NMe_2)(SbMe_2)$, formed only 2 : 1 complexes $[M\{o\text{-}C_6H_4(NMe_2)(SbMe_2)\}_2X_2]$ ($M = Pd$ or Pt; $X = Cl$, Br or I) with palladium(II) or platinum(II) halides. These were formulated as square planar with Sb_2X_2 donor sets, probably with cis stereochemistry [720,721]. All attempts to form $[M(L-L)_2]^{2+}$ or $M(L-L)X_2$-type complexes were unsuccessful, although $[Pt\{o\text{-}C_6H_4(NMe_2)(SbMe_2)\}_2Cl]BPh_4$ was isolated by reaction of the dichloride with $AgNO_3$ and $NaBPh_4$ [721]. Rhodium(III) halides also form complexes of 2 : 1 stoichiometry $Rh\{o\text{-}C_6H_4(NMe_2)(SbMe_2)\}_2X_3$ (X = Cl or Br), which are monomeric non-electrolytes, and presumed to contain Sb_2NX_3 donor sets (**34**) [722]. Attempts to prepare Co(II) or Ni(II) complexes of this amine-stibine failed [723,724]. The case of nickel is interesting in that (low-spin) square planar and square pyramidal complexes of the distibine (q.v.) amine–phosphine and amine–arsine analogues are known [724]. It is likely that the ligand field strength of the amine–stibine is too weak to cause spin-pairing, and that the stibine group has no affinity for the hard high-spin nickel(II).



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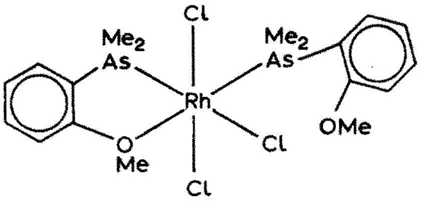
In marked contrast to the amine–stibine, the ligands (α-picolyl)dimethylstibine (picstib), (8-quinolyl)dimethylstibine (quinstib), and R,S-(8-quinolyl)methylphenylstibine (R,S-quinstib), chelate as NSb donors to palladium(II) and platinum(II) halides in $[MX_2(L-L)]$ (M = Pd or Pt; X = Cl, Br or I) [725]. The ligand field strength based upon the UV–visible spectra of the palladium chlorocomplexes is $o\text{-}C_6H_4(SbMe_2)_2 \sim$ quinstib > picstib > R,S-quinstib. The thiocyanate complexes exhibit linkage isomerism, and based upon the IR spectra were formulated $Pt(picstib)(SCN)_2$, Pd(quinstib)(SCN)(NCS) and Pt(quinstib)(SCN)(NCS). The picstib and quinstib ligands also functioned as chelates towards Cr, Mo and W carbonyls in $M(CO)_4(L-L)$, which were made by irradiation of the appropriate $M(CO)_6$ and L–L in tetrahydrofuran [725].

7.3 Oxygen ligands

(2-Methoxyphenyl)stibines $(2\text{-}MeOC_6H_4)_{3-n}R_nSb$, often behave only as monodentate Sb donors, and several examples of this have been mentioned in Sect. 4.3. Typical examples are the complexes $Pd\{o\text{-}C_6H_4(OMe)(SbMe_2)\}_2X_2$ [121,720] and $Pt\{o\text{-}C_6H_4(OMe)(SbMe_2)\}_2X_2$ [121,721] (X = Cl, Br or I), which are cis planar species with Sb_2X_2 donor sets. Similar planar complexes with the ligand coordinated only through antimony were formed by the three ligands $(2\text{-}MeOC_6H_4)_{3-n}Ph_nSb$ (n = 0, 1 or 2) [121]. The bulky ligand tris(2-methoxyphenyl)stibine gave only trans isomers with both Pd(II) and Pt(II) chlorides, whilst $Pt\{2\text{-}MeOC_6H_4)_{3-n}Ph_nSb\}_2Cl_2$

($n = 1$ or 2) have cis geometry. However, Pd$\{2\text{-MeOC}_6\text{H}_4)_{3-n}\text{Ph}_n\text{Sb}\}_2\text{Cl}_2$ ($n = 1$ or 2) appeared to exist in both cis and trans forms in solution, since in the ^{1}H NMR spectra, they exhibited two MeO resonances, which varied in relative intensity with changes in the solvent, but which were not affected by addition of free ligand, suggesting ligand exchange is slow on the NMR time scale. The Pd$\{(2\text{-MeOC}_6\text{H}_4)\text{Ph}_2\text{Sb}\}_2\text{Cl}_2$ was probably cis in the solid state, but the solid Pd$\{(2\text{-MeOC}_6\text{H}_4)_2\text{PhSb}\}_2\text{Cl}_2$ exhibited three ν(Pd—Cl) stretching vibrations consistent with a mixture of cis and trans isomers [121]. The observed pattern of cis/trans isomers is generally consistent with the preference for cis geometry exhibited by stibine donors and by Pt > Pd, except where the ligands' steric properties force a trans arrangement. Attempts to isolate halide-bridged $\text{M}_2\text{Cl}_4(\text{SbR}_3)_2$ complexes with the methoxyphenylstibines caused decomposition with reduction to the metal.

An initial study [722] of the rhodium complexes of o-$\text{C}_6\text{H}_4(\text{OMe})(\text{SbMe}_2)$ reported the formation of red-orange Rh$\{o\text{-C}_6\text{H}_4(\text{OMe})(\text{SbMe}_2)\}_3\text{Br}_3$ and yellow-orange Rh$\{o\text{-C}_6\text{H}_4(\text{OMe})(\text{SbMe}_2)\}_2\text{Cl}_3$, the latter with an Sb_2OCl_3 donor set. A detailed reinvestigation found that both yellow Rh$\{o\text{-C}_6\text{H}_4(\text{OMe})(\text{SbMe}_2)\}_3\text{Cl}_3$ and red-brown Rh$\{o\text{-C}_6\text{H}_4(\text{OMe})(\text{SbMe}_2)\}_2\text{Cl}_3$ could be isolated, depending upon the Rh : L ratio used, but that for $(2\text{-MeOC}_6\text{H}_4)_{3-n}\text{Ph}_n\text{Sb}$ ($n = 0$, 1 or 2), only the tris(ligand) complexes could be obtained. The ^{1}H NMR spectrum of Rh$\{o\text{-C}_6\text{H}_4(\text{OMe})(\text{SbMe}_2)\}_3\text{Cl}_3$ exhibited a single OMe resonance consistent with a fac geometry, whilst the Rh$\{o\text{-C}_6\text{H}_4(\text{OMe})(\text{SbMe}_2)\}_2\text{Cl}_3$ has a structure analogous to **35**, a geometry established for the corresponding complex of o-$\text{C}_6\text{H}_4(\text{OMe})(\text{AsMe}_2)$ by an X-ray study [725]. The Rh$\{(2\text{-MeOC}_6\text{H}_4)_{3-n}\text{Ph}_n\text{Sb}\}_3\text{Cl}_3$ were tentatively assigned as mer isomers on the basis of the far IR spectra [121], and this was supported for the ligand with $n = 2$ by the ^{1}H NMR spectrum, which had two MeO resonances in the ratio 2 : 1. However, for the complexes of the bulkier ligands, the ^{1}H NMR MeO resonances were very broad and seemed to contain several components, which probably result from restricted rotation about the Rh—Sb bonds. Despite this evidence of steric crowding, all attempts to form 2 : 1 complexes with one OMe group binding in place of the third stibine failed. The reaction of Rh$\{o\text{-C}_6\text{H}_4(\text{OMe})(\text{SbMe}_2)\}_2\text{Cl}_3$ with CO gave brown Rh$\{o\text{-C}_6\text{H}_4(\text{OMe})(\text{SbMe}_2)\}_2$-(CO)$\text{Cl}_3$ (**36**), and the reaction was reversed by bubbling N_2 through the solution.



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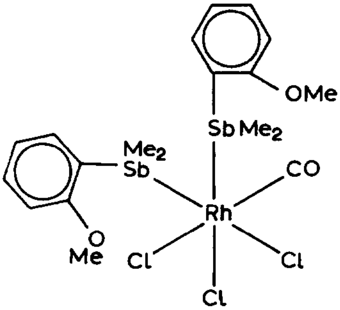
All four methoxyphenylstibines gave only IrL_3Cl_3 complexes, which were probably mer isomers [121].



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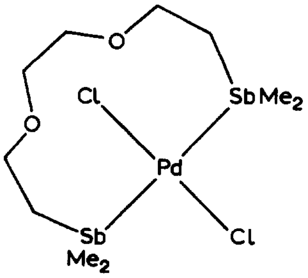
Several complexes of the potentially tetradentate distibinediether $Me_2Sb(CH_2)_2O(CH_2)_2O(CH_2)_2SbMe_2$ (dsde) have been prepared. The greenish-yellow $Pd(dsde)Cl_2$ was formulated as trans square-planar **37** with the ligand bound as a bidentate trans chelate similar to those formed by long-backboned diphosphine and diarsine ligands [121]. Other complexes of this ligand of uncertain structure were $Rh(dsde)Cl_3$, $Ir(dsde)Cl_3$, and $Ru(dsde)(CO)Cl_2$, which do not seem to contain coordination of the ether function, and $Os_2Cl_8(dsde)$, which probably contained the ligand bonding as an O,Sb chelate to two osmium centres [121].



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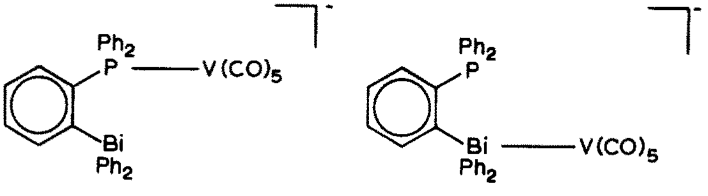
7.4 Phosphorus and arsenic ligands

The most used ligands falling into this category are the *o*-phenylene chelates $o\text{-}C_6H_4(SbR_2)(ER_2)$ (E = P or As; R = Me or Ph), various tripod tetradentates such as $Sb(CH_2CH_2CH_2EMe_2)_3$ and $Sb(o\text{-}C_6H_4ER_2)_3$, and a small number of bismuth analogues. It is convenient to deal with the bidentates and multidentates separately.

7.4.1 Bidentates

Talay and Rehder [727] prepared complexes derived from $\mathrm{V(CO)_6}$ and $(\eta^5\text{-Cp})\mathrm{V(CO)_4}$ with $o\text{-}\mathrm{C_6H_4(SbPh_2)(EPh_2)}$ ($\mathrm{E = P}$ or As) and $o\text{-}\mathrm{C_6H_4(PPh_2)(BiPh_2)}$, and compared their properties with the diphosphine and diarsine analogues. The isolated complexes included the expected cis chelate $[\mathrm{V(CO)_4(L{-}L)}]^-$ and two isomers of $[\mathrm{V(CO)_5(L{-}L)}]^-$, with the monodentate coordinated ligand bonded through either donor (**38**). The complexes were characterised by ^{51}V, ^{31}P NMR and IR spectroscopy. From $(\eta^5\text{-Cp})\mathrm{V(CO)_4}$, the corresponding $(\eta^5\text{-Cp})\mathrm{V(CO)_2(L{-}L)}$ and $(\eta^5\text{-Cp})\mathrm{V(CO)_3(L{-}L)}$ were obtained, the latter again as coordination isomers with monodentate L–L. The ligands $o\text{-}\mathrm{C_6H_4(PPh_2)_2}$ and $o\text{-}\mathrm{C_6H_4(AsPh_2)_2}$ generally behaved as chelates in these systems, and the formation of complexes with monodentate bound ligands by the heavier donor analogues was attributed mainly to steric strain, which was also evident in the trends seen in the ^{51}V NMR shieldings.



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The first stibine complexes of chromium(III) halides were isolated with $o\text{-}\mathrm{C_6H_4(PMe_2)(SbMe_2)}$, and were of type $[^n\mathrm{Bu_4N}][\mathrm{Cr}\{o\text{-}\mathrm{C_6H_4(PMe_2)(SbMe_2)}\}\mathrm{Cl_4}]$ and $\mathrm{Cr}\{o\text{-}\mathrm{C_6H_4(PMe_2)(SbMe_2)}\}_{1.5}\mathrm{X_3}$ ($\mathrm{X = Cl}$ or Br), the latter being formulated as *trans*-$[\mathrm{Cr}\{o\text{-}\mathrm{C_6H_4(PMe_2)(SbMe_2)}\}_2\mathrm{X_2}][\mathrm{Cr}\{o\text{-}\mathrm{C_6H_4(PMe_2)(SbMe_2)}\}\mathrm{X_4}]$ [728]. The red paramagnetic Mo(V) complex $[\mathrm{MoOCl_3}\{o\text{-}\mathrm{C_6H_4(AsMe_2)(SbMe_2)}\}]$ was prepared from $\mathrm{MoOCl_3(THF)_2}$ and the ligand in benzene, and the pink Mo(IV) complex *trans*-$[\mathrm{MoOCl}\{o\text{-}\mathrm{C_6H_4(AsMe_2)(SbMe_2)}\}_2]\mathrm{BPh_4}$ from $\mathrm{MoOCl_2(PMe_2Ph)_3}$ and the ligand in ethanol [729]. The Mo(IV) complex did not exchange cleanly with LiBr or LiI, but with KCNS it formed $[\mathrm{MoO(NCS)}\{o\text{-}\mathrm{C_6H_4(AsMe_2)(SbMe_2)}\}_2]\mathrm{BPh_4}$. One example of a tungsten(V) complex, the blue $\mathrm{WOCl_3}\{o\text{-}\mathrm{C_6H_4(AsMe_2)(SbMe_2)}\}$, is known [730].

A red-black powder $(\eta^5\text{-Cp})\mathrm{Mn(CO)_2}\{o\text{-}\mathrm{C_6H_4(PPh_2)(BiPh_2)}\}$ was formed from $(\eta^5\text{-Cp})\mathrm{Mn(CO)_3}$ and the ligand, and exists as a mixture of isomers with the ligand bonded either through P or Bi [727]. Extremely moisture-sensitive cream complexes $\mathrm{Mn}\{o\text{-}\mathrm{C_6H_4(AsMe_2)(SbMe_2)}\}_2\mathrm{X_2}$ ($\mathrm{X = Cl}$, Br or I) were formed by reaction of $\mathrm{MnX_2}$ with the ligand in THF under rigorously anhydrous conditions [703]. The high-spin d^5 complexes hydrolyse rapidly in air, and the ESR spectra were consistent with a trans structure.

No iron or ruthenium complexes have been described, but the brown *trans*-$\mathrm{OsO_2Cl_2}\{o\text{-}\mathrm{C_6H_4(PMe_2)(SbMe_2)}\}$ was obtained from $\mathrm{OsO_4}$, HCl and the ligand [435]. The cobalt(III) complexes *trans*-$[Co\{o\text{-}C_6H_4(PMe_2)(SbMe_2)\}_2X_2]Y$ (X = Cl, Br or I; Y = BF_4 or I) were generally similar to, although rather more stable than the distibine complexes [707]. The orange-brown $[Co\{o\text{-}C_6H_4(PMe_2)(SbMe_2)\}_3][BF_4]_3$ was prepared by air oxidation of a mixture of $Co(MeCO_2)_2$ and the ligand in ethanol, followed by treatment with HBF_4 [707].

Rhodium(III) complexes $[Rh(L{-}L)_2X_2]X$ (L–L = $o\text{-}C_6H_4(PPh_2)(SbPh_2)$ or $o\text{-}C_6H_4(AsPh_2)(SbPh_2)$; X = Cl or Br) have been prepared by reaction of the ligand with the appropriate RhX_3 [731]. From RhI_3, only $Rh(L{-}L)I_3$ complexes could be obtained, which are probably halide-bridged dimers since they have molecular weights in $CHCl_3$ intermediate between those required for monomers and dimers. Related $[Rh\{o\text{-}C_6H_4(PPh_2)(SbPh_2)\}Cl_3]_2$ and $[Rh\{o\text{-}C_6H_4(AsPh_2)(SbPh_2)\}Br_3]_2$ were obtained as by-products of the synthesis of the 2 : 1 complexes [731].

The ligands $o\text{-}C_6H_4(PMe_2)(SbMe_2)$ [710] and $o\text{-}C_6H_4(AsMe_2)(SbMe_2)$ [51] formed square pyramidal, brown $[Ni(L{-}L)_2X]Y$ (X = Cl, Br or I; Y = X, BF_4 or ClO_4) and planar $[Ni(L{-}L)_2](ClO_4)_2$ on mixing the constituents in ethanol. Also prepared were $[Ni\{o\text{-}C_6H_4(AsMe_2)(SbMe_2)\}_2NO_3]NO_3$, $[Ni\{o\text{-}C_6H_4(AsMe_2)(SbMe_2)\}_2NCS]BPh_4$, and $Ni\{o\text{-}C_6H_4(PMe_2)(SbMe_2)\}Cl_2$ [51,710]. The complexes are generally very similar to the familiar complexes of $o\text{-}C_6H_4(AsMe_2)_2$. A square pyramidal cation is also present in $[Ni\{o\text{-}C_6H_4(AsMe_2)(SbMe_2)\}\{MeAs(CH_2CH_2CH_2AsMe_2)_2\}]Br_2$ [732].

Square pyramidal, purple $[Ni\{o\text{-}C_6H_4(PPh_2)(SbPh_2)\}_2X]ClO_4$ (X = Cl, Br, I or NCS) were made by heating NiX_2, $[Ni(H_2O)_6](ClO_4)_2$ and the ligand in *n*-butanol [50]. Interestingly, the nickel(II) perchlorate complex was not the expected planar material, but the purple $[Ni\{o\text{-}C_6H_4(PPh_2)(SbPh_2)\}_2(H_2O)][ClO_4]_2$, which is five-coordinate and square-pyramidal on the basis of its UV–visible spectrum. Although there was UV–visible spectroscopic evidence for interaction between nickel(II) halides and $o\text{-}C_6H_4(AsPh_2)(SbPh_2)$ in CH_2Cl_2/*n*-BuOH solution, the only complex isolated was the greenish-black $[Ni\{o\text{-}C_6H_4(AsPh_2)(SbPh_2)\}_2I]_2[NiI_4]$, which was easily decomposed by hydroxylic solvents, demonstrating the poor donor ability of this very soft ligand [50]. Whereas ligands such as $o\text{-}C_6H_4(PPh_2)_2$ and $o\text{-}C_6H_4(AsPh_2)_2$ readily formed planar $Ni(L{-}L)X_2$ complexes, compounds of 1 : 1 stoichiometry were obtained only with difficulty for $o\text{-}C_6H_4(PPh_2)(SbPh_2)$ [50]. The brown $Ni\{o\text{-}C_6H_4(PPh_2)(SbPh_2)\}Br_2$ and greenish-black $Ni\{o\text{-}C_6H_4(PPh_2)(SbPh_2)\}I_2$ were prepared by heating the ligand with excess nickel(II) halide in *n*-butanol, when they precipitated. These materials were paramagnetic ($\mu = 2.2$ (Br), 3.0 (I) B.M.), which, coupled with their UV–visible spectra, suggested the iodocomplex probably had a polymeric octahedral structure, whilst the bromide may contain both planar and octahedral environments [50,733]. The red *trans*-$[Ni\{o\text{-}C_6H_4(PMe_2)(SbMe_2)\}_2Br_2]ClO_4$ is the only isolated Ni(III) stibine complex, and was made by bromine oxidation of the Ni(II) analogue; the corresponding chloride could not be made [710]. An attempt to oxidise this complex further (to Ni(IV)) was unsuccessful although diphosphine and diarsine complexes are known [734].

Yellow, planar palladium(II) and platinum(II) complexes M{o-$C_6H_4(AsPh_2)(SbPh_2)$}X_2 (X = Cl, Br, I or SCN) were formed directly from MX_4^{2-}, but with o-$C_6H_4(PPh_2)(SbPh_2)$ the initial products were Magnus-type salts [M{o-$C_6H_4(PPh_2)(SbPh_2)$}$_2$][MX_4], which rearranged to the monomers on boiling in N,N-dimethylformamide [731]. The platinum thiocyanate complexes and Pd{o-$C_6H_4(AsPh_2)(SbPh_2)$}$(SCN)_2$ contain S-bonded ligands, but the other palladium complex was formulated Pd{o-$C_6H_4(PPh_2)(SbPh_2)$}(NCS)(SCN) in the solid state, although in CH_2Cl_2 solution it too contained only Pd-SCN linkages [731]. Within the series of ligands o-$C_6H_4(EPh_2)(E'Ph_2)$ (E,E' = P, As or Sb) there is a general trend from *N*CS to *S*CN coordination with ligand donor P → As → Sb, and with metal Pd → Pt [731,734a]. The M{o-$C_6H_4(PPh_2)(SbPh_2)$}$_2X_2$ (M = Pd or Pt; X = Cl, Br or I) made by reaction of MX_4^{2-} with excess ligand in ethanol were 1 : 1 electrolytes in solution, whereas the diphosphine analogues had higher conductivities indicating partial ionisation of the second halide [731]. There was no evidence of a tendency to dissociate one bidentate ligand in solution, which was observed with the o-$C_6H_4(AsPh_2)_2$ complexes [734]. In contrast, the M{o-$C_6H_4(AsPh_2)(SbPh_2)$}$_2X_2$ could not be obtained, only the 1 : 1 complexes being isolated even with a large excess of ligand. Five-coordinate [M{o-$C_6H_4(AsPh_2)(SbPh_2)$}$_2$X]ClO_4 were isolated in the presence of excess $LiClO_4$, but they easily lost one bidentate ligand on treatment with X^-, which showed that the ligand o-$C_6H_4(AsPh_2)(SbPh_2)$ could not compete successfully with halide ions for the cationic M^{2+} centre [731]. The planar [M{o-$C_6H_4(PPh_2)(SbPh_2)$}$_2$][ClO_4]$_2$ were obtained by treatment of acetone solutions of the dichlorides with excess $HClO_4$, but again the arsine–stibine analogues were not formed.

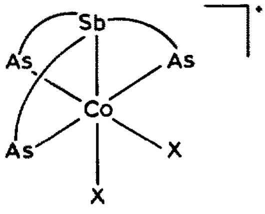
The reaction of o-$C_6H_4(PPh_2)(BiPh_2)$ with $PdCl_4^{2-}$ produced black decomposition products, no doubt due to fission of the Bi—C bonds [735].

7.4.2 *Tetradentates*

The tripodal tetradentates of interest in this section have apical antimony and three arsenic or phosphorus donor arms, $Sb(CH_2CH_2CH_2AsMe_2)_3$ or Sb(o-$C_6H_4ER_2)_3$ ($ER_2 = PPh_2$, $AsPh_2$ or $AsMe_2$). They have mostly been investigated in comparison with the corresponding ligands with apical P or As atoms to establish the varying electronic effects resulting from changing donor atoms and strain within the chelate rings. Most effort has been devoted to cobalt, nickel and palladium complexes.

One ruthenium complex has been obtained, Ru{Sb(o-$C_6H_4AsPh_2)_3$}Cl_2, a yellow solid made from $RuCl_3 \cdot nH_2O$ [736].

Trigonal bipyramidal deeply coloured cobalt(II) complexes [Co{Sb(o-$C_6H_4PPh_2)_3$}X]BPh_4 (X = Cl, Br, I or NCS) were obtained by reaction of the ligand with $CoX_2(PPh_3)_2$ followed by addition of $NaBPh_4$ [737]. The complexes have magnetic moments of ca. 2 B.M., and the electronic spectra were assigned in terms of a Jahn–Teller distorted C_{3v} symmetry by comparison with those of the tetraphosphine analogue. In contrast, the $Sb(CH_2CH_2CH_2AsMe_2)_3$ ligand did not produce isolable complexes of Co(II), but air oxidation of a mixture of the ligand, CoX_2 (X = Cl, Br, I or NCS) and $LiClO_4$ in ethanol readily gave the cobalt(III) complexes $[Co\{Sb(CH_2CH_2CH_2AsMe_2)_3\}X_2]ClO_4$ which have cis octahedral structures **39** [738].



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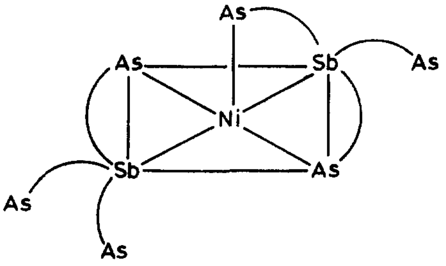
The nickel(II) complexes of four antimony tripods have been examined [57,58,739–741]. The UV–visible spectra of the blue-black trigonal bipyramidal $[Ni\{Sb(o\text{-}C_6H_4EPh_2)_3\}X]BPh_4$ (E = P or As; X = Cl or I) were compared [57] with those of the analogous ligands with apical P or As donors, and the ligand field strength showed an anomalous variation with apical donor $P > Sb > As$ (rather than the $P > As > Sb$ expected). The longer-backboned ligand $Sb(CH_2CH_2CH_2AsMe_2)_3$ also formed blue-black trigonal bipyramidal complexes $[Ni\{Sb(CH_2CH_2CH_2AsMe_2)_3\}X]BPh_4$ (X = Cl, Br, I, NO_3 or NCS) and the red $[Ni\{Sb(CH_2CH_2CH_2AsMe_2)_3\}CN]BPh_4$ [58]. The electronic spectra of these complexes showed a normal spectrochemical series with X, but again a comparison with the complexes of similar ligands with apical P or As donors revealed anomalous effects. Here, the lowest energy transitions in the chloro and cyano complexes have a normal dependence $P > As > Sb$, whilst for the bromocomplexes the order is $P > As \sim Sb$, and for the iodides $P > Sb > As$ [58]. Extension of these studies to the o-phenylene-backboned $Sb(o\text{-}C_6H_4AsMe_2)_3$ again resulted in the preparation of blue or purple trigonal bipyramidal $[Ni\{Sb(o\text{-}C_6H_4AsMe_2)_3\}X]Y$ (X = Cl, Br, I, NCS or NO_3; Y = X or BPh_4), and here the UV–visible spectra of all the complexes exhibited the anomalous energy dependence $As < Sb$ [740]. These effects have been discussed at length, and it was proposed that two effects were operating. Firstly, the presence of the large antimony at the apex of the ligand coupled with the varying interdonor backbone length $CH_2CH_2CH_2 > o\text{-}C_6H_4$ resulted in the angle L′–M–L (L′ = apical donor atom, L = equatorial donor atom) decreasing and compression of the apical donor atom down onto the metal, where it exerts an anomalously large ligand field [57,58,740,741]. Secondly, the effect of the halogen co-ligand on the ligand field has been suggested to be a nephelauxetic effect. The UV–visible spectra of the $[Ni\{Sb(CH_2CH_2CH_2AsMe_2)_3\}X]BPh_4$ also vary with applied pressure, and the complexes have been proposed as internal pressure calibrants [742].

In marked contrast to tripodal P_4 or As_4 ligands which formed trigonal bipyramidal $[Ni(ligand)Y]^{n+}$ ($Y = H_2O$, $n = 2$ or $Y = ClO_4$, $n = 1$), the ligand $Sb(o\text{-}C_6H_4AsMe_2)_3$ reacted with nickel(II) perchlorate irrespective of the M : L ratio used to form deep blue $[Ni\{Sb(o\text{-}C_6H_4AsMe_2)_3\}_2][ClO_4]_2$, which on the basis of its UV–visible spectrum was assigned a square pyramidal structure (**40**) [739,740]. Palladium complexes $[Pd\{Sb(o\text{-}C_6H_4AsMe_2)_3\}X]Y$ (X = Cl, Br, or SCN; Y = X or BPh_4) were isolated as orange-red crystals; a study of their UV–visible spectra compared with those of the tetraarsine analogues, revealed similar anomalous trends to those found in the nickel complexes above [55].



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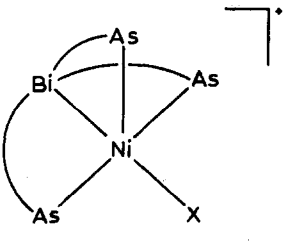
These studies on antimony tripods have been briefly extended to bismuth analogues. The ligand $Bi(o\text{-}C_6H_4AsMe_2)_3$ reacted with NiX_2 and $NaBPh_4$ in ethanol to form brown or blue-black $[Ni\{Bi(o\text{-}C_6H_4AsMe_2)_3\}X]BPh_4$ (X = Cl, Br or I) [70,743]. The UV–visible spectra led to the conclusion that these materials had a square pyramidal geometry, in contrast to the trigonal bipyramidal structures found with tripods containing P, As or Sb apical atoms. Although a trigonal bipyramidal geometry with an even greater compression was expected for bismuth compared with antimony (see above), it seems that the large bismuth could not occupy the apical position of a trigonal bipyramid, and that the less strained structure (**41**) was adopted. The spectra support the coordination of the bismuth to the metal centre. A green $[Co\{Bi(o\text{-}C_6H_4AsMe_2)_3\}Cl]BPh_4$ was also isolated, but attempts to form nickel halide complexes of the related ligand $Bi(CH_2CH_2CH_2AsMe_2)_3$ resulted in blue-green solutions characteristic of a trigonal bipyramidal geometry, which decomposed rapidly. The two ligands behaved differently towards nickel(II)



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perchlorate in ethanol in that a deep blue trigonal bipyramidal $[Ni\{Bi(CH_2CH_2CH_2AsMe_2)_3\}(H_2O)][ClO_4]_2$ and a brown $[Ni_2\{Bi(o\text{-}C_6H_4AsMe_2)_3\}_3][ClO_4]_4$ formed irrespective of the Ni : L ratio used [70].

Palladium(II) halides brought about Bi—C bond fission of reaction with $Bi(o\text{-}C_6H_4AsMe_2)_3$ and $NaBPh_4$, forming a black solid and the yellow $[Pd(AsMe_2Ph)_3Cl]BPh_4$ could be isolated from the solution [744].

8. SPECTROSCOPIC AND STRUCTURAL PROPERTIES

In this section we consider the results from specific techniques which shed light upon the metal–antimony bonding in stibine complexes. The limited number of examples and the even more limited data makes it impossible to draw many conclusions about metal–bismuthine bonding, but where trends have been discerned, they will be treated in Sect. 9. As we pointed out in the introduction, the properties of the quadrupolar antimony nuclei preclude the use of Sb NMR spectroscopy to study stibine complexes.

8.1 Antimony-121 Mössbauer spectroscopy

The spectra are recorded using the 37.2 keV transition $7/2 \rightarrow 5/2$, and in non-cubic fields eight line spectra are expected, although the natural line width of 2.1 mm s^{-1} means that only a broad band envelope is observed. Whilst data can be obtained at 80 K, cooling both source and sample to liquid helium temperatures is preferable to improve spectral quality. The technique has been applied to a considerable number of Sb(III) and Sb(V) compounds [745], but only a few studies of stibines or stibine complexes have appeared. Relative to the standard $Ca^{121}SnO_3$, the isomer shifts of free triorganostibines are ca. -9 mm s^{-1}, and on coordination the isomer shifts become less negative, ca. -7 mm s^{-1}. Oxidation of Sb(III) to Sb(V) results in a change of isomer shift to more positive values (in R_3SbX_2 to ca. -7 to -4 mm s^{-1}), and thus coordination formally parallels the change on oxidation as expected, since both lead to a reduced electron density at the antimony nucleus. Some representative data are shown in Table 7, and some typical spectra are shown in Fig. 27.

The interpretation of the data has been critically discussed by McAuliffe and Parish [149] who point out that the spectra reflect the charge density on the antimony rather than the Sb—M bond as a whole. The spectra may also fail to identify different closely related environments for coordinated stibines, for example for *mer*-$RhCl_3(Ph_3Sb)_3$ a two-site fit was not statistically better than a single site fit, despite the presence of $Sb_{trans\,Sb}$ and $Sb_{trans\,Cl}$ centres. In several series of palladium and platinum complexes, the isomer shifts could be used to infer stereochemistry (cis vs. trans) at the metal centre, but the conclusions were tentative [149]. For example, the smooth change in isomer shift with co-ligand in the series $Pt(Ph_3Sb)_2X_2$ $(X = Cl > NO_2 > I)$ is consistent with cis structures for all three, whereas the

TABLE 7

^{121}Sb Mössbauer data [107,149,316,745,746][a]

Compound	δ (mm s^{-1})[b]	e^2qQ/h (mm s^{-1})[c]
Ph_3Sb	−9.35	16.2
$(o\text{-}MeC_6H_4)_3Sb$	−9.77	17.4
$(p\text{-}MeC_6H_4)_3Sb$	−9.37	17.0
Me_3Sb	−8.72	16.3
$Fe(CO)_4(Ph_3Sb)$	−6.62	9.0
$Fe(CO)_3(Ph_3Sb)_2$	−6.65	10.9
$PdCl_2(Ph_3Sb)_2$	−7.31	12.0
$PdI_2(Ph_3Sb)_2$	−7.23	10.7
$Pd(NO_2)_2(Ph_3Sb)_2$	−7.04	9.6
$PtCl_2(Ph_3Sb)_2$	−6.44	9.5
$PtI_2(Ph_3Sb)_2$	−6.78	9.3
$Pt(NO_2)_2(Ph_3Sb)_2$	−6.73	9.3
$PtCl_2(Cy_3Sb)_2$	−7.65	8.2
$Pt(Et_3Sb)_2Cl_2$	−6.66	8.0
$RhCl_3(Ph_3Sb)_3$	−7.14	10.7

[a] Slightly different values have been reported by different workers, who have also used different standards.

[b] Isomer shift relative to $CaSnO_3$ shifts converted from other standards where necessary.

[c] Quadrupole coupling constants.

$Pd(Ph_3Sb)_2X_2$ exhibit a series $NO_2 > I > Cl$, probably suggesting a trans configuration for the halides but cis for the nitro complex. Overall the experimental demands and relatively limited stereochemical information obtainable have combined to limit studies of coordination complexes.

8.2 X-ray structural data

The available X-ray data are collected in Table 8. Individual structures have been discussed in appropriate places in the text, and here an overview of this data is given. Attempts to extract significant trends from the data largely founder upon the disparate nature of the complexes studied, and it is clear that the data are much too limited from which to draw conclusions about the nature of the M—Sb bond.

Comparison of the *d*(M—Sb) in $Fe(CO)_4(R_3Sb)$ (R = Me, Ph or ^{t}Bu) and $Ru(CO)_4(R_3Sb)$ (R = Me or Ph) reveals that the differences are not significant between R = Me or Ph, but that the Fe—Sb bond is significantly longer in the $^tBu_3Sb$ complex [98–100,318,377]. In the osmium complexes $Os(CO)_4(Ph_3Sb)$, *trans*-$Os(Ph_3Sb)_4Cl_2$ and *mer*-$Os(Ph_3Sb)_3Br_3$, the Os—Sb bond length increases with increasing osmium oxidation state (the variations appear significant and not simply due to different coordination number or trans ligand). This is the usual effect observed

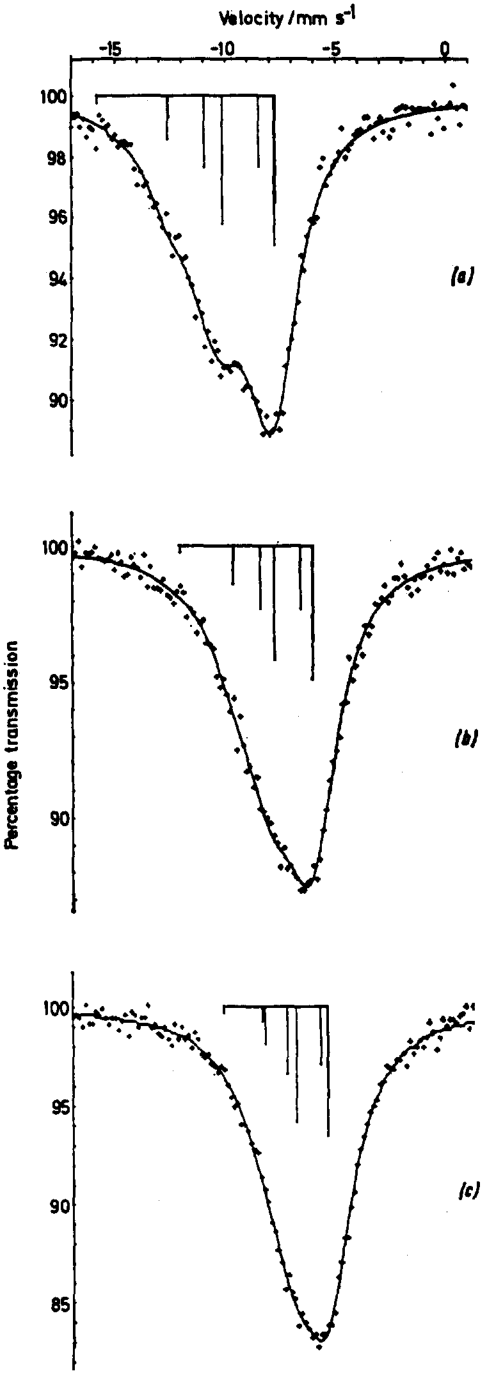

Fig. 27. ^{121}Sb Mössbauer spectra of (a) Ph_3Sb, (b) $Pd(Ph_3Sb)_2Cl_2$, and (c) $PtCl_2(Ph_3Sb)_2$. (From ref. 149 by permission of the Royal Society of Chemistry.)

TABLE 8

X-ray structural data on stibine complexes

Complex	*d*(M–Sb) (Å)	Fig.	Ref.
Fe(CO)$_4$(Me$_3$Sb)	2.49(02)		98
Ru(CO)$_4$(Me$_3$Sb)	2.619(1)	1	99
Fe(CO)$_4$(^{t}Bu$_3$Sb)	2.547(1)	2	100
[Ag(^{t}Bu$_3$Sb)$_2$]$^+$	2.69(2)		161
Cr(CO)$_5$(Ph$_3$Sb)	2.6170(3)		205
[W(CO)$_3$I$_3$(Ph$_3$Sb)]$^-$	2.720(3)	3	242
Re$_2$(CO)$_7$(μ-PPh$_2$)(μ-SbPh$_2$)(Ph$_3$Sb)	2.671(1)	4	295
ReCl$_2$(NO)$_2$(Ph$_3$Sb)$_2$	2.711(8)	5	296
Re$_2$H$_6$(Ph$_3$Sb)$_5$	2.5570(7)		
	2.5678(7)		
	2.5876(7)		
	2.5908(7)		
	2.5962(7)	6	300
Fe(CO)$_4$(Ph$_3$Sb)	2.472(1)	7	318
Fe(CO)$_4$Fe(μ-SbPh$_2$)Fe(CO)$_3$Ph(Ph$_3$Sb)	2.515(?)	8	321
(η^5-Cp)Mn(CO)$_2$Fe$_2$(CO)$_6$(Ph$_3$Sb)	2.506(5)	9	325
[(η^5-Cp)Fe(CO)$_2$(Ph$_3$Sb)]PF$_6$	2.477(1)	10	350
Ru(CO)$_4$(Ph$_3$Sb)	2.623(1)		377
trans-Ru(Ph$_3$Sb)$_4$Cl$_2$	2.625(1)–2.632(1)		
	(2 molecules in cell)	11	416
Os(CO)$_4$(Ph$_3$Sb)	2.612(2)	12	314
trans-Os(Ph$_3$Sb)$_4$Cl$_2$	2.611(2)–2.630(2)		416
mer-Os(Ph$_3$Sb)$_3$Br$_3$	2.640(2)		
	2.644(2)		
	2.654(2)	13	441
Co(NO)(CO)$_2$(Ph$_3$Sb)	2.480(1)	14	457
Co(DMGH)$_2$Cl(Ph$_3$Sb)	2.55(5)		470
Rh(C$_4$(CF$_3$)$_4$)Cl(Ph$_3$Sb)$_2$	2.586(1)		
	2.584(1)		484
Rh(MeCO)(CO)(Ph$_3$Sb)$_3$	2.552(2)		
	2.272(2)		
	2.579(2)		493
Rh{PhC(O)CHC(O)Ph}Ph$_2$(Ph$_3$Sb)$_2$	2.551(2)		
	2.588(2)		494
Rh(DMGH)$_2$(Ph$_3$Sb)Cl	2.553(2)		502
Rh$_2$(μ-MeCO$_2$)$_4$(Ph$_3$Sb)$_2$	2.732(4)	15	530
Rh$_2$(μ-PhCONH)$_4$(Ph$_3$Sb)$_2$	2.681(1)		532
Rh$_2$(μ-MeCONH)$_{4-x}$(μ-MeCO$_2$)$_x$(Ph$_3$Sb)$_2$	2.699(2)		533
RhCl$_2$(Ph)(Ph$_3$Sb)$_3$	2.582(2)		
	2.594(2)		
	2.706(2)	16	539
RhCl$_2$(Ph)(Ph$_3$Sb)$_2$(MeCN)	2.360(2)		
	2.588(1)	17	540
Pd(Ph$_3$Sb)$_2$I$_2$	2.578(1)	18	612

TABLE 8 (*continued*)

Complex	d(M–Sb) (Å)	Fig.	Ref.
$[Pd(\eta^5\text{-}Cp)(Ph_3Sb)_2]PF_6$	2.506(1) 2.527(1)	19	632
$Pd_2(MeCO_2)_4(Ph_3Sb)_2$	2.508(4) 2.509(4)	20	634
$Pd_3(MeCO_2)_4Ph_2(Ph_3Sb)_2$	2.473(4)	21	634
$CuCl(Ph_3Sb)_3 \cdot CHCl_3$	2.548(2) 2.550(2) 2.564(2)	22	639
$[Cu\{(p\text{-}FC_6H_4)_3Sb\}_4]BF_4$	2.556(1) 2.547(1) (× 3)	23	640
$[Au(Ph_3Sb)_4]ClO_4$	2.658(2) 2.656(2)	24	661
$[Au(Ph_3Sb)_4][AuPh_2]$	2.585(12)–2.669(14) (3 independent molecules)		663
$[Au(Ph_3Sb)_4][Au\{2,4,6\text{-}C_6H_2(NO_2)_3\}_2]$	2.647(1) 2.649(1) 2.653(1) 2.655(1)		662
$Cr(CO)_5(Ph_3Bi)$	2.705(1)		205
$[(\eta^5\text{-}Cp)Fe(CO)_2(Ph_3Bi)]BF_4$	2.570(1)	25	106
$[Co\{o\text{-}C_6H_4(SbMe_2)_2\}_2Cl_2]_2[CoCl_4]$	2.505(1) 2.478(1)	26	707

with group 15 donor ligands, and is attributable to weaker binding of the neutral ligand as the metal orbitals contract with increasing formal charge. The difficulties of drawing conclusions about the nature of the M–Sb bonding from the available X-ray data are nicely illustrated by the cases of $Cu(Ph_3Sb)_3Cl$ (d(Cu–Sb) = 2.554(5) Å (ave.)) described by the authors as "very long" [639], whilst for $[Cu\{(p\text{-}FC_6H_4)_3Sb\}_4]BF_4$ (d(Cu–Sb) = 2.552(3) Å (ave.)) was described as "very short" and indicative of a significant $d\pi$–$d\pi$ component in the bonding [640].

The effect of coordination upon the geometry of the stibine also appears to be of marginal significance, at least for Ph_3Sb. Electron diffraction data on Me_3Sb [747] revealed d(Sb–C) = 2.163(3) Å and C–Sb–C = 94.1°, which can be compared with $Ru(CO)_4(Me_3Sb)$ d(Sb–C) = 2.149(7) Å although the C–Sb–C has increased to 102.6(3)° [99]. For Ph_3Sb, the X-ray crystal structure [748] showed d(Sb–C) = 2.155(9) Å and C–Sb–C = 95.1(3)–98.0(3)°, and very similar dimensions are reported [749] for $(p\text{-}MeC_6H_4)_3Sb$, d(Sb–C) = 2.141(3) Å and C–Sb–C = 97.3(1)°. For those Ph_3Sb complexes where the dimensions of the coordinated ligands have been determined with sufficient precision, the d(Sb–C) bond lengths are generally within 3–4σ of the free ligand value and the C–Sb–C angles lie in the range 97–101°.

It is only fair to record that the data are almost completely limited to Ph_3Sb complexes, and of the reported structures, approximately half either do not give detailed data on the ligands or the data are not of high precision.

One notable study is that of Carty et al. [205] who obtained structural data on the isomorphous series of complexes, $Cr(CO)_5(EPh_3)$ (E = P, As, Sb or Bi), and found that, although the individual differences were small, the C—E—C angles decreased* (E = P, 102.6°; E = As, 101.4°; E = Sb, 99.2°; E = Bi, 98.7°) and the Cr—E—C angles increased (E = P, 115.6°; E = As, 116.6°; E = Sb, 117.9°; E = Bi, 118.9°), which was interpreted as evidence for increasing s character in the Cr—E bond as group 15 was descended.

8.3 *UV–visible spectra*

Goggin et al. [144] studied the UV–visible spectra of various series of palladium(II) and platinum(II) complexes, and established the position of R_3Sb ligands in the spectrochemical series as $Cl < R_2Te < R_2Se \sim R_3Sb < R_2S \sim H_2O < R_3As \sim NH_3 < R_3P < P(OR)_3$.

The expected series Sb < As < P has been found to hold for a number of series of bidentate ligands [35,42,50,51,707,731]. It is notable that, although less than those of the analogous diphosphine or diarsine, the ligand field generated by $o\text{-}C_6H_4(SbMe_2)_2$ is substantial, and it certainly deserves to be classified as a strong field ligand.

When antimony is at the apex of a tripodal tetradentate ligand, its large size and the geometric constraints of the chelate ligand cause compression of the antimony onto the metal, resulting in an anomalously great ligand field and sometimes in a reversal of the expected spectrochemical series [737–741]. These effects were discussed in more detail in Sect. 7.4.2.

Consistent with the low electronegativity of antimony, ligand-to-metal charge transfer transitions (LMCT) in stibine complexes of heavy metals such as Ru, Ir or Os, occur at lower energy than those of phosphine or arsine analogues, and in extreme cases such as $Ir(Ph_3Sb)_2Cl_4$ are found in the near IR region [123,124,436,439,443].

9. COMPARISONS WITH OTHER GROUP 15 LIGANDS

This final section aims to provide an overview of the steric and electronic properties of stibine and bismuthine ligands, and the differences between them and the more intensively studied phosphines and arsines. However, the data on bismuthines are extremely limited, whilst that on stibines mainly relate to Ph_3Sb. The very different chemistries of PMe_3 and PPh_3 [1,3] illustrate the limited view which would result if the triaryl ligand was taken as the archetypal phosphine. Unfortunately, the

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* Average values are given.

chemistry of trialkylstibines has been neglected, the data are fragmented and in some cases rather old. Similarly, examples of stibine donors bound to hard metal centres, either early transition metals in positive oxidation states or later group metals in high oxidation states, are limited to a few complexes of distibines or mixed donor ligands.

9.1 Steric properties

The usual approach to discussing the steric properties of phosphines is the cone angle concept of Tolman [750], which is readily extended to other ligands. Since the Tolman model is geometrically based [750], it is easily extended to the heavier donor analogues by allowing for the larger size of the donor atoms $P < As < Sb < Bi$, and the corresponding increase in $d(M{-}E)$. McAuliffe [12] has tabulated the results of such calculations for common group 15 ligands, and shows that the cone angles of stibines are between 2° and 5° less than those of the corresponding phosphines, with bismuthines having cone angles smaller again by a similar amount. This decrease in bulk is one factor in the higher coordination numbers observed in many systems. The apparently weaker coordinating power and the tendency to monodentate coordination found in $o\text{-}C_6H_4(SbPh_2)(EPh_2)$ ($E = P$ or As), $o\text{-}C_6H_4(PPh_2)(BiPh_2)$ and $Ph_2SbCH_2SbPh_2$ compared with $o\text{-}C_6H_4(EPh_2)_2$ or $Ph_2PCH_2PPh_2$ [695,713,727,731] is partly due to electronic factors, but also due to steric strain within the chelate ring due to the larger donor atoms. Steric effects are very evident in the anomalous spectroscopic properties of. complexes of the tripodal $Sb(CH_2CH_2CH_2ER_2)_3$ and $Sb(o\text{-}C_6H_4ER_2)_3$ ligands (Sect. 7.4).

9.2 Electronic properties

The familiar model for the M—P bond in tertiary phosphines is the σ-donor π-acceptor model of Chatt [751]. Over the intervening 40 years, this model has been intensively tested against a wide range of experimental observations, examined by increasingly powerful calculations, debated and refined (see refs. 1, 752 and 753 for reviews). In spite of this interest, the nature of the M—P bond remains disputed. Against this background, it is not to be expected that the much less studied M—Sb bond can be unequivocably described, and literature discussion focuses on differences from the M—P analogue.

In the period 1950–1970, many spectroscopic and some thermodynamic studies were carried out in attempts to elucidate the nature of the group 15 ligand—metal bond, the stibine and bismuthine components in such studies (where they were included at all) being usually represented by only Ph_3Sb and Ph_3Bi. The conclusions reached were often expressed in terms of varying σ-donor and π-acceptor powers of the ligand [752]. More recent work has been more cautious, recognising that variations in an experimentally observed parameter often reflect changes in the complex as a whole, and that distinction of steric and electronic effects, let alone factoring out the latter into σ and π effects, is extremely difficult.

The general pattern to emerge from these studies is clear. Stibines are moderate σ donors, and the π acceptor component* is less significant than in phosphines or arsines. The tendency noted previously towards the adoption of higher coordination numbers in stibine complexes will certainly be facilitated by smaller cone angles, but its driving force is probably reduced electron donation to the metal centre, which is compensated by binding more ligands. Stibines also have a marked tendency to adopt a cis stereochemistry (or perhaps to avoid a trans Sb–M–Sb arrangement), which may correlate with the decreased trans influence $P > As > Sb$ [84,202,595]. It should be noted that studies in a wide variety of systems (see, for example, refs. 77, 84, 114 and 439) have indicated that changing the R substituents can have a similar or greater effect than changing the donor atom from phosphorus to arsenic, although changing the donor from As to Sb has a much more notable effect.

This review has attempted to collect together, and where possible collate, available data on stibine and bismuthine complexes. We conclude by pointing out that substantial areas remain underexplored, particularly complexes of the early transition metals in positive oxidation states, and systematic studies of trialkylstibines in general.

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* The π acceptor orbitals on antimony are likely to be the Sb–C σ^* or their admixture with the Sb 5d, comparable with recent results on the phosphorus π acceptor orbitals [1].

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