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Review

Developments in the coordination chemistry of stibine ligands

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Contents

Abstract

Developments in the chemistry of stibine and bismuthine ligands in the period 1991–2005 are reviewed. The article describes in turn, new ligand syntheses, ligand properties including bonding and steric effects, *trans* influence and *trans* effects. The recent identification of monostibines as bridging ligands is also discussed. This is followed by sequential review of the metal complexes of tertiary monostibines, distibines, polydentates and bismuthines; compounds containing direct Sb—Sb or Bi—Bi bonds are excluded.

Keywords: Antimony ligands; Stibines; Metal complexes; Distibines; Bismuthines

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1. Introduction

Studies of the coordination chemistry of stibine ligands began over 80 years ago, but stibines have always received much less attention than phosphorus or arsenic analogues. In part this may be traced to their more difficult syntheses (except for the simplest R_3Sb), weak binding power to 3d metals in positive oxidation states, and to the perception that their complexes differed from those of phosphines only "by degree", i.e. poorer ligands but not fundamentally different [1]. (A similar perception also applied to group 16 ligands and similarly delayed the development of selenoether and telluroether coordination chemistry for many years [2].) Although early studies of stibine complexes utilised trialkylstibines [1], work in the period post 1960 often used only $SbPh_3$ as a "token" stibine in work focused on phosphine and arsine complexes. This was unfortunate in that $SbPh_3$ is among the weaker donor stibines and was not particularly suited to the spectroscopic techniques available. X-ray structural studies were also rare in this period, less than 10 structures of stibine complexes had been reported by 1980. The studies which incorporated cursory examination of $SbPh_3$ complexes in larger works focused on the lighter analogues, inevitably tended to see similarities and rarely explored the differences in any detail.

Bismuthines remain the Cinderellas among group 15/16 ligands, weakly coordinating and containing reactive Bi–C bonds, which are easily broken. Whilst an extensive coordination chemistry is unlikely, it should be pointed out that almost all the work has been with $BiPh_3$ and studies are mostly even more cursory that with stibines [1]; only one bismuthine complex had been characterised by an X-ray study by 1990.

In the last 15 years or so a number of detailed studies have demonstrated that stibines are not simply "weakly coordinating phosphines", but that they have significantly different electronic properties, and as a result, a markedly different coordination chemistry. The most important single development in group 15 coordination chemistry in this period was the discovery by Werner and co-workers [3] that SbR_3 can behave as a bridging ligand between two rhodium centres, a bonding mode subsequently extended to PR_3 and AsR_3, but in these latter cases the syntheses require metathesis of the lighter ligands into the stibine complexes.

Distibine ligands have been known for over 30 years, but their study has been restricted to a few research groups, none are commercially available and their often difficult syntheses seem to have limited studies. Recent studies (below) show that they have sufficient differences to lighter analogues to warrant the effort. At the time of writing only one tristibine is known, [4] and antimony and bismuth are the only donor atoms in group 15 or 16 yet to be incorporated into macrocycles.

One of us co-authored a review of stibine and bismuthine coordination chemistry [1], which covered the literature up to ca. 1991 and the present article updates literature coverage to work published up to mid-2005. We have reviewed recently the synthesis of (As), Sb and Bi ligands elsewhere [5] and only cover in Section 2 work which has appeared in the last 4 years. Previous reviews of stibine and bismuthine complexes are listed in these earlier works [1,5]. We have excluded discussion of the ligand properties of species with direct Sb–Sb bonds such as $R_2Sb–SbR_2$ or $(RSb)_n$, of R_2Sb^- anions and their bismuth equivalents: recent coverage of this chemistry is available in several articles by Breunig and co-workers [6–9].

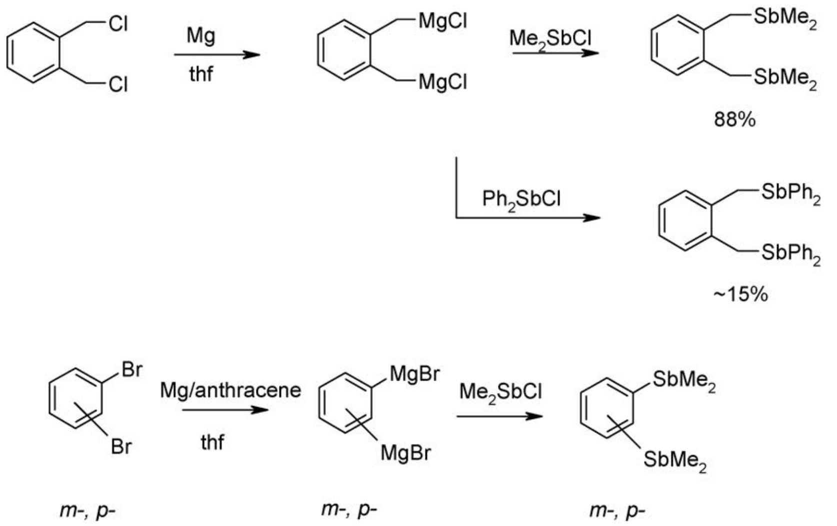
2. Stibine and bismuthine ligands

The two main routes for introducing antimony groups into ligands utilise either electrophilic (halostibines) or nucleophilic (stibide anions) reagents [1,5]. Due to their thermal instability and oxygen sensitivity, primary ($RSbH_2$) or secondary (R_2SbH) stibines have been little used as synthons. The synthesis, isolation and X-ray structures of $[R_2SbLi(thf)_3]$ (R = Ph or mesityl) made from R_2SbH and BuLi) and $[{}^tBu_2SbK$(pentamethyldiethylenetriamine)] (cyclo-$({}^tBuSb)_4$ + K) have been described [10]. However, metallation of primary stibines is less clear-cut. The 2,4,6-triisopropylphenylstibine, $({}^iPr_3C_6H_2)SbH_2$ was obtained as colourless needles by reduction of the corresponding dichlorostibine with $LiAlH_4$, and is metallated cleanly by BuLi to form $({}^iPr_3C_6H_2)SbHLi$ as a yellow powder [11]. The primary stibine is indefinitely stable under nitrogen and decomposed on heating only at 195 °C. In contrast, $PhSbH_2$ reacts with BuLi in the presence of $Me_2NCH_2CH_2NMe_2$ (temen) to give the Zintl anion $[Sb_7Li_3(temen)_3]$ [10]. The synthesis and structure of the very crowded $(2,4,6\text{-}{}^iPr_3C_6H_2)_3Sb$ ($<$C–Sb–C = 106.7°) have been reported [12].

The usual route to α,ω-distibinoalkanes is via reaction of stibide nucleophiles with the appropriate dihaloalkane [1,5]. The reaction of $C(CH_2Cl)_4$ with $NaSbPh_2$ in liquid ammonia yields $C(CH_2Cl_2)_2(CH_2SbPh_2)_2$ which has been the subject of an X-ray structure determination; substitution of the remaining chlorine does not appear to be possible [13]. Notably only three of the chlorines of $C(CH_2Cl)_4$ are replaced by reaction with $NaAsMe_2$ in thf [14]. The 1,3-$(PhC{\equiv}C)_2Sb(CH_2)_3Sb(C{\equiv}CPh)_2$ has been prepared from $PhC{\equiv}CLi$ and $Cl_2Sb(CH_2)_3SbCl_2$ and the X-ray structure reported [15].

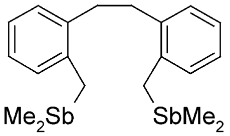
For distibines with other than $-(CH_2)_n-$ backbones, the yields are often very poor ($o\text{-}C_6H_4(SbMe_2)_2$ is a notable example [5]), and the reaction conditions are crucial to obtaining viable quantities of ligand. The reaction of $o\text{-}C_6H_4(CH_2Br)_2$ with $NaSbMe_2$ in liquid ammonia gave only 6% yield of $o\text{-}C_6H_4(CH_2SbMe_2)_2$, however using $o\text{-}C_6H_4(CH_2MgCl)_2$ and Me_2SbCl in thf resulted in an 88% yield of the distibine (Scheme 1) which usually does not require distillation [16].

In concentrated thf solution the diGrignard undergoes C–C coupling, and the new distibine $\{-CH_2\text{-}o\text{-}C_6H_4CH_2SbMe_2\}_2$ (I) has been obtained by kugelröhr distillation from the resulting mixture in high vacuum. (I) was structurally characterised as the $[Me_3PtI\{\{-CH_2\text{-}o\text{-}C_6H_4CH_2SbMe_2\}_2\}]$ complex [17]. The reaction of $NaSbPh_2$ with $o\text{-}C_6H_4(CH_2Br)_2$ failed to give any of the distibine, but the reaction of Ph_2SbCl with $o\text{-}C_6H_4(CH_2MgCl)_2$ gave $o\text{-}C_6H_4(CH_2SbPh_2)_2$ as a waxy solid (15%). High yields of *m*- and $p\text{-}C_6H_4(CH_2SbMe_2)_2$ were obtained via the appropriate diGrignard reagent [16]. Good yields (>50%) of the *m*- and *p*-phenylene distibines (*m*- or $p\text{-}C_6H_4(SbMe_2)_2$) are also obtainable via the a diGrignard route (Scheme 1) [16] but unfortunately this approach cannot be



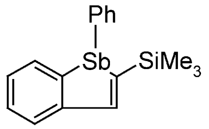
Scheme 1. Xylyl and phenylene distibines.

extended to o-$C_6H_4(SbMe_2)_2$ for which a high yield synthesis remains elusive.



(I)

Although inversion barriers at the heteroatom increase as group 15 is descended, studies of chiral stibines are rare. The racemic Sb-chiral (±)-1-phenyl-2-trimethylsilylstibindole (II) has been been complexed with di-μ-chlorobis[(*S*)-2-[1-(dimethylamino)ethyl]phenyl-C,N]dipalladium (III) and the resulting diastereoisomeric palladium complexes separated by chromatography [18]. The structures of the two isomers have been determined [18]. A series of R[2-(*S*)-(1-dimethylaminoethyl)phenyl(*p*-tolyl)stibines (R = Ph, 1-naphthyl, 9-phenanthryl) (IV) have been prepared and similarly resolved via their palladium complexes [19].



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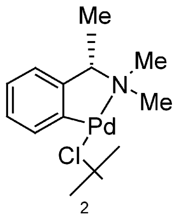

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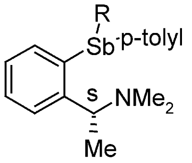

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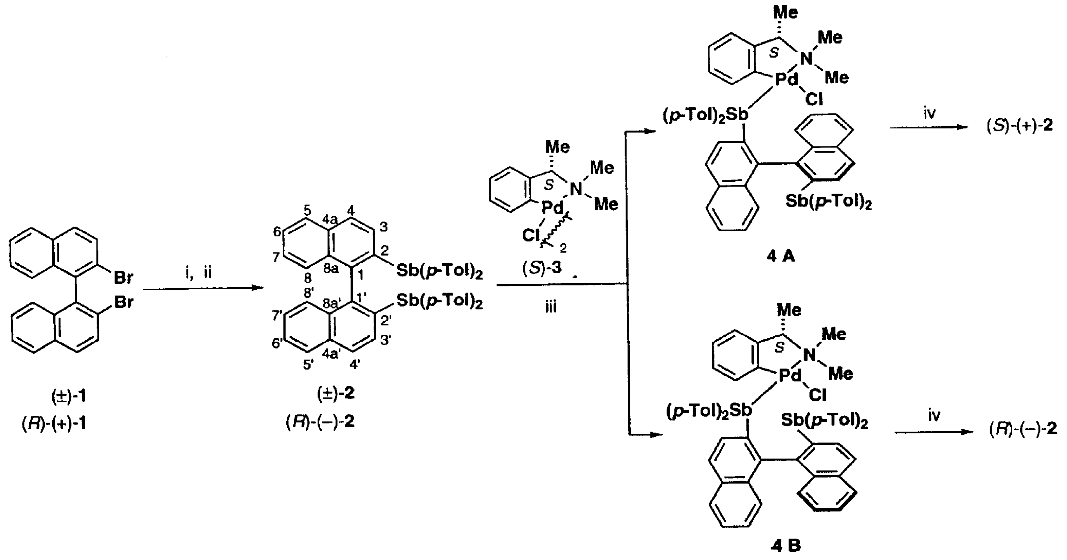
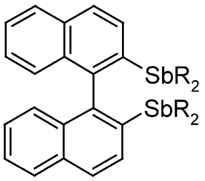


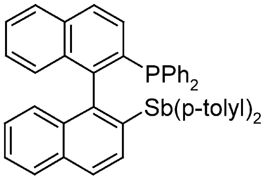
Reagents and conditions: (i) *tert*-butyllithium, ether, −80°C, 1 h; (ii) $(p\text{-Tol})_2SbBr$, ether, −80 to 0°C, 4 h, 65%; (iii) dichloromethane, room temp., 5 min, quantitative; (iv) 1,2-bis(diphenylphosphano)ethane, dichloromethane, room temp., 10 min, 94–96%

Scheme 2. Chiral distibines from ref. [20] by permission of Elsevier S.A.

Chiral distibines based upon the binaphthyl backbone (V) have been obtained recently (Scheme 2) [20,21]. These are readily made from the dilithiated binaphthyl and the appropriate R_2SbBr and resolved via their palladium complexes, with subsequent demetallation by $Ph_2PCH_2CH_2PPh_2$. The related P, Sb ligand (VI) has been prepared and resolved [22].



(V)



(VI)

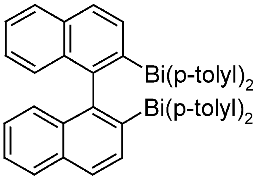
Attempted reduction of $(2,4,6\text{-}^i Pr_3C_6H_2)BiCl_2$ with $LiAlH_4$ gave $(2,4,6\text{-}^i Pr_3C_6H_2)Bi{=}Bi(2,4,6\text{-}^i Pr_3C_6H_2)$ rather than the primary bismuthine [11]. The chiral dibismuthine (VII) has been obtained as a racemic mixture by a similar route to the antimony analogue, but attempts to resolve it via the usual palladium reagent failed [22].

3. Spectroscopic and structural data

The application of spectroscopic techniques to the study of stibine and bismuthine complexes mostly resembles that in many other areas of coordination chemistry. This section deals with a limited number of aspects specific to these systems.

3.1. NMR

Although all naturally occurring antimony and bismuth isotopes have nuclear spins $I > 0$, reasonable absolute frequencies, and good sensitivities,[1] they also have substantial quadrupole moments, and in the low symmetry environments found in stibines and bismuthines and their complexes, fast quadrupolar relaxation results in unobservably broad resonances. The application of NMR spectroscopy in this area therefore devolves onto ^1H, ^{13}C or metal nuclei and many examples will be found in Sections 6 and 7. The fast quadrupolar relaxation of the antimony and bismuth nuclei also removes any spin–spin couplings to heteronuclei. One notable feature of the ^{13}C NMR data is that alkyl-carbon atoms directly bonded to Sb or Bi have low frequency chemical shifts, often to low frequency of TMS, a “heavy atom effect” also seen with neighbouring elements including Pb, Te and I [23]. For arylstibines, the *ipso*-C is typically found in the region ca. δ 133–140, but there has been some confusion about the *ipso*-C resonance in arylbismuthines, values ranging from ca. δ 130–155 having been quoted. Re-examination of the $^{13}C\{^1H\}$ spectrum of purified $BiPh_3$ found the *ipso*-C resonance at 155.5 which shifts only slightly on coordination of the bismuthine [24]. The ready decomposition in solution of many stibine and especially bismuthine complexes, means that often resonances are present from decomposition products and this can be highly misleading.



(VII)

3.2. Mass spectrometry

The relatively weak C—Sb and C—Bi bonds often result in extensive fragmentation, although the problems have been reduced for the complexes by the introduction of softer ionisation methods like FAB, APCI or ES^+. Bismuth is monoisotopic (^{209}Bi), but for antimony the presence of two abundant isotopes differing by 2 a.m.u. (^{121}Sb 57.3%, ^{123}Sb 42.7%) produces characteristic isotope patterns, which are extremely useful in identifying fragment ions and unequivocally deducing the number of antimony atoms present.

3.3. Mőssbauer spectroscopy

The application of the 37.2 keV transition $7/2 \rightarrow 5/2$ of ^{121}Sb to study the antimony environment in stibine complexes was discussed in a previous review [1]. Although a few more examples of the application of this technique have been described (Section 6), the broad lines, the limited stereochemical information obtainable, and the sophisticated equipment required, means that use of the technique has been restricted to a few groups.

3.4. X-ray crystallography

As in other areas of molecular chemistry, the last 15 years have seen a great increase in the quantity of X-ray crystallographic work. At the time of the previous review [1] ca. 40 examples of stibine complexes (almost all containing $SbPh_3$) and two bismuthine complexes had been characterised by single crystal X-ray studies. The much greater number of examples now reported, and the often higher precision has made it possible to look in some detail at systematic trends. The results of this are discussed in Section 4.

4. Ligand properties

4.1. Bonding and steric effects

The last 50 years have seen an enormous amount of work exploring the nature of the transition metal-phosphorus bond in

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[1] ^{121}Sb $I = 3/2$ 57.3%, $\Xi = 23.93$ MHz, $Q = -0.53 \times 10^{-28}$ m^2, $D_c = 5.2 \times 10^2$; ^{123}Sb $I = 3/2$ 42.7%, Ξ 12.96 MHz, $Q = -0.68 \times 10^{-28}$ m^2, $D_c = 1.11 \times 10^2$; ^{209}Bi $I = 9/2$, 100%, $\Xi = 16.07$ MHz $Q = -0.4 \times 10^{-28}$ m^2, $D_c = 7.7 \times 10^2$. J. Emsley, The Elements, Oxford, 1989.

tertiary phosphine complexes, and the models that have resulted are then carried over to M–AsR_3 or M–SbR_3 bonds with minor modifications. It is not appropriate to review all this work here, we merely summarise the current view which is that the M–PR_3 bond has a σ component involving donation of the lone pair to the metal and a π component involving transfer of metal electron density into an orbital with P–C σ^* character or a symmetry allowed combination of P–C σ^* and 3d orbitals [25]. A consequence of this model is that increased π acceptance leads to a shorter M–P but a longer P–C bond and some small increase in the C–P–C angle. The successful test of this model is via X-ray crystallographic data on redox pairs $[ML_nX_y]^{0/+}$ [25], although the differences are small, and only slighter greater than experimental uncertainty in the bond lengths. For main group metals or d^0 transition metals only the σ component is present. The bonding models developed for phosphines are carried over to the heavier analogues with some modifications. For example, the ns/np orbitals become more separated in energy as group 15 is descended, most obviously demonstrated in the C–E–C angles along the series PPh_3 103°, $AsPh_3$ 100°, $SbPh_3$ 96°, $BiPh_3$ 94°; as the E–C bonds have a higher p character. The weaker bonding as the series is descended was attributed to higher s character in the lone pair, which has less directional properties and is less available. Reduced π acceptance by the heavier analogues is usually attributed to lower electronegativity of E and more diffuse orbitals.

A detailed study of M-PPh_3 fragments by Orpen [26] utilising some 1860 examples taken from the CSD, found a correlation of the P–C distance with <C–P–C, but concluded that on coordination to a transition metal the geometry of PPh_3 was little changed. During studies of distibinomethane complexes, where X-ray structures of a number of complexes containing M(η^1-$Ph_2SbCH_2SbPh_2$) units were determined, it was notable that whilst the geometry of the "free" –$SbPh_2$ group was little changed from that of the uncoordinated distibine, the coordinated groups uniformly showed an increase in C–Sb–C of ≤8° [27]. This is rationalised in terms of greater Sb p character in the M–Sb bond and correspondingly, less p and more s character in the Sb–C bonds (on a hybridisation model the bonding in the SbC_3 group in the free molecule which is predominently antimony p^3 changes on coordination towards sp^3). A survey of a much larger number of M–$SbPh_3$ complexes from the CSD showed this effect was characteristic of stibine complexes, in that on coordination the C–Sb–C angles widen, and also the Sb–C bonds shorten [28]. The results are shown graphically in Fig. 1 [28]. Note that the last point potentially conflicts with predictions that increased M–Sb π-bonding would lengthen Sb–C. Often the quoted Sb–C bond lengths are not of high precision, and we know of no studies of the structures of redox pairs containing stibines. The effects are even more pronounced in M-BiR_3 (although examples are even fewer) [24]. Recently, structural data have become available on [R_3M-ER_3] (M = Ga or In; E = Sb or Bi) (see Section 6.7) which also show an increase in <C–E–C on coordination, and since these have no π component to the bonding, this is strong support for the effect being due to changes in the orbital composition of the σ-bonds.

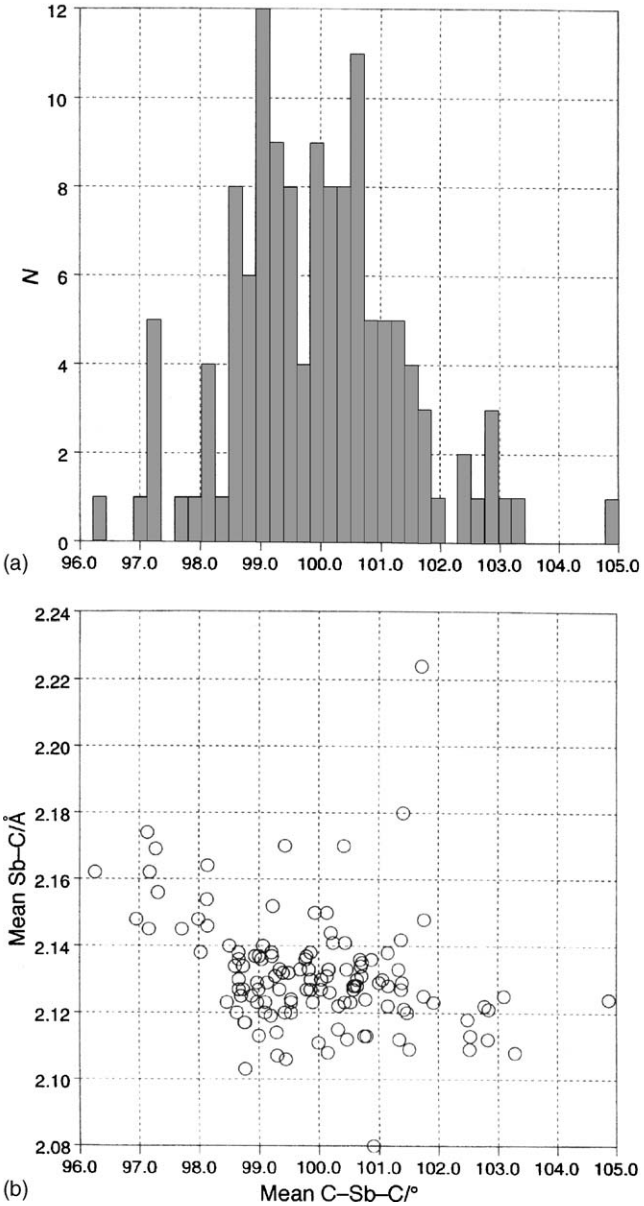


Fig. 1. (a) Histogram showing the average C–Sb–C angle (°) for Ph_3Sb–E (E = transition element); (b) scattergram plot of d(Sb–C) versus average C–Sb–C angle. From ref. [28] by permission of the Royal Society of Chemistry.

Methods of experimentally ranking the electronic properties of group 15 ligands are well known, e.g. Tolman's electronic parameter based upon observation of the υ(CO) (a_1) stretching mode in [$Ni(CO)_3L$] [29], or the δ(^{13}C) NMR resonance of the carbonyl groups in the same complexes [30]. Both criteria applied to a variety of stibines and distibines show that such ligands place less electron density into the π^*(CO) orbitals than phosphine analogues, and the experimental values also show the usual trends with R group [16,31]. The failure of some bismuthines to form nickel carbonyl complexes rules out this approach, but similar data from [$W(CO)_5(ER_3)$] place bismuthines lower in ability than stibines to transfer electron density to the carbonyls [32]. The high toxicity of nickel carbonyl makes its routine use unattractive, and it has been suggested that Vaska type complexes *trans*-[$Rh(CO)(ER_3)_2Cl$] could be used instead to rank the properties of the ER_3 ligands [33,34], but whilst this seems to work well for phosphines, there are anomalies in the data with AsR_3 and SbR_3 complexes.

Steric effects of group 15 ligands are usually treated via Tolman's cone angle model [35]. Tolman's original work was based only upon the effects of R groups upon the cone angles in phosphines, but subsequently cone angles for arsines and stibines were calculated, and the listing [36] shows that as group 15 is descended the cone angles decrease by a few degrees. Typically the rather smaller cone angles inferred for stibines has often been used to explain higher coordination numbers in their complexes. There are two questions related to this assumption: firstly the quoted cone angles are only slightly smaller, but more significantly, given the widening of the <C–Sb–C on coordination, the magnitude of which varies from complex to complex (see above), it is unclear that the "real cone angle" of a stibine is smaller, or even what value should be taken as the norm.

Whilst the dominance of steric factors with very bulky ligands and of electronic factors with small ligands in low coordination number environments is usually clear, the debate continues about how to separate electronic and steric effects and their relative significance in most complexes between these extremes.

Among the observed differences noted in stibine complexes compared to lighter analogues are:

1. Higher coordination numbers.
2. Less dissociation in solution.
3. More labile ligands.
4. Different *cis–trans* isomer distributions.

Whilst one cannot rule steric effects contributing to the observed differences, most of these can be rationalised in terms electronic effects, i.e. stibines placing less electron density on the metal centres than the phosphine or arsine analogues, which in turn can be related to both reduced σ donation and reduced π acceptance. These quite different electronic properties would account for the points above and for the very different organometallic chemistry promoted by stibines [3]. How the recent observation of bridging stibines fits into these bonding models must await data on a larger number of systems.

4.2. *Trans effect and trans influence*

There has been recent interest in the relative position of group 15 ligands in these two series. The *trans* effect (the effect of a coordinated ligand on the rate of substitution of the ligand *trans* to it in a molecule) has been mostly studied for planar Pt(II) complexes. The kinetics of iodide displacement in $[PtI_3L]^-$ (L = PPh_3, $AsPh_3$, $SbPh_3$) by pyridine or substituted pyridines have been studied by stopped-flow spectrophotometry [37,38] and result in a *trans* effect series $SbPh_3 > PPh_3 > AsPh_3$.

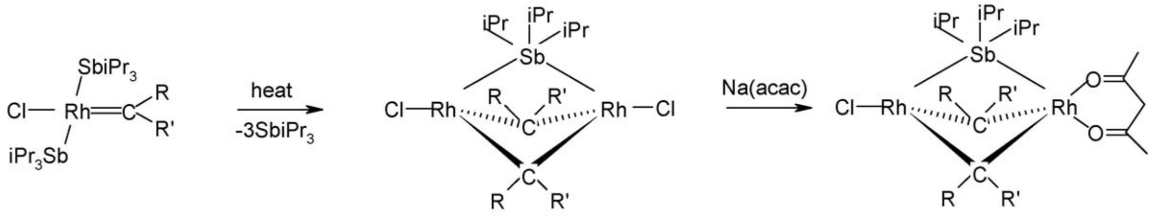
Detailed rationalisation of this series needs data on a larger range of systems, and we note that a study of the rate of water displacement in *trans*-$[Ru(NH_3)_4L(H_2O)]^{2+}$ by imidazole gave a *trans* effect series $PPh_3 > AsPh_3 > SbPh_3$ [39] suggesting that the metal centre plays a significant role.

The *trans* influence (the effect of a coordinated ligand on the M–L bond strength/length *trans* to it) has been explored in the past using IR/Raman or NMR data and it was usually concluded that the *trans* influence decreased down group 15. The increasing availability of high quality X-ray data allows direct comparison of a common M–L bond as a function of varying *trans* ligands. Steric effects and interactions between *cis* ligands are hard to eliminate from comparisons and when only small differences are apparent in the experimental data, these qualifications should be remembered. It is generally accepted that group 15 ligands are higher in the *trans* influence series that thioethers or halides, and current interest has revolved around disputes of the order within group 15. To limit data to the best studied systems, square planar Pt(II), one can compare Pt–I bonds *trans* to EPh_3 in the three compounds $[PtI_3(EPh_3)]^-$ which are E = P (2.662(3) Å), E = As (2.6585(8) Å), E = Sb (2.637(2) Å) [37,38], giving the series of increasing *trans* influence as $PPh_3 > AsPh_3 > SbPh_3$. In *cis*-$[PtBr_2(PPh_3)(SbPh_3)]$ the $Pt–Br_{trans\,Sb}$ is 2.573(3) Å and $Pt–Br_{trans\,P}$ 2.583(3) Å, which are barely different within the 3σ criteria [40], and it notable that in this complex the angles about Pt are distorted <P–Pt–Br = 177°, but Sb–Pt–Br = 171°. Comparison of a wider range of systems often shows little difference on $M–L_{trans\,E}$ as ER_3 is varied, probably indicating how difficult it is to separate out a single effect in real systems.

The $[M(CO)_5(EPh_3)]$ (M = Cr, Mo, W, E = P, As, Sb, Bi) have been studied in great detail and X-ray structures have been determined for all 12 complexes which are isomorphous ([32,41,42] and refs therein). Comparison of the distances $M–C_{trans\,E}$ for fixed M show small and erratic changes and no clear pattern emerges. Similarly comparing the A_1 υ(CO) frequency for the CO group *trans* to EPh_3 shows values which differ by $\leq 5\,cm^{-1}$ for fixed M, and an irregular pattern as E is varied [32,41]. It seems that the electron distribution within the $M(CO)_5$ unit is little changed, possibly since both σ donation and π acceptance are believed to diminish down group 15 it may be that the effects approximately cancel out in these compounds. However, if one examines the ^{13}C NMR spectra, specifically the $^1J(^{13}C–^{183}W)$ coupling constants in $[M(CO)_5(EPh_3)]$, one finds that whilst the values on the *cis*-CO's are invariant (∼126 Hz), those on the $CO_{trans\,E}$ diminish Bi (183 Hz) > Sb (162 Hz) > As (155 Hz) > P (140 Hz) which are consistent with a clear *trans* influence diminishing as group 15 is descended ([32] and references therein).

5. Bridging stibines, the unique Rh–(μ-SbR_3)–Rh systems

Standard textbooks usually contain a list of π-acids, the common examples including CO, NO, RNC, PR_3, AsR_3 and SbR_3, which coordinate as σ-donors and π-acceptors to a wide variety of metal centres. In addition to binding as a terminal ligand, carbon monoxide has been known for many years to be able to bridge two (or more) metal centres, and both symmetric and asymmetric (semi-bridging) linkage modes have been identified by X-ray crystallography. In marked contrast, despite the thousands of phosphine complexes characterised (and a significant but smaller number of arsines and stibines), group 15 donor ligands were only found in terminal positions. The view naturally



Scheme 3. The bridging coordination modes of stibines.

became accepted (although never theoretically justified) that bridging by neutral ER_3 ligands did not happen. This view has been changed by the initially serendipitous discovery by Werner and co-workers, who found that on heating, the green rhodium(I) carbene *trans*-[RhCl(Sb^{i}Pr$_3$)$_2$(=CPh$_2$)] (Rh–Sb = 2.5843(5), 2.5633(5) Å) turned red, forming [Rh$_2$Cl$_2$(Sb^{i}Pr$_3$)(=CPh$_2$)$_2$] (Scheme 3), and a subsequent X-ray study showed that the latter contained both bridging carbene and bridging stibine ligands (Fig. 2) (Rh–Sb = 2.6868(5), 2.6695(5) Å) [43,44]. Subsequent work showed the Sb^{i}Pr$_3$ could be exchanged for $SbMe_3$, $SbEt_3$ or $SbBz_3$, which also entered the bridging position [44,45]. Treatment of [Rh$_2$Cl$_2$(μ-Sb^{i}Pr$_3$)(μ-=CPh$_2$)$_2$] with one equivalent of Tl(acac) gave [Rh$_2$Cl(acac)(μSb^{i}Pr$_3$)(μ-=CPh$_2$)$_2$] (Fig. 3) in which the stibine (and the carbene) bridges are asymmetric (Rh1–Sb = 2.498(1) Å, Rh2–Sb = 2.846(1) Å) [46]. The further elegant work of Werner's group is described in detail in a very recent review [3], which also records how routes were found [47–51] to introduce bridging PR_3 and recently $AsMe_3$ groups via displacement of the SbR_3. In view of this detailed account by the author [3], we will not describe the work further in the present article.

All the examples of complexes with bridging ER_3 ligands thus far are of rhodium and also have carbene bridges. It remains to be established if this coordination mode can be extended to other metal systems (Pd and Ir seem the most likely targets), and whether ER_3 ligands alone (or with a M–M bond) can link two metal centres. The fact that bridging group 15 ligands proved elusive for so long, probably indicates that a large number of examples will not be found, but the remarkably robust rhodium systems, suggest that other examples should be forthcoming if the right synthetic strategy can be found.

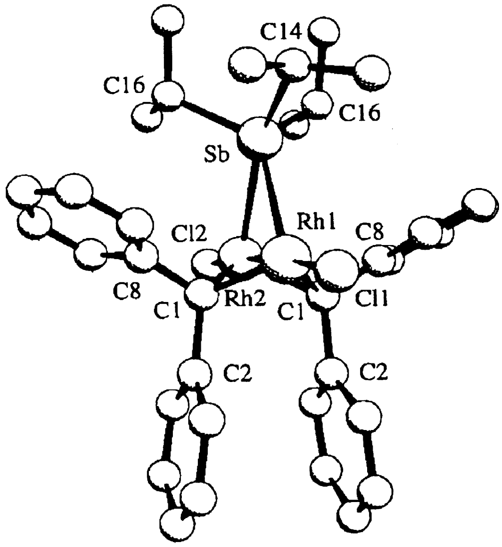


Fig. 2. Structure of [Rh$_2$Cl$_2$(=CPh$_2$)$_2$(Sb^{i}Pr$_3$)] from ref. [44] by permission of VCH-Wiley.

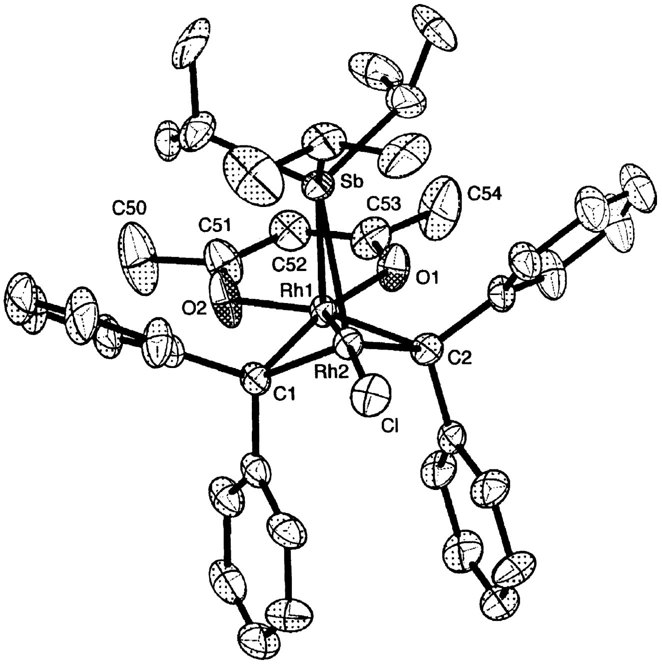


Fig. 3. Structure of [Rh$_2$Cl(acac)(=CPh$_2$)$_2$(Sb^{i}Pr$_3$)] from ref. [44] by permission of VCH-Wiley.

6. Tertiary monostibine complexes

6.1. Groups 3–5

The stibine complexes of these elements remain very little explored. There are no compounds with group 3 metals, and apart from a few substituted vanadium carbonyl complexes, groups 4 and 5 are represented by some ill-defined halide adducts mentioned in the older literature [1]. An example of the latter is the purple complex formulated $TiCl_4(SbPh_3)$, recently used to moderate the Lewis acidity of $TiCl_4$ in some organic transformations [52]. No characterisation of the complex was given in the report.

Orange [Et$_4$N][Ta(CO)$_5$(SbPh$_3$)] is formed by displacement of the ammonia from [Et$_4$N][Ta(CO)$_5$(NH$_3$)] with $SbPh_3$ in liquid ammonia [53].

Table 1
Seven coordinate Mo(II) or W(II) complexes

Compound	Comment	Ref.
$[\{Mo(\mu\text{-}I)Br(CO)_3(SbPh_3)\}_2]$		[58]
$[MoIBr(CO)_3(SbPh_3)L]$	L = PPh_3, $AsPh_3$, $SC(NMe_2)_2$, MeCN	[58]
$[MoCl(GeCl_3)(CO)_3(SbPh_3)L]$	L = $SbPh_3$, MeCN,	[59]
$[MoCl(GeCl_3)(CO)_2(SbPh_3)L_2]$	L = PPh_3, MeCN,	[59]
$[MI_2(CO)_3(imidazole)(SbPh_3)]$	M = Mo, W	[60]
$[WCl(ICl_2)(CO)_3(SbPh_3)(MeCN)]$		[61]
$[\{W(\mu\text{-}Cl)(ICl_2)(CO)_3(SbPh_3)\}_2]$		[61]
$[M_2I_4(CO)_6(SbPh_3)\{MeC(CH_2PPh_2)_3\}]$	M = Mo, W	[62]
$[WI_2(CO)_3(L)(SbPh_3)]$	L = MeCN, EtCN, BuCN, $PhCH_2CN$, 1,2-$C_6H_4(CH_2CN)_2$	[63,64,69]
$[MI_2(CO)_3(4,4'\text{-bipy})(SbPh_3)]$	M = Mo, W	[65]
$[MI_2(CO)_3(pyrazole)(SbPh_3)]$		[66]
$[MoClI(CO)_3(SbPh_3)_2]$		[67]
$[WI(CO)_3(S_2PCy_3)(SbPh_3)]$		[68]
$[MBr_2(CO)_3(MeCN)(SbPh_3)]$	M = Mo, W	[69]

6.2. Groups 6–7

The complexes of group 6 metals are mostly substituted carbonyl derivatives in oxidation states 0 (Cr, Mo or W) or II (Mo or W), and as in earlier groups the halide complexes remain little investigated. The $[M(CO)_5(SbMe_3)]$ (M = Cr, Mo or W) have been prepared, the first two from $[M(CO)_5(thf)]$ and $SbMe_3$ in thf, the last from $W(CO)_6$ and $SbMe_3$ in diglyme [54]. The ^{121}Sb Mőssbauer spectra of $[M(CO)_5(SbR_3)]$ (R = Me or Ph) have been recorded and the trends in isomer shift correlated with the relative σ donation from antimony, which appears to vary with the Allred-Rochow electronegativity of the metal centre [54]. The X-ray structures of $[M(CO)_5(SbPh_3)]$ (M = Mo or W) have been determined [41]. The structures of $(Me_3Si)_3Sb$ and $[Cr(CO)_5\{Me_3Si)_3Sb\}]$ have been compared [55]: notably the Si–Sb–Si angles open up by ca. 4° on coordination (see also Section 4).

A rare example of a Cr(III) stibine is $[CpCrCl_2(SbEt_3)]$ included in a larger study of the synthesis and spectroscopic properties of a series of such compounds with a wide variety of Lewis bases [56]. The $[CpMo(CO)_2(SbPh_3)_2]BF_4$ complex is obtained by oxidation of $[\{CpMo(CO)_3\}_2]$ with $[Fe(Cp)_2]BF_4$ in the presence of $SbPh_3$ [57].

There are a large number of seven-coordinate mixed ligand complexes of Mo(II) and W(II) reported by Baker and co-workers containing one or rarely two $SbPh_3$ groups. The interest from the point of view of the stibine is small but for completeness the new examples are listed in Table 1. Some triphosphine bridged dimers, for example $[WI_2(CO)(RC{\equiv}CR)\{PhP(CH_2CH_2PPh_2)_2\}L']$ (L′ = $MI_2(CO)_3(SbPh_3)$ M = W or Mo) have also been described [70]. The structures of $[WX_2(CO)_3(MeCN)(SbPh_3)]$ (X = Br or I) are best described as distorted capped trigonal prisms with one halide providing the cap on a rectangular face [69].

The reaction of $[Mn_2(CO)_{10}]$ with $SbPh_3$ and Me_3NO gave orange-brown $[Mn_2(CO)_9(SbPh_3)]$ shown by an X-ray structural study to be axially substituted (Fig. 4) [71]. Photolysis of a mixture of $[Mn_2(CO)_{10}]$ and $SbPh_3$ in toluene, followed by chromatography on silica gave $[Mn_2(CO)_9(SbPh_3)]$ and orange-yellow $[Mn_2(CO)_8(SbPh_3)_2]$. The latter was identified as an *ax*, *ax* isomer since it showed only a single CO stretch in the IR spectrum. Heating $[Mn_2(CO)_{10}]$ with $SbPh_3$ in boiling xylene gave little reaction [71], and old reports of a paramagnetic $[Mn(CO)_4(SbPh_3)]$ formed in this way appear erroneous [1].

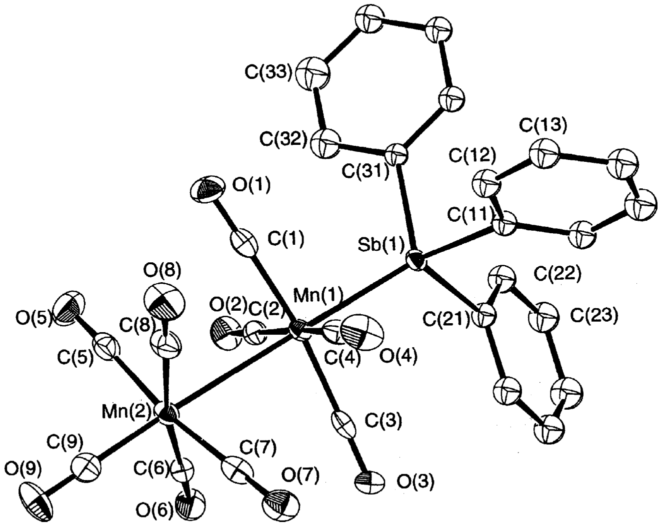


Fig. 4. Structure of $[Mn_2(CO)_9(SbPh_3)]$ from ref. [71] by permission of Elsevier Science S.A.

Photolysis of a mixture of $[Re_2(CO)_{10}]$ and $SbPh_3$ gave only *ax*-$[Re_2(CO)_9(SbPh_3)]$ consistent with the greater difficulty of displacing CO groups from the 5d metal centre [71]. The carbonyl cation $[Mn(CO)_5(SbPh_3)]CF_3SO_3$ is formed from $[Mn(CO)_5Cl]$, $AgCF_3SO_3$ and $SbPh_3$ in dichloromethane, and an X-ray study revealed a pseudo-octahedral cation. A detailed study of the $[Mn(CO)_5Cl]$-$SbPh_3$ reactions showed that when the reactants are stirred together in a 1:1 ratio in $CHCl_3$ at room temperature the product is *cis*-$[Mn(CO)_4Cl(SbPh_3)]$, whilst a 1:2 ratio refluxed in $CHCl_3$ gives *fac*-$[Mn(CO)_3Cl(SbPh_3)_2]$. Prolonged reflux of the latter partially converts it into the *mer-trans*-$[Mn(CO)_3Cl(SbPh_3)_2]$: no other isomers were observed. The identity of the isomers follows from their IR spectra and was confirmed for *mer-trans*-$[Mn(CO)_3Cl(SbPh_3)_2]$ by an X-ray structure, although there is disorder between the Cl and one CO group [71]. The corresponding reactions of $[Re(CO)_5Cl]$ with $SbPh_3$ are much slower and gave *cis*-$[Re(CO)_4Cl(SbPh_3)]$ and *fac*-$[Re(CO)_3Cl(SbPh_3)_2]$, although the latter does not isomerise on heating. The structure of *fac*-$[Re(CO)_3Cl(SbPh_3)_2]$ (Fig. 5) was also reported [71]. The dimer $[Re_2(\mu\text{-}Br)(\mu\text{-}PCy_2)(CO)_7(SbPh_3)]$ was the unexpected product from reaction of $Li[Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_7(PhCO)]$ with $[Ph_4Sb]Br$: in contrast Ph_4P^+ or Ph_4As^+ cations are metallated by the rhenium to give zwitterionic compounds [72].

The reaction of $[NBu_4][Re(NO)X_5]$ (X = Cl or Br) with $SbPh_3$ gave *mer*-$[Re(NO)X_2(SbPh_3)_3]$; recrystallisation of the bromocomplex from $CHCl_3$ produced a small yield of $[ReClBr_2(SbPh_3)_3]$ [73]. The corresponding reactions with PPh_3 and $AsPh_3$ yield $[ReCl_3(NO)L_2]$ (L = PPh_3, $AsPh_3$) compounds, the tri-substitution of the stibine being attributed by the

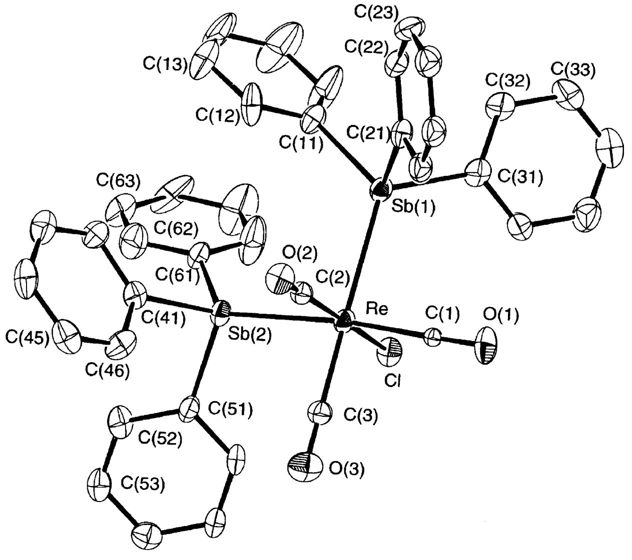


Fig. 5. Structure of *fac*-[Re(CO)$_3$Cl(SbPh$_3$)$_2$] from ref. [71] by permission of Elsevier Science S.A.

authors to the reduced steric demands of SbPh$_3$. It seems more likely to be due to the lower ability of the stibine to stabilise the higher oxidation state with nitrosyl co-ligands. The *mer-trans*-[ReCl$_2$Br(SbPh$_3$)$_3$] complex is also known [74].

6.3. Group 8

The reaction of Me$_3$SbBr$_2$ with [Fe(CO)$_3$(PPh$_3$)]$^{2-}$ gave *trans*-[Fe(CO)$_3$(PPh$_3$)(SbMe$_3$)] [75], whilst [Fe$_4$(CO)$_{13}$]$^{2-}$ gave a low yield of the known complex [Fe(CO)$_4$(SbMe$_3$)] [76]. The ^{57}Fe and ^{121}Sb Mőssbauer spectra of [Fe(CO)$_4$L] (L = SbMe$_3$ SbPh$_3$) have been reported [54].

A number of organo-iron complexes have been described, most as parts of large compilations containing other group 15 ligands: [(η^5-C$_9$H$_7$)Fe(CO)$_2$(SbPh$_3$)]BF$_4$ [77], [(η^5-^{t}Bu$_2$C$_5$H$_3$)Fe(CO)(SbPh$_3$)(SCOR)], [(η^5-^{t}BuC$_5$H$_4$)Fe(CO)(SbPh$_3$)(SCOR)], [(η^5-C$_5$H$_5$)Fe(CO)(SbPh$_3$)(SCOR)] [78], [(η^5-C$_5$H$_5$)Fe(CO)(SbPh$_3$)(SeCOR)] [79], [(η^5-C$_5$H$_5$)Fe{P(OMe)$_3$}$_2$(SbPh$_3$)]PF$_6$ (X-ray structure) [80].

Orange [Ru(CO)$_4$(SbMe$_3$)] is conveniently made by photolysis of a mixture of Ru$_3$(CO)$_{12}$ and SbMe$_3$ in hexane [54]. One product from the reaction of Ru$_3$(CO)$_{12}$ and SbPh$_3$ at room temperature was [(Ph$_2$Sb)Ru$_3$(CO)$_{10}$(PhCO)] identified by a crystal structure determination [81]. In contrast, [Ru$_3$(CO)$_{10}$(Ph$_2$PCH$_2$PPh$_2$)] and SbPh$_3$ give the simple substitution product [Ru$_3$(CO)$_9$(Ph$_2$PCH$_2$PPh$_2$)(SbPh$_3$)] [81]. The mixed metal tetrahedral core cluster anion [H$_2$Ru$_3$Ir(CO)$_{12}$]$^-$ undergoes loss of one carbonyl group from Ru on reaction with SbPh$_3$; the product is readily protonated to the neutral trihydride [H$_3$Ru$_3$Ir(CO)$_{11}$(SbPh$_3$)] [82]. Other stibine clusters include [Ru$_4$Se$_2$(CO)$_{10}$(SbPh$_3$)] [83] and the alkylidyne [H$_3$Ru$_3$(μ^3-CNMeBz)(CO)$_7$(SbPh$_3$)$_2$] [84].

There are many studies of organo-ruthenium complexes, most based upon (η^5-C$_5$H$_5$)Ru or (η^6-arene)Ru cores which contain SbPh$_3$, often as one in a series of neutral donor types. In many of these the stibine plays a minor spectator role or fills a coordination site, and the chemical interest in the complexes is located elsewhere. A range of such complexes is listed in Table 2 for completeness.

The [(η^5-C$_5$H$_5$)Ru(SbPh$_3$)(MeCN)$_2$]PF$_6$, on heating in nitromethane solution, rearranges into a number of products, two of which contain η^6-Ph coordination of the stibine, [(η^5-C$_5$H$_5$)Ru(η^6-C$_6$H$_5$SbPh$_2$)]$^+$ and [(η^5-C$_5$H$_5$)Ru(η^6-C$_6$H$_5$SbPh$_2$)Ru(η^5-C$_5$H$_5$) (SbPh$_3$)(MeCN)]$^{2+}$; in the latter, one ruthenium is bonded to the Cp ring, the MeCN and Sb-coordinated stibine, whilst the second has a sandwich structure composed of the Cp and the phenyl group of the stibine [96].

The [(η^5-C$_5$Me$_5$)Ru(Sb^{i}Pr$_3$)Cl$_2$] is made by reaction of [{(η^5-C$_5$Me$_5$)RuCl$_2$}$_2$] with Sb^{i}Pr$_3$ (Fig. 6) and is reduced by

Table 2
Oreanoruthenium complexes

Complex	Comment	Ref.
[Ru(C$_{10}$H$_{16}$)(SbPh$_3$)Cl$_2$]	C$_{10}$H$_{16}$ is a bis(allyl)	[85]
[(η^6-C$_6$Me$_6$)Ru(SbPh$_3$)Cl$_2$]		[86]
[{(η^5-C$_5$H$_5$)Ru(SbPh$_3$)$_2$}$_2$ μ-pyrazine][PF$_6$]$_2$		[87]
[(η^6-*p*-cymene)Ru(SbPh$_3$)Cl$_2$]		[88]
[(η^6-*p*-cymene)Ru(SbCy$_3$)Cl$_2$]		[89]
[(η^5-C$_5$H$_5$)Ru(NO)(SbPh$_3$)Cl]		[90]
[(η^5-C$_5$H$_5$)Ru(SbR$_3$)(MeCN)$_2$]PF$_6$	R = Ph, ^{n}Bu	[91,92]
[(η^5-C$_5$H$_5$)Ru(SbPh$_3$)$_2$Cl]	Reaction with alkynes	[93]
[(η^5-C$_5$H$_5$)Ru(SbPh$_3$)L]	L = *N*-cyanodithiocarbimate(2-)	[94]
[(η^5-C$_5$H$_5$)Ru(SbPh$_3$)L]BF$_4$	L = various diamines	[95]
[(η^5-C$_5$H$_5$)Ru(SbPh$_3$)L]BF$_4$	L = pyridyl-azine type ligand	[96]
[(η^5-C$_5$H$_5$)Ru(SbPh$_3$)$_{3-n}$(MeCN)$_n$]PF$_6$	n = 1, 2	[97]
[(η^6-*p*-cymene)Ru(SbPh$_3$)$_2$Cl]BF$_4$		[98]
[(η^6-arene)Ru(SbPh$_3$)(L)Cl]BF$_4$	Arene = C$_6$H$_6$, C$_6$Me$_6$, *p*-cymene, L = 1-(4-cyanophenyl)imidazole	[99]
[(η^5-C$_5$H$_5$)Ru(SbPh$_3$)L]PF$_6$	L = maleonitriledithiolate	[100]
[Ru(CO)$_2$(SbPh$_3$)(η^5-7,8-C$_2$B$_9$H$_{11}$)]		[101]
[(η^6-arene)Ru(SbPh$_3$)$_2$H]BF$_4$	Arene = C$_6$H$_6$, C$_6$Me$_6$, *p*-cymene	[102]
[(η^5-C$_5$Me$_5$)Ru(SbPh$_3$)(H$_2$)$_2$]BF$_4$		[103]
[(η^5-C$_5$Me$_5$)Ru(SbPh$_3$)$_2$H$_2$]BAr$_4$		[103]
[(η^5-C$_5$Me$_5$)Ru(SbPh$_3$)$_2$H]		[103]
[RuH(CO)(SbPh$_3$){S$_2$C$_2$(CN)$_2$}Ru(SbPh$_3$)(η^5-C$_5$H$_5$)]		[104]

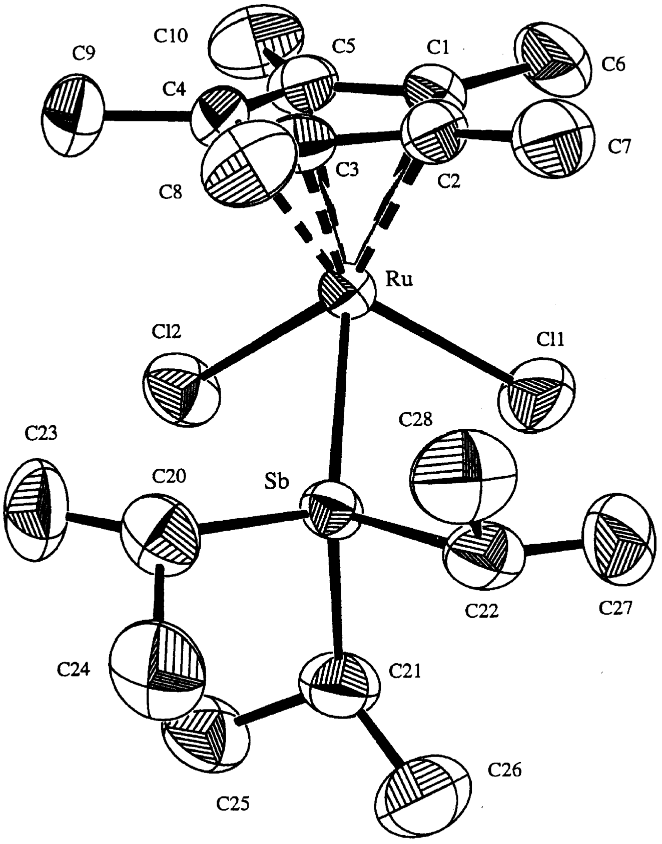


Fig. 6. Structure of [(η^5-C_5Me_5)$RuCl_2$(Sb^iPr_3)] from ref. [105] by permission of VCH.

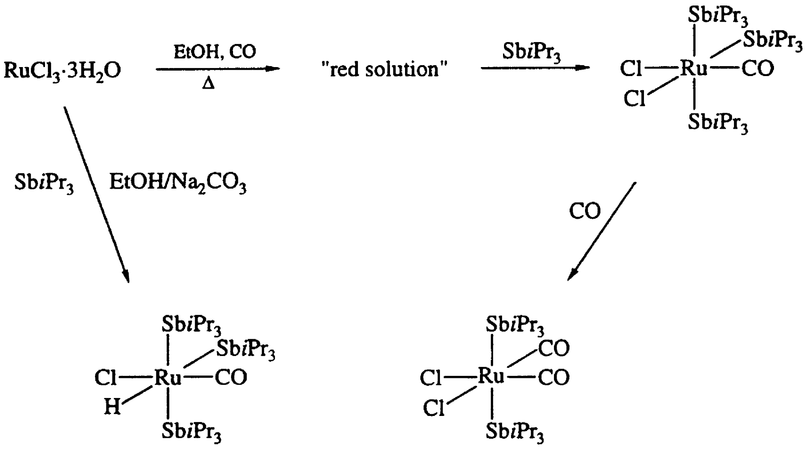
Mg/Hg to the 16e [(η^5-C_5Me_5)Ru(Sb^iPr_3)Cl] [105]. The latter is better made from [{(η^5-C_5Me_5)RuCl}$_4$] and four equivalents of Sb^iPr_3, and adds CO to form [(η^5-C_5Me_5)Ru(Sb^iPr_3)(CO)Cl]. Using only two equivalents of Sb^iPr_3 in the first reaction affords the unsymmetrical dimer, [(η^5-C_5Me_5)Ru(Sb^iPr_3)(μ-Cl)$_2$Ru(η^5-C_5Me_5)] [105].

Treatment of [{$RuCl_2$(COD)}$_n$] with Sb^iPr_3 in ^{i}PrOH in the presence of Na_2CO_3 gives [RuH_2(H_2)(Sb^iPr_3)$_3$], which is converted to [RuHCl(H_2)(Sb^iPr_3)$_3$] by HCl [106]. [RuH_2(H_2)(Sb^iPr_3)$_3$] reacts with CO to give the monocarbonyl [Ru(CO)(H)$_2$(Sb^iPr_3)$_3$] and with C_2H_4 a mixture of [RuH_2(C_2H_4)$_2$(Sb^iPr_3)$_2$] and [RuH_2(C_2H_4)(Sb^iPr_3)$_3$] which cannot be separated, although under an argon atmosphere the latter is the only product [107]. Propene and [RuH_2(H_2)(Sb^iPr_3)$_3$], form the bis(allyl) [Ru(η^3-C_3H_5)$_2$(Sb^iPr_3)$_2$] the structure of which shows an essentially tetrahedral geometry at Ru. From [{Ru(*p*-cymene)Cl_2}$_2$] and Sb^iPr_3 the [Ru(*p*-cymene)(Sb^iPr_3)Cl_2] forms, converted by more ligand in the presence of NH_4PF_6 to [Ru(*p*-cymene)(Sb^iPr_3)$_2$Cl]PF_6, but all attempts to displace the *p*-cymene were unsuccessful [106]. From $RuCl_3{\cdot}3H_2O$ and Sb^iPr_3 in ethanol it is possible to isolate [Ru(CO)HCl(Sb^iPr_3)$_3$], [Ru(CO)$_2$$Cl_2$($Sb^iPr_3$)$_2$] or [Ru(CO)$Cl_2$($Sb^iPr_3$)$_3$] depending upon the reaction conditions (Scheme 4) [106], the structure of the last being determined by an X-ray study. [Ru(CO)HCl(Sb^iPr_3)$_3$] gives the stibine substitution product [Ru(CO)HClL(Sb^iPr_3)$_2$] (L = $MeO_2CC{\equiv}CCO_2Me$) with the ester, and with $NaBH_4$ the dihydride, [Ru(CO)H_2L(Sb^iPr_3)$_2$]. The products with PhC≡CH and $HC{\equiv}CCPh_2OH$ are the alkynyl and allenylidene complexes [Ru(CO)(C≡CPh)Cl(Sb^iPr_3)$_3$] [Ru(CO)($CCCPh_2$)Cl_2(Sb^iPr_3)$_2$], respectively [106].

A number of acetylacetonate complexes have been described by Bennett et al., including *cis*-[Ru(acac)$_2$(cyclooctene)($SbPh_3$)], *cis*-[Ru(acac)$_2$($SbPh_3$)$_2$], [108] *cis*-[Ru(acac)$_2$(C_2H_4)($SbPh_3$)] [109]; $AgPF_6$ oxidises *cis*-[Ru(acac)$_2$(cyclooctene)($SbPh_3$)] to the blue Ru(III) analogue *cis*-[Ru(acac)$_2$(cyclooctene)($SbPh_3$)]PF_6.

The reaction of [Ru(η^3-C_3H_5)$_2$(Sb^iPr_3)$_2$] with $MeCO_2H$ produces the binuclear [Ru_2($MeCO_2$)$_4$((Sb^iPr_3)$_4$(H_2O)], whilst reaction with acacH gave *cis*-[Ru(acac)$_2$(Sb^iPr_3)$_2$] [110]. The Sb^iPr_3 in the latter is easily displaced even by bulky phosphines to form *cis*-[Ru(acac)$_2$(Sb^iPr_3)$_{2-n}$(P^iPr_3)$_n$] ($n = 1, 2$) and with PhC≡CH the vinylidene *cis*-[Ru(acac)$_2$(Sb^iPr_3)(=C=CPh)] [110]. The mixed ligand [RuHCl{Sb(CH_2Ph)$_3$}(PCy_3)$_2$] is also known [111].

The formation of 6-coordinate [Ru($SbPh_3$)$_4$$Cl_2$], and the absence of any evidence for the existence of [Ru($SbPh_3$)$_3$$Cl_2$], which contrasts with the ready formation of [Ru(PPh_3)$_3$$Cl_2$] has been demonstrated [112]. The iodoruthenium(II) systems replicate this difference in that reaction of [Ru(H_2O)$_6$]$^{2+}$ with



Scheme 4. Some Ru stibine complexes from ref. [106] by permission of Wiley-VCH.

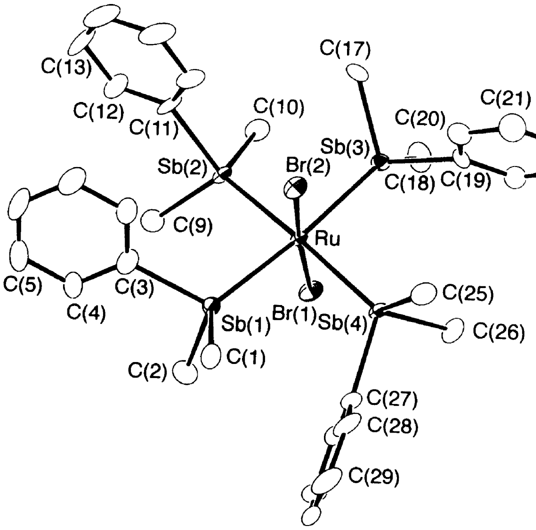


Fig. 7. Structure of *trans*-[Ru(SbPhMe$_2$)$_4$Br$_2$] from ref. [114] by permission of the Royal Society of Chemistry.

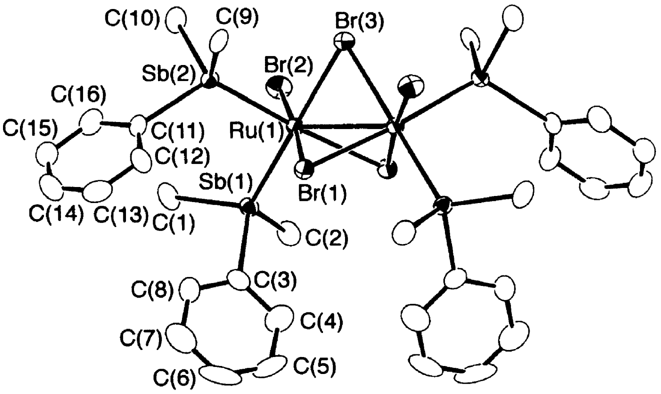


Fig. 8. Structure of [Ru$_2$Br$_5$(SbPhMe$_2$)$_4$] from ref. [114] by permission of the Royal Society of Chemistry.

SbPh$_3$ and NaI gives *trans*-[Ru(SbPh$_3$)$_4$I$_2$], whereas PPh$_3$ produces [Ru(PPh$_3$)$_3$I$_2$] which from its low temperature ^{31}P NMR spectrum appears to be square pyramidal [113]. The *trans*-[Ru(SbPh$_3$)$_4$I$_2$] is oxidised to *trans*-[Ru(SbPh$_3$)$_4$I$_2$]BF$_4$ by HNO$_3$/HBF$_4$. In contrast, SbMe$_2$Ph and RuCl$_3$·nH$_2$O (in the presence of KX for X = Br or I) in ethanol give *trans*-[Ru(SbMe$_2$Ph)$_4$X$_2$] (Fig. 7) [114]. These undergo reversible 1e oxidations at rather more positive potentials than phosphine or arsine analogues, and chemical oxidation with HNO$_3$/HBF$_4$ led to the isolation of the solid *trans*-[Ru(SbMe$_2$Ph)$_4$X$_2$]BF$_4$ [114]. A few purple rhomb crystals obtained during crystal growing attempts from solutions of *trans*-[Ru(SbMe$_2$Ph)$_4$Br$_2$] proved to be [Ru$_2$Br$_5$(SbMe$_2$Ph)$_4$] (Fig. 8) the only known stibine member of the 11e (formal bond order = 1/2) series of mixed valence dimers [Ru$_2$X$_5$(ER$_3$)$_4$] [114]. The structure of *trans*-[Ru(NO)Cl$_3$(SbPh$_3$)$_2$] (disordered NO/Cl) was reported [115]. It has been claimed that photochemical degradation of this complex yields *trans*-[Ru(NO)Cl$_3$(OSbPh$_3$)$_2$] [116] but the evidence for a stibine oxide is tenuous and seems to rely upon (the erroneous) analogy with phosphine or arsine oxide compounds.

Medicinal applications of ruthenium complexes have been developed in recent years. Examples of mixed ligand complexes developed for medicinal purposes include [Ru(SbPh$_3$)$_2$Cl$_2$(*N*,*S*-1,9-dimethylpurine-6-thione)] whose structure consists of *trans* chlorines with the N,S coordinated thione *trans* to SbPh$_3$ [117]. Other complexes studied include *trans*-[RuCl$_2$(SbPh$_3$)$_2$(L)$_2$] (L = 1,4-pyrazine, 3,5-dimethylpyridine, 4-methylpyrimidine, *N*-methylimidazole) [117,118].

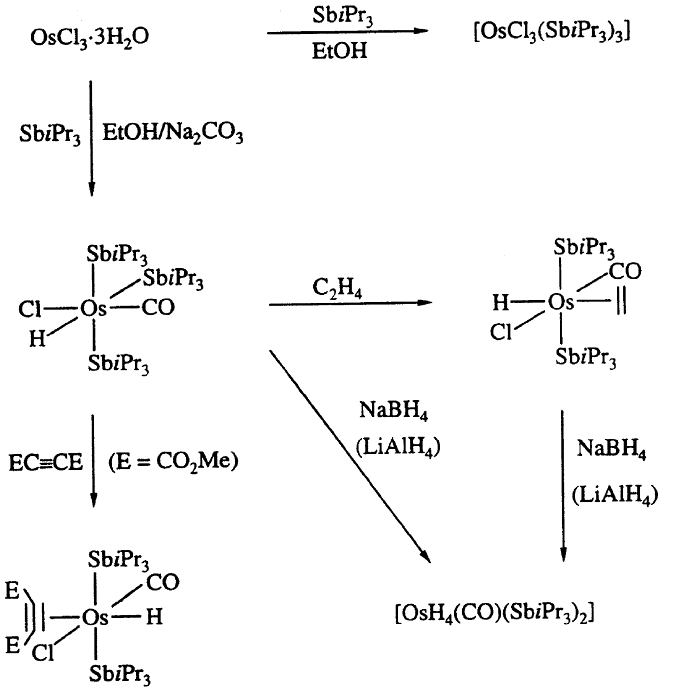
Group 15 substituted osmium carbonyl clusters remain an active area of cluster chemistry. Bromination of the triangular [Os$_3$(CO)$_{11}$(SbPh$_3$)] results in M–M ring opening to give two isomers of linear [Os$_3$(CO)$_{11}$Br$_2$(SbPh$_3$)] [119]. One isomer was structurally characterised as [Br$_2$Os(CO)$_3$Os(CO)$_4$Os(CO)$_4$(SbPh$_3$)], whilst the second form is [BrOs(CO)$_4$Os(CO)$_4$Os(CO)$_3$Br(SbPh$_3$)] established by spectrosocopic comparison with the structurally characterised PPh$_3$ analogue [119]; in both the SbPh$_3$ occupies an axial position on the terminal osmium.

The reaction of [Os$_3$(CO)$_{10}$(μ-H)(μ-SbPh$_2$)] with EPh$_3$ (E = P, As, Sb) leads to [Os$_3$(CO)$_{10}$H(μ-SbPh$_2$)(EPh$_3$)] in which the Os–Os bond bridged by the stibide has broken with the H bonding to one osmium and the EPh$_3$ to the other [120]. NMR studies indicate a second isomer is present in solution, probably reflecting a different site for the incoming neutral ligand. Thermolysis of [Os$_3$(CO)$_{11}$(SbPh$_3$)] in refluxing hydrocarbons gave a variety of more complex clusters containing fragmentation products of the stibine. Crystallographically identified examples included [Os$_3$(μ-SbPh$_2$)(μ-H)(μ-C$_6$H$_4$)(CO)$_9$] [Os$_6$(μ^3-SbPh)(μ-C$_6$H$_4$)(CO)$_{20}$] and [Os$_6$(μ^4-Sb)(μ-SbPh$_2$)(μ-H)(μ-C$_6$H$_4$)$_2$(C$_6$H$_5$)(CO)$_{16}$]. Further reaction of some of these species with SbPh$_3$ or alkenes has been described [121,122]. The syntheses and structures of the naphthol substituted clusters [Os$_3$(CO)$_7$(μ-H)$_2$(μ^3-OC$_{10}$H$_6$)(SbPh$_3$)$_2$] and [Os$_3$(CO)$_8$(μ-H)(μ^2-OC$_{10}$H$_7$)(SbPh$_3$)$_2$] have been reported [123].

Pentafluoronitrosobenzene (C$_6$H$_5$NO), reacts with the cluster [Os$_3$(CO)$_{10}$H$_2$(SbPh$_3$)] to give [Os$_3$(CO)$_{10}$H(SbPh$_3$)(ONC$_6$F$_4$O)] in which the pentafluorophenyl group has been specifically oxidised at the para position to give a quinone-like product [124]. The bis(trifluormethyl)nitroxide radical adds to [Os$_3$(CO)$_{10}$H$_2$(SbPh$_3$)] to form [Os$_3$(CO)$_{10}$H(SbPh$_3$){ON(CF$_3$)$_2$}]; protonic acids (HX) cleave the ON(CF$_3$)$_2$ (as HON(CF$_3$)$_2$) to leave [Os$_3$(CO)$_{10}$H(SbPh$_3$)X] [125,126].

The dimeric [Os$_2$(μ-Cl)$_2$Cl$_2$(η^6-1,3,5-C$_6$H$_3$Me$_3$)$_2$] is cleaved by Sb^{i}Pr$_3$ to [OsCl$_2$(η^6-1,3,5-C$_6$H$_3$Me$_3$)(Sb^{i}Pr$_3$)] which reacts with propargyl alcohols to form allenylidenes [OsCl(η^6-1,3,5-C$_6$H$_3$Me$_3$)(Sb^{i}Pr$_3$)(=C=C=CR$_2$)]PF$_6$ [127]. The [OsCl$_2$(η^6-1,3,5-C$_6$H$_3$Me$_3$)(Sb^{i}Pr$_3$)] is also formed from Sb^{i}Pr$_3$ and the carbene [OsCl$_2$(η^6-1,3,5-C$_6$H$_3$Me$_3$)(=CPh$_2$)] [128].

The reaction of OsCl$_3$·3H$_2$O with Sb^{i}Pr$_3$ gives a variety of formally Os(II), (III) or (IV) derivatives (Scheme 5) [106]. The reduction of [OsI$_6$]$^{2-}$ with SbPh$_3$ in refluxing ethanol affords the fawn Os(II) complex *trans*-[Os(SbPh$_3$)$_4$I$_2$] [129], which contrasts with the corresponding reactions with [OsX$_6$]$^{2-}$ (X = Cl, Br) where reduction stops at Os(III). However nitric acid in aqueous HBF$_4$ oxidises *trans*-[Os(SbPh$_3$)$_4$I$_2$] to chocolate



Scheme 5. Some Os stibine complexes from ref. [106] by permission of Wiley-VCH.

brown *trans*-$[Os(SbPh_3)_4I_2][BF_4]$. $K[OsCl_4(acac)]$ and $SbPh_3$ in ethanol gave *trans*-$[OsCl_2(acac)(SbPh_3)_2]$ (the *trans* groups are the stibines) [130].

The osmium(VI) nitrido complex $[OsNCl_3(SbPh_3)_2]$ reacts with $[\{Rh(COD)Cl\}_2]$ to form the bimetallic $[Cl_3(SbPh_3)_2OsNRhCl(COD)]$ which was structurally characterised and has a linear nitrido-bridge [131]. A green Os(VI) $[OsO_2Cl_2(SbPh_3)_2]$ complex has been reportedly obtained from OsO_4/Ph_3Sb in EtOH/HCl [132], but it seems from the preparative route and the properties that this substance is probably the well known *mer*-$[OsCl_3(Ph_3Sb)_3]$ [133].

6.4. Group 9

In contrast to the preceding 3d metals, the new chemistry of tertiary stibines with cobalt is mostly in the higher oxidation state Co(III) rather than in substituted carbonyl derivatives. Three new carbonyl complexes are $[(\mu^3\text{-}CPh)Co_3(CO)_7(SbPh_3)_2]$ [134], $[BuOC(O)Co(CO)_3(SbPh_3)]$ [135] and $[(\mu^3\text{-}CPh)Co_3(CO)_8(SbPh_3)]$ [136].

Cobalt(II) isonitrile complexes yellow-green $[Co(RNC)_4(SbPh_3)_2][ClO_4]_2$ (R = Bu or *N*-hexyl) with magnetic moments corresponding to one unpaired electron (and hence low-spin tetragonal d^7 species) are formed from $[Co(RNC)_5]^{2+}$ and $SbPh_3$ in EtOH [137]. On standing in solution it is claimed that they transform into paramagnetic complexes formulated as $[Co(RNC)_4(OSbPh_3)_2][ClO_4]_3$, containing Co(III) with an intermediate spin state (ca. 3.3–3.7 μ_B). There is no direct evidence for the presence of $OSbPh_3$ and since in the 'free' state all stibine oxides are oxygen bridged oligomers, the formulations are highly speculative. The "$OSbPh_3$" is displaced by R_3P to form diamagnetic $[Co(RNC)_4(PR_3)_2]^{3+}$ [138].

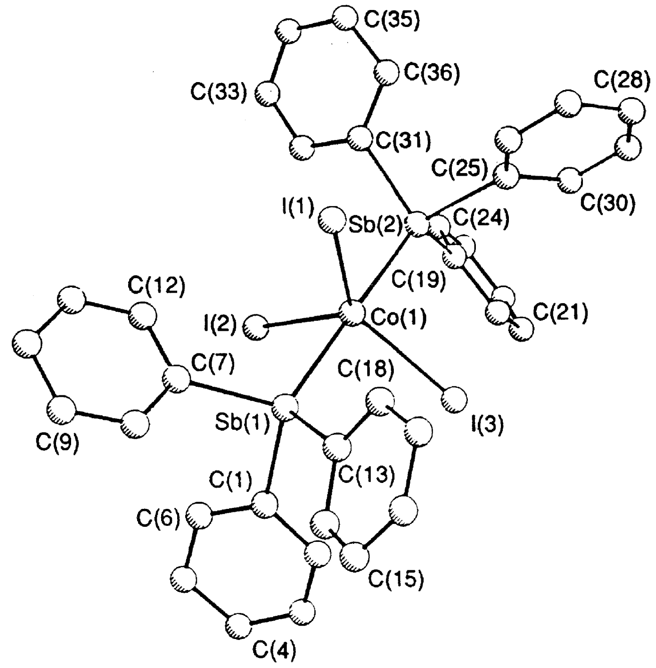


Fig. 9. Structure of $[Co(SbPh_3)_2I_3]$ from ref. [143] by permission of the Royal Society of Chemistry.

Cobaloxime complexes include $[Co(HDMG)_2\{Sb(p\text{-tolyl})_3\}X]$ (H_2DMG = dimethylglyoxime; X = Cl or NCS) both of which were characterised by X-ray studies [139]. The kinetics of water substitution in $[Co(HDMG)_2(H_2O)R]$ by $SbPh_3$ and the displacement of $SbPh_3$ from $[Co(L)_2(SbPh_3)]$ (L = 4,5-dichloro-1,2-benzodiiminato) have been reported [140,141].

The most interesting new cobalt stibines are $[Ph_3SbI][Co(SbPh_3)I_3]$ [142] and $[Co(SbPh_3)_2I_3]$ [143]. The former green cobalt(II) complex is formed by reaction of cobalt powder with Ph_3SbI_2 in diethyl ether and probably contains a tetrahedral anion by analogy with the crystallographically characterised PPh_3 complex. On standing for two weeks the reaction mixture containing $[Ph_3SbI][Co(SbPh_3)I_3]$ deposits green-black crystals with the structure in Fig. 9, a trigonal bipyramidal Co(III) complex. The magnetic moment of this complex (4.4 μ_B) is not understood. Notably $[Co(PR_3)_2X_3]$ (X = Cl or Br) are formed by NOX oxidation of $[Co(PR_3)_2X_2]$ ($PR_3 = PMe_3, PEt_3, \neq PPh_3$) but not by halogen oxidation and no iodo-complexes are known [144], which makes the $[Co(SbPh_3)_2I_3]$ extremely unusual.

There is a substantial stibine chemistry of rhodium. The unique chemistry of $Rh(\mu\text{-}SbR_3)Rh$ systems is described in Section 5, while the chemistry of terminally coordinated stibines is described here.

The chemistry of Vaska analogues *trans*-$[Rh(CO)(ER_3)_2X]$ is extensive, but the older literature on *trans*-$[Rh(CO)(SbPh_3)_2Cl]$ is confused and contradictory [1]. A reinvestigation [145] shows that reaction of $[\{Rh(CO)_2Cl\}_2]$ with the stibine in a 2:1 $SbPh_3$:Rh ratio in diethyl ether at 0 °C produces yellow *trans*-$[Rh(CO)(SbPh_3)_2Cl]$, whilst a 4:1 ratio in acetone affords red $[Rh(CO)(SbPh_3)_3Cl]$. The structures of both complexes have been determined (Fig. 10).

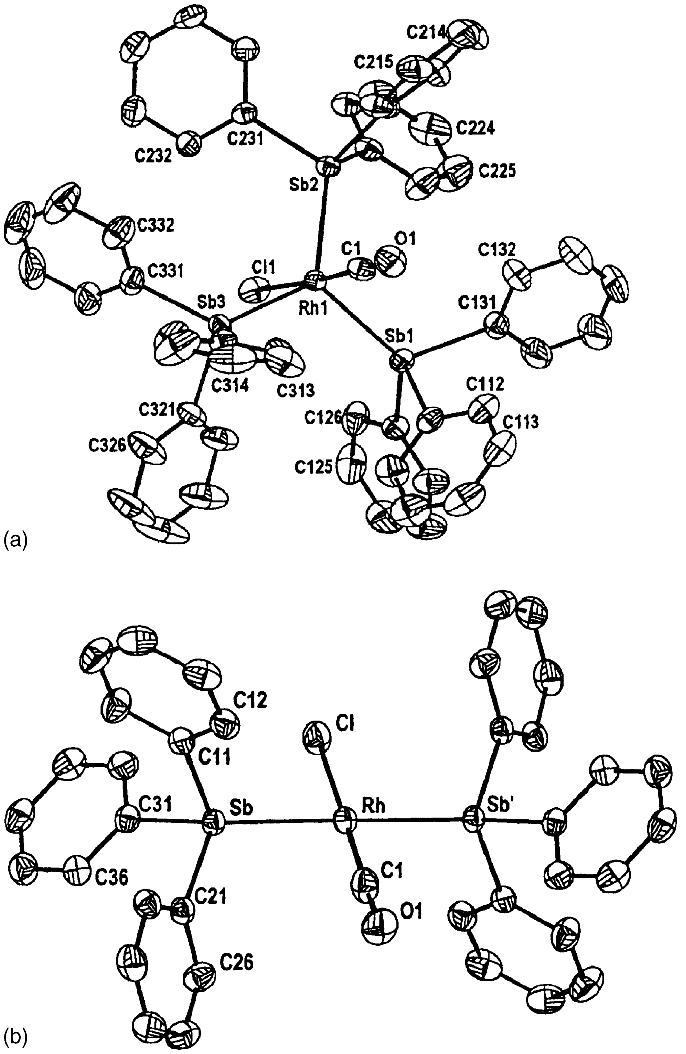


Fig. 10. (a and b) Structures of $[Rh(CO)Cl(SbPh_3)_3]$ and $[Rh(CO)Cl(SbPh_3)_2]$ from ref. [145] by permission of Elsevier S.A.

For the C_3 symmetric planar complex Rh–Cl = 2.315(3) Å, Rh–C(O) = 1.797(3) Å, Rh–Sb = 2.5655(2) Å which can be compared with the corresponding values in the trigonal bipyramidal complex Rh–Cl = 2.410(2) Å, Rh–C(O) = 1.875(7) Å, Rh–Sb = 2.5981(5) Å [145]. In solution, solvent dependent equilibria are present. The structure of the tbp $[Rh(CO)(SbPh_3)_3I]$ has also been determined [146] Rh–I = 2.7159(8) Å, Rh–C(O) = 1.825(6) Å, Rh–Sb = 2.5962(4) Å. The *trans*-$[Rh(CO)(SbMePh_2)_2Cl]$ has also been prepared [147].

Oxidative addition of MeI to $[Rh(CO)(SbPh_3)_3Cl]$ gave $[Rh(CO)(SbPh_3)_2I_2(Me)]$, the structure of which shows *trans*-stibines and *cis*-iodines [145]. The reaction of $[Rh(CO)(SbPh_3)_3Cl]$ with propargyl halides ($RC{\equiv}CCH_2X$, X = Cl or Br) produces $[Rh(CO)(SbPh_3)_2ClX(CH_2C{\equiv}CR)]$, but with $HC{\equiv}CCH_2X$ (X = $PhSO_3$, *p*-tolSO_3) the products are allenyl species $[Rh(CO)(SbPh_3)_2ClX(CH{=}C{=}CH_2)]$; under other reaction conditions rhodiacyclopentene-2-ones form [148–150]. Sulfur dioxide adducts, $[Rh_2(CO)_2(SO_2)(SbPh_3)_2Br_2]$ and $[Rh_2(CO)_2(SO_2)_3(SbPh_3)_2I_2]$, have been reported [151].

An extensive organometallic chemistry of rhodium supported by tri(isopropyl)stibine has been developed by Werner et al. and provides many examples of differing reactivities or products compared to those obtained in the phosphine systems, reflecting the very different electronic properties of the stibine. In a review focused on stibines it is not possible to describe the detailed organometallic chemistry, rather we attempt to describe the types of compounds reported and illustrate some of the differences from lighter group 15 ligand examples. The reaction of $[\{Rh(C_2H_4)_2Cl\}_2]$ with Sb^iPr_3 forms *trans*-$[Rh(C_2H_4)(Sb^iPr_3)_2Cl]$ or *trans*-$[Rh_2(C_2H_4)_2(Sb^iPr_3)_2(\mu\text{-}Cl)_2]$ depending on the molar ratio of reagents [152,153]. The ethene is easily displaced from the former by CO, CNR, $RC{\equiv}CR$, etc. (L) to give corresponding *trans*-$[Rh(L)(Sb^iPr_3)_2Cl]$, whilst dihydrogen gives 5-coordinate $[RhH_2(Sb^iPr_3)_2Cl]$, and the structure of *trans*-$[Rh(CNMe)(Sb^iPr_3)_2Cl]$ was determined. Whilst *trans*-$[Rh(C_2H_4)(As^iPr_3)_2Cl]$ reacts with $RC{\equiv}CH$ to give *trans*-$[Rh(RC{\equiv}CH)(As^iPr_3)_2Cl]$ which isomerise to the vinylidenes *trans*-$[Rh(RHC{=}C{=})(As^iPr_3)_2Cl]$, *trans*-$[Rh(C_2H_4)(Sb^iPr_3)_2Cl]$ does not afford vinylidenes but catalyses the formation of *E*-enynes $RC{=}CHC{\equiv}CR$ [153].

Diazoalkanes $RR'CN_2$ (R,R′ = Ph_2, $PhCF_3$, $Ph(C_6H_4X)$, etc.) react with *trans*-$[Rh(C_2H_4)(L)_2Cl]$ (L = PR_3, As^iPr_3) to give $[Rh(RR'CN_2)(L)_2Cl]$ which on heating or photolysis produce dinitrogen complexes *trans*-$[Rh(N_2)(L)_2Cl]$. However reaction of the diazoalkanes with *trans*-$[Rh(C_2H_4)(Sb^iPr_3)_2Cl]$ at low temperatures followed by warming leads to the carbene complexes *trans*-$[Rh({=}CRR')(Sb^iPr_3)_2Cl]$ from which the Sb^iPr_3 is easily displaced by PR_3, As^iPr_3, or $SbEt_3$ (L′) or diphosphines $(L')_2$ to form the corresponding $[Rh(RR'C{=})(L')_2Cl]$. The structures of *trans*-$[Rh({=}CRR')(L'')_2Cl]$ (L″ = P^iPr_3 and Sb^iPr_3) were determined and compared (Fig. 11) [154,155]. The geometric differences are small, suggesting that the different chemistries supported by the two ligands is largely a response to different electronic properties.

The *trans*-$[Rh({=}CRR')(Sb^iPr_3)_2Cl]$ react with NaCp to form the half-sandwich complexes $[Rh(\eta^5\text{-}C_5H_5)({=}CRR')(Sb^iPr_3)]$ from which the stibine is readily displaced by PR_3, CO CNR, etc. to form the corresponding adducts [156]. The formation of related half-sandwich compounds [157], complexes where the arene is functionalised with a pendant donor group for example, as in $C_6H_5(CH_2)_nPR_2$ [158–160], and the reaction of these complexes with electrophiles [161] have been described. The *trans*-$[Rh({=}CPh_2)(L)_2Cl]$ (L = P^iPr_3, Sb^iPr_3) react with PF_3 to cleave the carbene, forming *trans*-$[Rh(PF_3)(L)_2Cl]$, but with $[Rh(\eta^5\text{-}C_5H_5)({=}CRR')(L)]$, for L = P^iPr_3 the carbene is displaced giving the insertion product $[Rh(\eta^5\text{-}C_5H_4CHPh_2)(PF_3)(P^iPr_3)]$, but for L = Sb^iPr_3 simple displacement gives $[Rh(\eta^5\text{-}C_5H_5)({=}CPh_2)(PF_3)]$[162]. Some η^5-indenyl complexes $[Rh(\eta^5\text{-}C_9H_7)(Ph_2C{=})(L)]$ (L = PR_3, Sb^iPr_3) have been prepared from the *trans*-$[Rh({=}CPh_2)(L)_2Cl]$ and C_9H_7K and the structure of the stibine determined; on treatment with CO, the carbene inserts into one the the CH bonds in the 5-membered indenyl ring [163].

The $[Rh(\eta^5C_5Me_5)Cl(SbPh_3)(L)]PF_6$ (L = 1-(4-cyanophenyl)-imidazole) and $[Rh(\eta^5C_5Me_5)(SbPh_3)(L)]BPh_4$ (L =

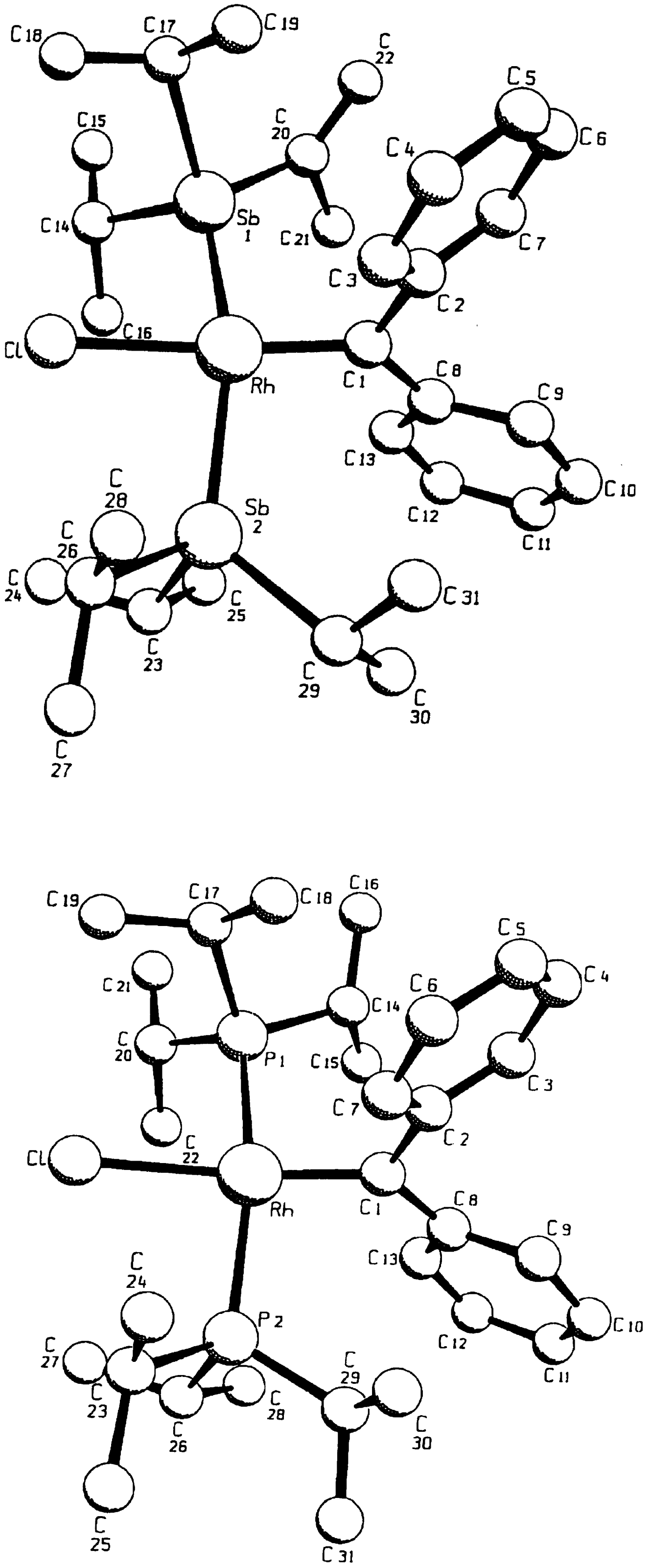


Fig. 11. Structures of [RhCl(Ph$_2$C=)(^{i}Pr$_3$Sb)$_2$] and [RhCl(Ph$_2$C=)(^{i}Pr$_3$P)$_2$] from ref. [154] by permission of VCH.

various thiourea monoanions)have been described [164,165]. The complex *trans*-[Rh{η^1-OSO$_2$(CF$_3$)}(C$_2$H$_4$)(Sb^{i}Pr$_3$)$_2$] has been prepared [166].

The [RhCl$_2$(σ-Ph)(SbPh$_3$)$_3$] has proved a useful synthon for a variety of Rh(III) complexes. An X-ray structure of [RhCl$_2$(σ-Ph)(SbPh$_3$)$_3$] (EtOAc) showed slight conformational differences in the substituent groups compared with the structure found previously in an acetone solvate [167]. When the complex reacts with PPh$_3$ the stibines are displaced, but the product is an unusual 5-coordinate complex [RhCl$_2$(σ-Ph)(PPh$_3$)$_2$] [168]. Other complexes made by displacement of stibine ligands from this compound and structurally characterised include [RhCl$_2$(σ-Ph)(pyrazine)$_2$(SbPh$_3$)], [RhCl$_2$(σ-Ph)(cyanoethylpyrrole)(SbPh$_3$)$_2$], [RhCl$_2$(σ-Ph)(purine-6-thione)(SbPh$_3$)], [RhCl$_2$(σ-Ph)(1,3-thiazole)$_n$(SbPh$_3$)$_{3-n}$] (n = 1 or 2) [169,170].

The Vaska analogue *trans*-[IrCl(CO)(SbPh$_3$)$_2$] is conveniently made from ^{n}Bu$_4$N[Ir(CO)$_2$Cl$_2$] and the stibine in thf under an atmosphere of CO [171]. One entry into the iridium chemistry of Sb^{i}Pr$_3$ is by reaction with [{Ir(C$_8$H$_{14}$)$_2$Cl}$_2$] in hexane under hydrogen which produces *mer-cis*-[Ir(H)$_2$Cl(Sb^{i}Pr$_3$)$_3$] [172]. Further reaction with CO or terminal alkynes yield [Ir(H)$_2$Cl(CO)(Sb^{i}Pr$_3$)$_2$] and [IrHCl(C≡CR)(Sb^{i}Pr$_3$)$_2$], respectively. From [{Ir(C$_2$H$_4$)$_2$Cl}$_2$] and SbR$_3$ the products are [IrCl(C$_2$H$_4$)(SbR$_3$)$_2$] (R = Me, Ph, ^{i}Pr) which have distorted trigonal bipyramidal structures (Fig. 12) [172].

Further substitution with NaCp, PhC≡CPh or tolylC≡CH afford [Ir(η^5-C$_5$H$_5$)(C$_2$H$_4$)(Sb^{i}Pr$_3$)], [IrCl(PhC≡CPh)(Sb^{i}Pr$_3$)$_2$] and [IrHCl(C$_2$H$_4$)(σ-C≡Ctolyl)(Sb^{i}Pr$_3$)$_2$], respectively [172]. Bridge-splitting in [{IrCl(C$_2$H$_4$)(P^{i}Pr$_3$)}$_2$] with Sb^{i}Pr$_3$ gives a near quantitative yield of *trans*-[IrCl(C$_2$H$_4$)(Sb^{i}Pr$_3$)(P^{i}Pr$_3$)], which reacts with R$_2$CN$_2$ to give the carbene *trans*-[IrCl(=CR$_2$)(Sb^{i}Pr$_3$)(P^{i}Pr$_3$)] [173,174]. The stibine is selectively replaced by As^{i}Pr$_3$ to give *trans*-[IrCl(C$_2$H$_4$)(As^{i}Pr$_3$)(P^{i}Pr$_3$)] [175]. The *trans*-

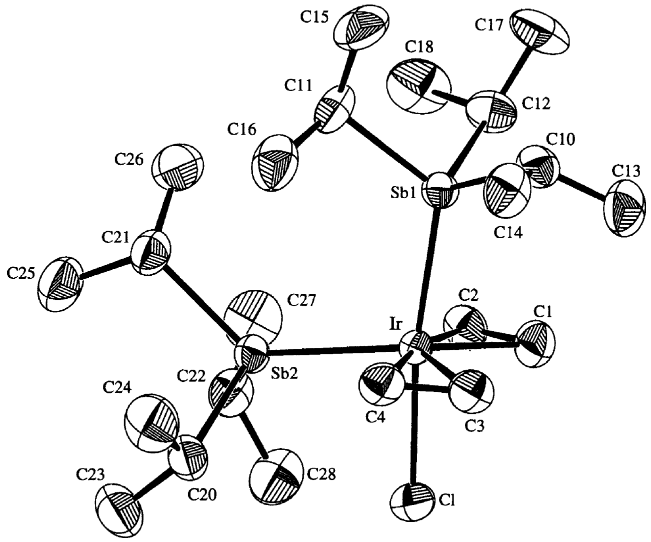


Fig. 12. Structure of [IrCl(C$_2$H$_4$)$_2$(^{i}Pr$_3$Sb)$_2$] from ref. [172] by permission of VCH.

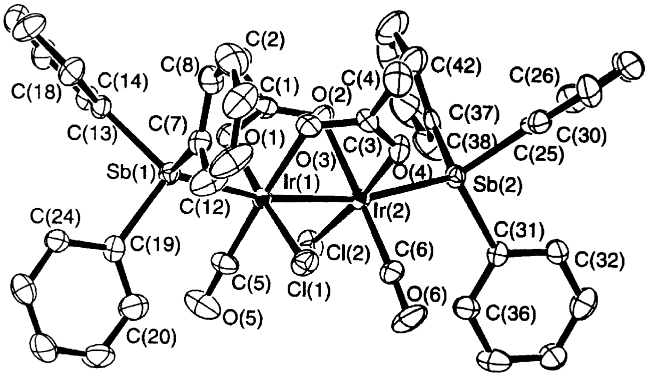


Fig. 13. Structure of $[Ir_2(\mu\text{-}O_2CMe)_2Cl_2(CO)_2(SbPh_3)_2]$ from ref. [178] by permission of Elsevier S.A.

$[IrCl(C_2H_4)(Sb^iPr_3)(P^iPr_3)]$ reacts with CO, H_2, RC≡CR to give substitution or oxidative addition products, but reacts with R_2CN_2 to give the carbenes *trans*-$[IrCl(=CR_2)(Sb^iPr_3)(P^iPr_3)]$ [173,174]. In contrast, *trans*-$[IrCl(C_8H_{14})(Sb^iPr_3)(P^iPr_3)]$ and diazoalkanes give the *trans*-$[IrCl(N_2CR_2)(Sb^iPr_3)(P^iPr_3)]$ without nitrogen loss [176]. The different ease of displacement of the group 15 ligands is used in reaction of *trans*-$[IrCl(=CR_2)(Sb^iPr_3)(P^iPr_3)]$ with NaCp which cleanly yields the $[Ir(\eta^5\text{-}C_5H_5)(=CR_2)(P^iPr_3)]$ [176].

$[IrCl(C_8H_{14})(Sb^iPr_3)_2]$ rearranges rapidly in hexane solution into the hydrido(allyl) $[IrHCl(\eta^3\text{-}C_8H_{13})(Sb^iPr_3)_2]$, and treatment of this complex with propene or 1-hexene result in generation of the appropriate allyl [176]. The preparations of $[IrCl(CO)_2(Sb^iPr_3)_2]$ and $[IrHCl_2(Sb^iPr_3)_2]$ were also described [176]. Bis(butadiene)iridium(I) complexes $[Ir(C_4H_6)_2(L)]^+$ (L = P^iPr_3, As^iPr_3, Sb^iPr_3) were obtained by displacement of cyclooctene from $[Ir(C_4H_6)_2(C_8H_{14})]^+$ by the group 15 ligand [177].

A series of Ir(II) dimers $[Ir_2(\mu\text{-}O_2CMe)_2Cl_2(CO)_2(L)_2]$ (L = PPh_3, PCy_3, $P(OPh)_3$, $AsPh_3$, $SbPh_3$) have been obtained by reaction of the group 15 ligands with $[Ir_2(\mu\text{-}O_2CMe)_2Cl_2(CO)_2]$ [178]. The structure of the stibine complex is shown in Fig. 13 and comparison with structures of other members of the series shows that the Ir–Ir distance depends on the group 15 ligand. The complexes undergo reversible 1e oxidations at potentials, which vary inversely with the σ-donor power of the neutral ligand.

Formally Ir(V) cations $[Ir(\eta^5\text{-}C_5Me_5)Me_3L]OSO_2CF_3$ (L = PMe_3, PPh_3, $AsPh_3$, $SbPh_3$, etc.) are formed from $[Ir(\eta^5\text{-}C_5Me_5)Me_3(OSO_2CF_3)]$ and the ligands [179].

6.5. Group 10

The synthesis of $[Ni(SbPh_3)_4]$ from $SbPh_3$ and either [Ni(1,5-cyclooctadiene)$_2$] [180] or a mixture of $NiCl_2{\cdot}6H_2O$ and $NaBH_4$ in ethanol [181] have been described. The latter reaction conducted under a CO atmosphere affords a convenient synthesis for $[Ni(CO)_2(SbPh_3)_2]$ [181]. The electronic absorption and emission spectra of a series of $[NiL_4]$ (L = $AsPh_3$, $SbPh_3$, etc.) complexes have been recorded and assignments proposed [181]. The reaction of [Ni(2-methylallyl)(1,5-cyclooctadiene)][B(3,5-$C_6H_3(CF_3)_2)_4$] with excess $SbPh_3$ in CH_2Cl_2 produces the 5-coordinate [Ni(2-methylallyl)$(SbPh_3)_3$][B(3,5-$C_6H_3(CF_3)_2)_4$] [182] (Fig. 14), which contrasts with the complexes formed by PPh_3 or $AsPh_3$ which are 4-coordinate bis(ligand) species. The complexes are extremely efficient styrene oligomerisation catalysts, the degree of oligomerisation varying with the group 15 ligand, with the stibine producing the highest yield of dimer.

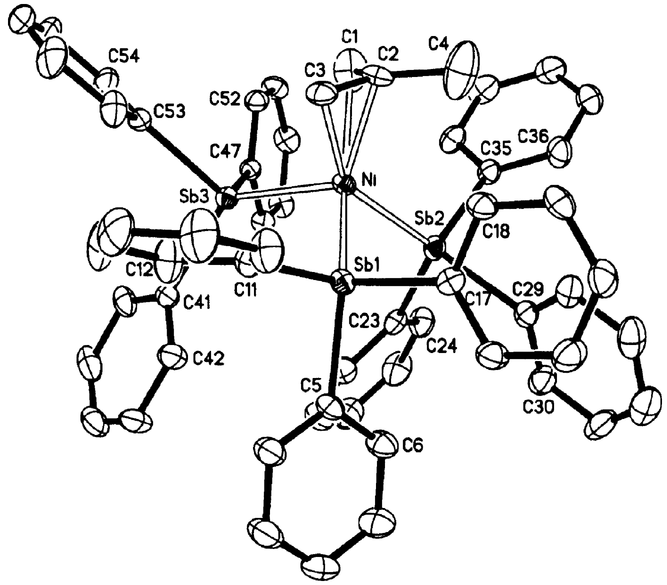


Fig. 14. Structure of $[Ni(\eta^3\text{-}CH_2C(Me)CH_2)(SbPh_3)_3]^+$ from ref. [182] by permission of the Royal Society of Chemistry.

A moderate amount of new work on palladium and platinum stibines has been reported, almost all of which involves the divalent metal centres. A preliminary account of platinum(II) trimethylstibine complexes reported the synthesis and some characterisation of $[Pt(SbMe_3)_2(H_2O)_2](NO_3)_2$, $[Pt(SbMe_3)_2(NO_3)_2]$, $[Pt(SbMe_3)_4](NO_3)_2$, and $[Pt_2(\mu\text{-}OH)_2(SbMe_3)_4](NO_3)_2$ [183]. An X-ray determination showed the tetrakis cation to be planar but limited details were provided. The $[PdX_2(Sb^iPr_3)_2]$ (X = Cl, Br or I) and $[PtCl_2(Sb^iPr_3)_2]$ were prepared from $[MCl_2(RCN)_2]$ or by metathesis; only one isomer appears to be present in each; for the chlorides, the palladium complex is *trans*, the platinum *cis* [184]. As would be expected given the bulk of the ligand, the $[PdX_2\{Sb(o\text{-tolyl})_3\}_2]$ (X = Cl or Br) prepared from [PdX$_2$(COD)] and the ligand have *trans* structures [185]. Several X-ray structures of previously known planar Pd(II) and Pt(II) complexes have been determined in connection with studies of the *trans* influence and *trans* effect of stibines. These results are discussed in Section 4.2 and the structural data is listed in Table 3. The *cis*-$[PtBr_2(SbPh_3)_2]$ was made by the unusual reaction of $PtCl_2$ in thf with $[Ph_2SbBr_2]^-$; longer reactions times gave a mixture of $[PtBr(Ph)(SbPh_3)_2]$ and $[PtBr_3(SbPh_3)]^-$ [187].

The cleavage of Sb–C bonds in $SbPh_3$ appears to be particularly easy with Pd(II) chloro-compounds [187]. Thus reaction of $SbPh_3$ with [PdCl$_2$(COD)] or $PdCl_2$ gave *trans*-$[PdCl(\sigma\text{-}Ph)(SbPh_3)_2]$. The reaction using Na_2PdCl_4 gave mostly *cis*-$[PdCl_2(SbPh_3)_2]$ contaminated with small amounts of the chloro σ-phenyl complex [187]. Curiously, using

Table 3
X-ray structural data on Pd(II) and Pt(II) complexes

Complex	d(M—Sb) (Å)	d(M—X) (Å)	Ref.
$[Pt(SbMe_3)_4](NO_3)_2$	2.5579(6)–2.5619(9)		[183]
trans-$[PdX_2(Sb^iPr_3)_2]$	2.5721(7)	2.289(2)	[184]
trans-$[PdCl_2\{Sb(o\text{-tolyl})_3\}_2]$	2.5658(3)	2.3037(8)	[185]
trans-$[PdBr_2\{Sb(o\text{-tolyl})_3\}_2]$	2.5685(5)	2.4177(5)	[185]
cis-$[PtCl_2(SbPh_3)_2]$	2.491(1), 2.510(1)	2.354(3), 2.326(4)	[186]
trans-$[PtI_2(SbPh_3)_2]$	2.550(1), 2.554(1)	2.607(1), 2.597(1)	[186]
$[PtI_3(SbPh_3)]^-$	2.507(2)	2.596(2) (x2), 2.637(2)	[37]
cis-$[PtBr_2(SbPh_3)_2]$	2.513(1), 2.497(1)	2.470(2), 2.442(2)	[40]
trans-$[PtBr(Ph)(SbPh_3)_2]$	2.548(1),	2.496(2)	[40]
cis-$[PtBr_2(SbPh_3)(PPh_3)]$	2.463(2)	2.573(3), 2.583(2)	[40]
$[PtBr_3(SbPh_3)]^-$	2.496(2)	2.392(3), 2.431(4), 2.471(4)	[40]
trans-$[PdBr(Ph)(SbPh_3)_2]$	2.5421(5)	2.491(4)	[187]
trans-$[PdCl(Ph)(SbPh_3)_2]$	2.5568(5)	2.373(2)	[187]

$[PdBr_2(COD)]$ gave *trans*-$[PdBr(\sigma\text{-}Ph)(SbPh_3)_2]$ but $PdBr_2$ gave only *cis*-$[PdBr_2(SbPh_3)_2]$. The $SbPh_3$ ligands can be exchanged with PPh_3, $AsPh_3$, 2,2′-bipy, 1,10-phen in refluxing CH_2Cl_2 which provides a convenient route to other phenylpalladium complexes [188]. Whilst Pd(II) and Pt(II) complexes of tris(allyl)arsine or tris(methylallyl)arsine form readily, the reaction of $[PdCl_2(RCN)_2]$ with the corresponding stibines results in fragmentation with $[Pd_2Cl_2(L)_2]$ formed (L = allyl, 2-methylallyl) and the fate of the stibine residue is unknown [189]. Rather similar differences are observed on the reaction of tris(thienyl)-arsine and –stibine with Pd or Pt halides [190]. Whilst the arsine affords normal planar (As-coordinated ligand) complexes, the stibine is decomposed.

There are a number of mixed ligand complexes reported containing $SbPh_3$, usually as part of larger studies incorporating phosphines, arsines, *N*-heterocycles, etc. For completeness these are listed here: (those marked * include a X-ray crystal structure of the stibine complex) $[Pd_2(SC_6F_5)_2(Ph_2PCH_2PPh_2)(SbPh_3)_2]CF_3SO_3$ [191]; *cis*-$[Pt(SC_6F_5)_2(PhCCPh)(SbPh_3)]$ [192]; the salicylhydroxamates $[Pt\{OC_6H_4C(O)NOH(SbPh_3)_2]$ and $[Pt\{OC_6H_4C(O)NOH(SbPh_3)(4\text{-}MeC_6H_4N)]^*$ [193]; $[PdCl(Me_2NCH_2C_6H_4)(SbPh_3)]^*$ [194]; $[PtCl_2(C_4Me_4)(SbPh_3)]^*$ [195]; $[PtCl_2(C_4R_4)(SbPh_3)]$ [196]; $[PtCl\{(mesityl)_2PC_6H_2Me_2CH_2\}(SbPh_3)]$ [197].

Complexes of the racemic Sb-chiral (±)-1-phenyl-2-trimethylsilylstibindole (II) with di-μ-chlorobis[(*S*)-2-[1-(dimethylamino)ethyl]phenyl-C,N]dipalladium (III) have been mentioned in Section 2 and diastereoisomers separated by chromatography [17]. The structures of the two isomers have been determined [18].

Platinum(IV) halide complexes of stibines are very unstable [1], but much more stable complexes result with alkylplatinum(IV) acceptors. The reaction of $[Me_3PtI]_4$ with SbR_3 ($R_3 = Ph_3$, Me_2Ph, $MePh_2$) in $CHCl_3$ produced yellow *fac*-$[PtMe_3I(SbR_3)_2]$ which are stable at room temperature both as solids and in solution, but decompose with (mostly) elimination of ethane on heating. The complexes are characterised by ^{195}Pt NMR shifts in the region of δ −4300, and the structure of *fac*-$[PtMe_3I(SbPh_3)_2]$ was determined [198].

6.6. Group 11

Homoleptic $[Cu(SbR_3)_4]Y$ ($R_3 = Me_3$, Et_3, Ph_3, Me_2Ph, $MePh_2$, $Me_2(2\text{-}BrC_6H_4)$; $Y = BF_4$ or PF_6) have been prepared from $[Cu(MeCN)_4]Y$ and the appropriate ligand in CH_2Cl_2 [199,200]. All the complexes show sharp singlets in the ^{63}Cu solution NMR spectra, unaffected by addition of free ligand to the solutions [199]. Since resonances from the quadrupolar ($I = 3/2$) ^{63}Cu are only seen in cubic symmetry environments, this is compelling evidence for the presence of tetrahedral $CuSb_4$ species in solution, and is in marked contrast to the behaviour of phosphine analogues which show varying degrees of dissociation to lower coordination number species depending upon the particular phosphine present. ES^+ mass spectra of a solution of $[Cu(MeCN)_4]BF_4 + SbPh_3$ show the *tetrakis*-stibine cation is the dominant species irrespective of the ratio of reagents used [201]. X-ray crystal structures have been reported for Cu(I)–$SbPh_3$ complexes with M:L ratio's of 1:4, 1:3 and 1:2 [202–204]. The $[Cu(SbPh_3)_4]ClO_4$ contains the expected tetrahedral cation, but with two slightly different Cu–Sb distances 2.552(1), 2.577(1) Å. The structures of $[Cu(SbPh_3)_3I]$, $[Cu(SbPh_3)_3Br]\ CHCl_3$, $[Cu(SbPh_3)_3(ONO_2)]$ 1.5MeOH, also contain pseudo-tetrahedral coordination about the copper, the d(Cu–Sb) at ∼2.55 Å is invariant within the series of complexes. The $[Cu(SbPh_3)_2X]$ (X = Cl, Br, I), which crystallised from mixtures of CuX and $SbPh_3$ (1:2 ratio) in MeCN are dimers with bridging X groups completing a distorted tetrahedral geometry at the copper (Fig. 15).

The $[Cu(BH_4)(PPh_3)_2]$ complex reacts with CO_2 and $SbPh_3$ to produce the formate $[Cu(PPh_3)(SbPh_3)(O_2CH)]$ [205]. Mixed ligand $[Cu(SbPh_3)(thione)_2X]$ have been reported [206].

The silylstibine, $Sb(SiMe_3)_3$ functions as a source of $SbSiMe_3$ or Sb units in the large copper clusters such as $[Cu_{12}(SbSiMe_3)_6(PR_3)_6]$ or $[Cu_{45}Sb_{16}(PR_3)_{16}]$ formed from CuX, various PR_3 and $Sb(SiMe_3)_3$ [207].

Silver(I) stibine complexes are generally very similar to their Cu(I) analogues, apart from a tendency to light sensitivity, which results in many blackening over a period of days–weeks even as solids. The $[Ag(SbR_3)_4]BF_4$ ($R_3 = Me_3$, Et_3, Ph_3, Me_2Ph, $MePh_2$, $Me_2(2\text{-}BrC_6H_4)$) were made by combining the ligands

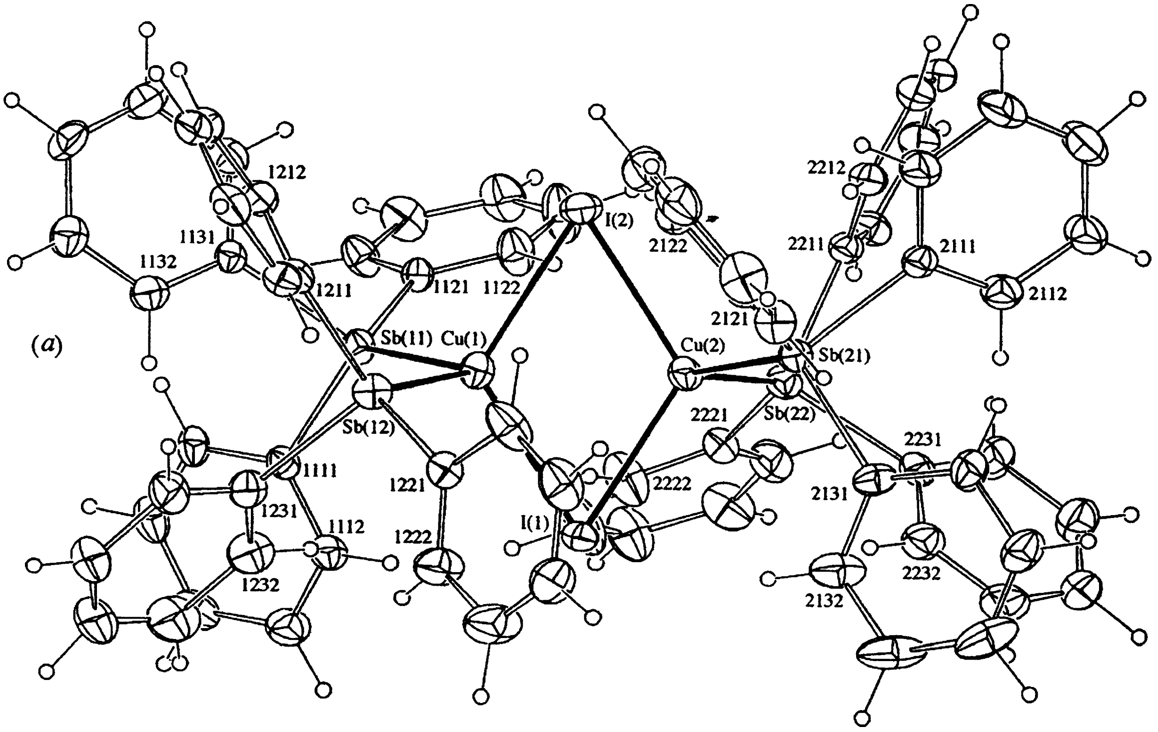


Fig. 15. Structure of [Cu(SbPh$_3$)$_2$I] from ref. [204] by permission of the Australian Chemical Society.

with AgBF$_4$ in acetone [200]. The ^{109}Ag NMR spectra were sharp singlets and unchanged in the presence of added ligand, indicating that the *tetrakis*-stibine cations are the only species present in significant amounts. ES$^+$ mass spectrometry of solutions of AgNO$_3$/SbPh$_3$ in MeCN show [Ag(SbPh$_3$)$_4$]$^+$ is the predominant species at high Ag:ligand ratios, but with less stibine present [Ag(MeCN)(SbPh$_3$)]$^+$ is the major ion [201].

A considerable amount of structural data is available for Ag(I) stibines. The [Ag(SbPh$_3$)$_4$]BF$_4$ has the expected tetrahedral cation with Ag–Sb = 2.720(1)–2.730(1) Å, marginally smaller than in the corresponding gold cation [200]. Very similar tetrahedral cations are present in the [Ag(SbPh$_3$)$_4$]Y (Y = ClO$_4$, NO$_3$, 1/2SiF$_6$ salts), although some disorder problems prevent very detailed comparisons [202]. Structures have also been reported for the [Ag(SbPh$_3$)$_3$Y] (Y = Cl, I, SCN, NCS (both linkage isomers characterised), CN, ONO$_2$) [208], and [(SbPh$_3$)$_2$Ag(μ-X)$_2$Ag(SbPh$_3$)$_2$] (X = Cl, Br, I) [209]. The 1:1 complex [Ag(SbPh$_3$)(NO$_3$)] also contains 4-coordinate silver in a chain polymer, each silver being coordinated to a stibine, one bidentate and one monodentate nitrate group (Fig. 16) [210].

Silver(I) nitrite forms two complexes with SbPh$_3$, [Ag(SbPh$_3$)(NO$_2$)] and [Ag(SbPh$_3$)$_3$(NO$_2$)], the former is a chain polymer with each silver chelated (O,O′) by a nitrite which is *N*-coordinated to the next Ag along the chain, each silver carrying one terminal stibine. The tris(stibine) is molecular with 5-coordinate silver (Sb$_3$O$_2$) [211]. A detailed re-examination of the AgCN–SbPh$_3$ system [212] found in addition to the reported [208] [Ag(SbPh$_3$)$_3$CN], a new structural type in [Ag(SbPh$_3$)$_2$CN] which contains an infinite 1D polymer with Ag(SbPh$_3$)$_2$ units bridged by cyanide groups. Silver bromate complexes [Ag(SbPh$_3$)$_x$(BrO$_3$)] (X = 1–4) have been isolated [213]. The complex with x = 4 has been shown by a crystallographic study to contain the expected tetrahedral AgSb$_4$ cation; the other three complexes have not been examined by X-ray methods, but are assumed to contain coordinated bromate, although the structural units are unclear.

A number of new mixed ligand Ag(I) systems containing SbPh$_3$ have been structurally and/or spectroscopically characterised, including those with cyanoximates [214], bis(1,2,3-triazol-1-yl)methane [215], tetrazoles [216] and carboranes [217]. The complexes of tris(2-thienyl)stibine and tris(2-furyl)stibine, [AgL$_2$(NO$_3$)] contain the ligands bonded only via antimony to 3-coordinate silver centres [218].

6.7. Groups 12–15

Little new work is reported from group 12. This includes the synthesis of [Cd(SbPh$_3$)$_2$(ClO$_4$)$_2$] [219], [Hg{Sb(mesityl)$_3$}X$_2$] and [Hg{Sb(*p*-EtOC$_6$H$_4$)$_3$}$_x$I$_2$] (x = 1, 2) [220].

At the time of the last review [1] knowledge of the reactions of stibines with p-block metals was limited to early studies which reported substituent scrambling or sometimes halogenation (to R$_3$SbX$_2$) but with no well characterised Lewis base complexes. The desire to develop single source precursors to III–V materials has resulted in some recent work in this area, which is summarised in two reviews [221,222].

Boron halide adducts of Sb(SiMe$_3$)$_3$ of type [BX$_3${Sb(SiMe$_3$)$_3$}] (X = Cl, Br, I) were made by combination of the constituents in pentane at low temperature [223]. The structures of all three were determined and contain a tetrahedral boron centre with B–Sb not significantly different

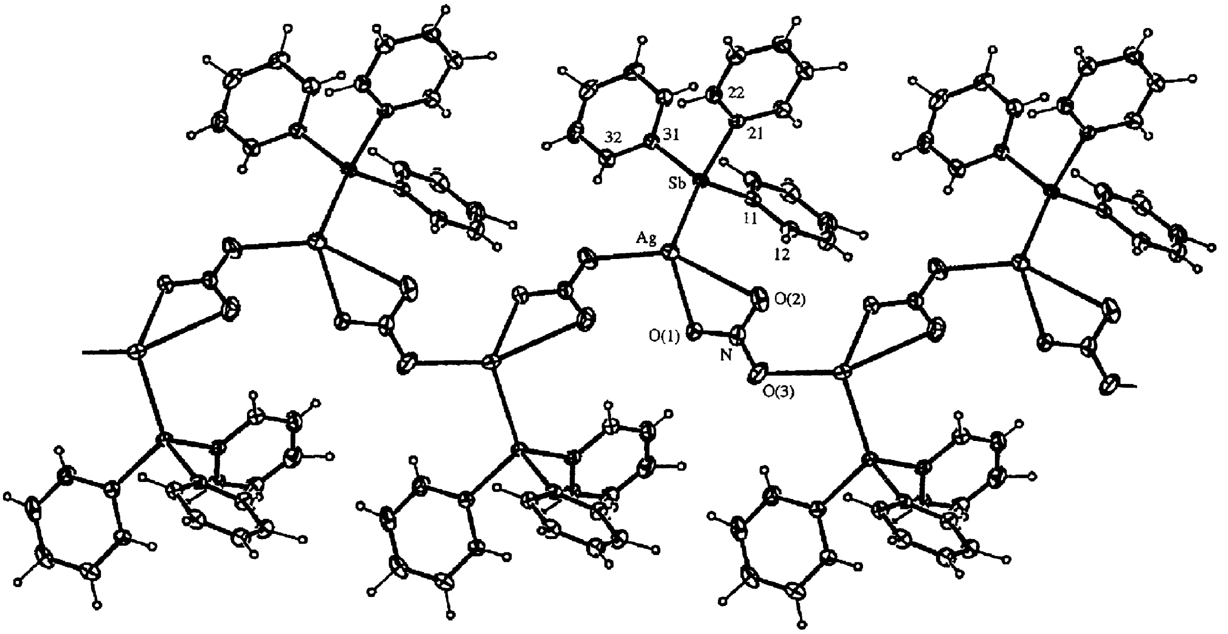


Fig. 16. Structure of [$AgNO_3(SbPh_3)$] from ref. [210] by permission of the Australian Chemical Society.

between the three adducts at ∼2.26 Å. The combination of R_3Al and the silylstibine, $Sb(SiMe_3)_3$ in a 1:1 ratio in the absence of a solvent formed colourless [$R_3Al\{Sb(SiMe_3)_3\}$] (R = Me, Et, ^{t}Bu) [224]. Adducts [$R_2AlCl\{Sb(SiMe_3)_3\}$] are also formed with R_2AlCl (R = Et, ^{t}Bu), but reaction of Me_2AlCl and $Sb(SiMe_3)_3$ resulted in elimination of $SiMe_4$ and formation of a 6-membered ring cyclo-[$MeAlCl\{Sb(SiMe_3)_2\}]_3$ [224]. The Al–Si bonds are 2.841(1) in [$Et_3Al\{Sb(SiMe_3)_3\}$] and 2.821(1), 2.798(1) Å in [^{t}$Bu_2AlCl\{Sb(SiMe_3)_3\}$] (there are two slightly different molecules in the unit cell). The combination of trialkylstibines and trialkylaluminiums produces [$(R_3Al(SbR'_3)$] (R = Me, Et, ^{t}Bu, R′ = Et, ^{n}Pr, ^{i}Pr, ^{s}Bu, ^{t}Bu) [225]. Structures were determined for [$(R_3Al(SbR'_3)$] (R = Me, Et, R′ = ^{t}Bu; R = ^{t}Bu, Et, R′ = ^{t}Bu, ^{i}Pr) (Fig. 17) and comparison of the Al–Sb bond lengths suggest steric factors are mainly responsible for slightly elongated bonds in the most crowded examples [225]. Comparisons of the structural and NMR data within a series of [$R_3Al(ER'_3)$] (E = P–Sb) and DFT calculations have been used to explore the factors which determine the relative stability of the adducts [226].

Matrix-isolation IR spectroscopy was used to identify [$Me_3Ga(SbH_3)$], the strength of the interaction between the components appears to be weaker than with PH_3 [227]. Trialkylgalliums and $Sb(SiMe_3)_3$ form [$R_3Ga\{Sb(SiMe_3)_3\}$] (R = Me, Et, ^{t}Bu) [228–231]. Two examples have been characterised by X-ray studies (R = Et, ^{t}Bu) and the Ga–Sb bond length is much longer in the ^{t}Bu complex (3.027(2) Å) compared to the Et (2.846(5) Å) attributed to steric crowding. In contrast to some of the aluminium systems where adducts are formed, reaction of Me_2GaCl, Et_2GaCl or ^{t}Bu_2GaCl with $Sb(SiMe_3)_3$ results in elimination of Me_3SiCl and formation of [$\{R_2GaSb(SiMe_3)_2\}_n$] or [$\{R_2Ga\{Sb(SiMe_3)_2\}GaR_2Cl\}_n$]; for R = Me or Et the complexes are dimers, but the molecularity of the ^{t}Bu complexes was not established.

Adducts of R_3Ga and R'_3Sb, [$R_3GaSbR'_3$] (R = ^{n}Bu, ^{t}Bu, R′ = Et, ^{n}Pr, ^{i}Pr, ^{t}Bu) are made by combination of the components and their NMR spectra and the structures of [^{t}$Bu_3Ga(SbEt_3)$] and [^{t}$Bu_3Ga(Sb^iPr_3)$] have been reported [232]. Pyrolysis of [$R_3Ga\{Sb(SiMe_3)_3\}$], [$\{R_2GaSb(SiMe_3)_2\}_n$] and [$R_3GaSbR'_3$] produce GaSb films the form depending on the temperature [229,233–235].

Weak adducts [$Me_3In(EH_3)$] (E = P, As or Sb) were identified by matrix-isolation IR spectroscopy at low temperatures [236]. Less is known about trialkylindium-group 15 base adducts than for their gallium analogues, but [$(Me_3SiCH_2)_3In\{Sb(SiMe_3)_3\}$]

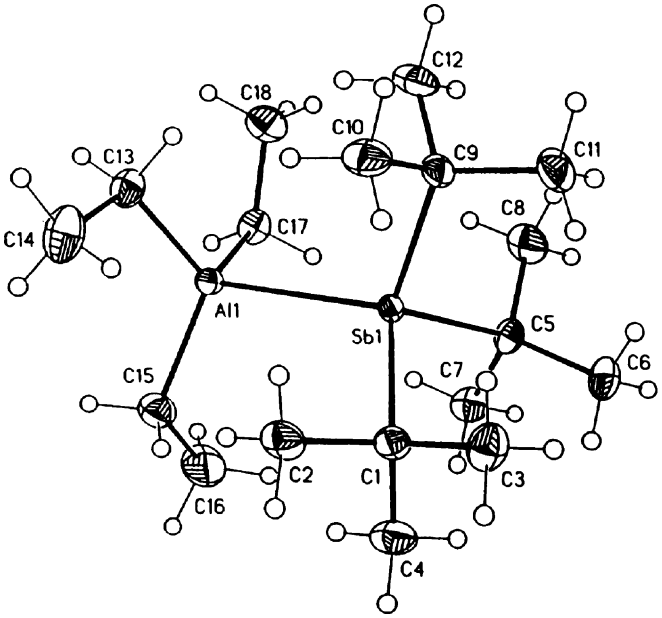


Fig. 17. Structure of [$Et_3Al(Sb^tBu_3)$] from ref. [226] by permission of Elsevier S.A.

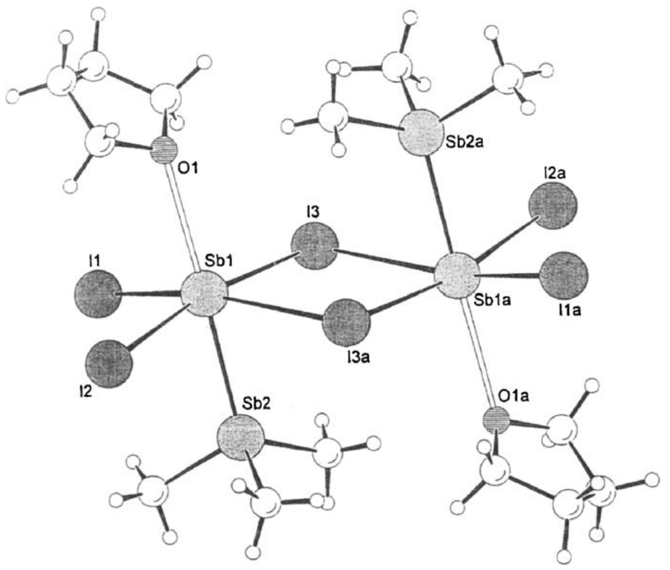


Fig. 18. Structure of $[\{SbI_3(thf)(SbMe_3)\}_2]$ from ref. [237] by permission of Wiley Interscience.

and $[(Me_3SiCH_2)_2In\{Sb(SiMe_3)_2\}]_2$ were made by reaction of the silylstibine with $(Me_3SiCH_2)_3In$ and $(Me_3SiCH_2)_2InCl$, respectively, and both have been structurally characterised [228]. The corresponding $[^tBu_3In\{Sb(SiMe_3)_3\}]$ is made by combination of the constituents and $[^tBu_2In\{Sb(SiMe_3)_2\}]_2$ from the ligand as $^tBu_2InCl$ [235].

There appears to be no new work on group 14–stibine complexes. In group 15 the reaction of Me_3Sb with SbI_3 in thf solution forms yellow rods of $[\{SbI_3(SbMe_3)(thf)\}_2]$ which have the structure shown in Fig. 18 [237]. The adduct $[MeI_2Sb(SbMe_3)]$ (Fig. 19) forms spontaneously by rearrangement of Me_2SbI at −20 °C in the absence of a solvent [238]. The structure may be described as containing a pyramidal Me_3Sb and a T-shaped $MeSbI_2$ (or a pseudo-tbp $MeSbI_2$ with axial iodines, the stibine, a Me and a lone pair equatorially disposed). The Sb–Sb distance 2.859(1), 2.868(1) Å (there are two slightly different molecules in the cell) approximates to a normal single bond. A related species is $[Me_3Sb–SbMe_2][\{SbMeBr_3\}_2]$ formed from Me_2SbBr [239].

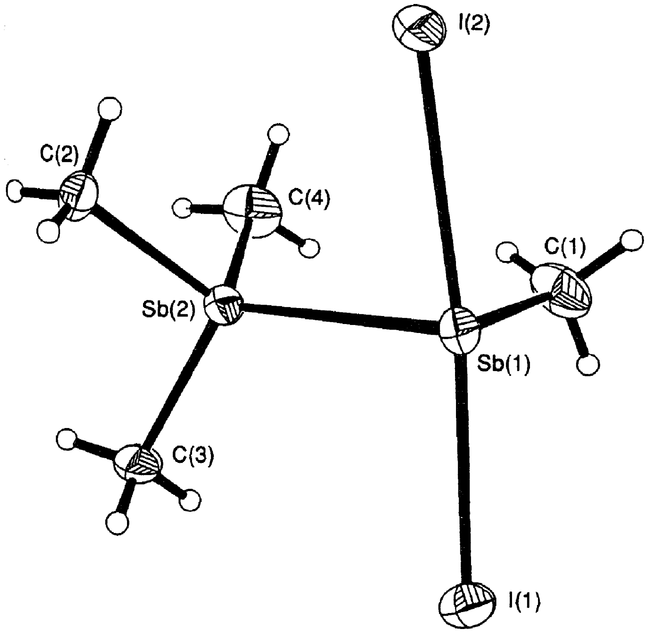


Fig. 19. Structure of $[MeI_2Sb(SbMe_3)]$ from ref. [238] by permission of the Royal Society of Chemistry.

7. Ditertiary stibine complexes

7.1. Distibinomethanes and related ligands

In this section the unique coordination chemistry of ligands of type $R_2SbYSbR_2$ ($Y = CH_2$, O, S) is described. The short interdonor linkage and the large size and weaker binding of the antimony atoms disfavour chelation to give a strained 4-membered ring, and monodentate or bridging bidentate are the common coordination modes. This contrasts with the much studied diphosphinomethanes where chelate formation is often found [240].

Some complexes of $Ph_2SbCH_2SbPh_2$ with group 6 carbonyls were described earlier [1], but with very limited data. A detailed re-examination prepared four types of complex, $[M(CO)_5(\eta^1\text{-}Ph_2SbCH_2SbPh_2)]$, $[(CO)_5M(\mu\text{-}Ph_2SbCH_2SbPh_2)M(CO)_5]$, *cis*-$[(CO)_4M(\mu\text{-}Ph_2SbCH_2SbPh_2)_2M(CO)_4]$, and *fac*-$[M(CO)_3(\eta^1\text{-}Ph_2SbCH_2SbPh_2)_3]$ (M = Cr, Mo, W) [27]. The $[M(CO)_5(\eta^1\text{-}Ph_2SbCH_2SbPh_2)]$ type result from combination of $[M(CO)_5(thf)]$ with the ligand in a 1:1 ratio, whilst a 2:1 ratio produces $[(CO)_5M(\mu\text{-}Ph_2SbCH_2SbPh_2)M(CO)_5]$ (M = Cr,W inexplicably Mo forms only the 1:1 complex). The traditional route to *cis*-tetracarbonyls by reaction of the ligand with *cis*-$[M(CO)_4(L)]$ (L = norbornadiene, $Me_2N(CH_2)_3NMe_2$, etc.) gives disubstituted metal centres, but in contrast to ligands with longer backbones, for the distibinomethane, the complexes are ligand bridged dimers *cis*-$[(CO)_4M(\mu\text{-}Ph_2SbCH_2SbPh_2)_2M(CO)_4]$. The *fac*-$[Mo(CO)_3(\eta^1\text{-}Ph_2SbCH_2SbPh_2)_3]$ was made from the ligand and $Mo(CO)_6$ in ethanol containing $NaBH_4$, *fac*-$[W(CO)_3(\eta^1\text{-}Ph_2SbCH_2SbPh_2)_3]$ from $[W(CO)_3(MeCN)_3]$ and *fac*-$[Cr(CO)_3(\eta^1\text{-}Ph_2SbCH_2SbPh_2)_3]$ unexpectedly from *cis*-$[Cr(CO)_4(norbornadiene)]$ and the ligand in ethanol. All complexes were characterised by IR, ^1H, $^{13}C\{^1H\}$ NMR and FAB MS, and structures of representative types are shown in Figs. 20–22 [27].

Attempts to confirm reports of molybdenum complexes containing chelating distibine [1] were unsuccessful. The pyrophoric $Me_2SbCH_2SbMe_2$ forms generally similar complexes, although pure examples with $\eta^1\text{-}Me_2SbCH_2SbMe_2$ proved very unstable, due both to the stronger donor power and the air-sensitivity of the "free" Me_2Sb-group [27]. Related complexes $[M(CO)_5(\eta^1\text{-}L)]$, $[(CO)_5M(\mu\text{-}L)M(CO)_5]$ and *cis*-$[(CO)_4M(\mu\text{-}L)_2M(CO)_4]$ ($L = Ph_2SbOSbPh_2$, $Ph_2SbSSbPh_2$) have been reported and structures of $[Cr(CO)_5(\eta^1\text{-}Ph_2SbSSbPh_2]$ and *cis*-$[(CO)_4Cr(\mu\text{-}Ph_2SbOSbPh_2)_2Cr(CO)_4]$ determined [241]. The $Me_2SbOSbMe_2$ straightforwardly gave *cis*-$[(CO)_4Cr(\mu\text{-}Me_2SbOSbMe_2)_2Cr(CO)_4]$, but $Me_2SbSSbMe_2$ reacts with $[Cr(CO)_4(norbornadiene)]$ to give

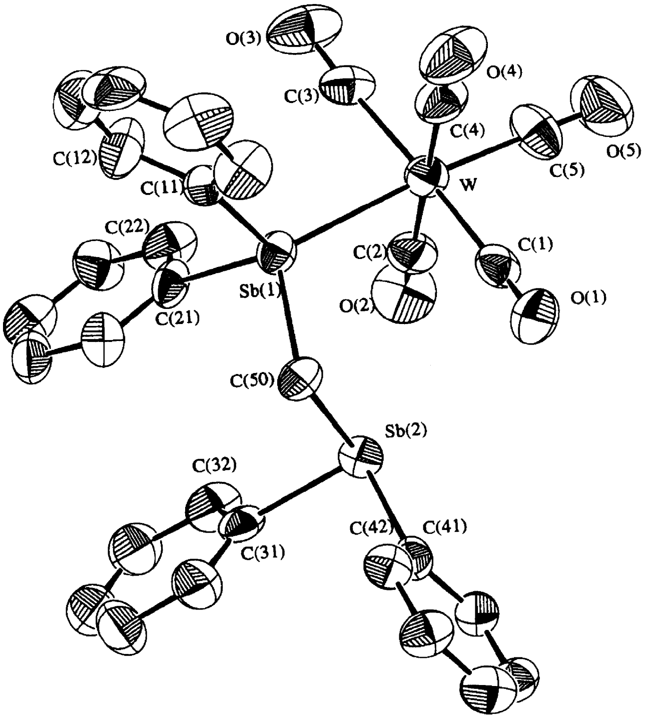


Fig. 20. Structure of $[W(CO)_5(Ph_2SbCH_2SbPh_2)]$ from ref. [27] by permission of the Royal Society of Chemistry.

cis-$[(CO)_4Cr(\mu\text{-}Me_2SbSSbMe_2)_2Cr(CO)_4]$ and $[Cr(CO)_4\{MeSb(SSbMe_2)_2\}]$ (Fig. 23) [242]. The last complex contains a tristibine, $MeSb(SSbMe_2)_2$, formed in a rearrangement which eliminates $SbMe_3$. Comparisons of the IR spectra of their carbonyl complexes suggest that the $R_2SbCH_2SbR_2$ are stronger σ-donors than the O or S bridged ligands.

$[Mn_2(CO)_8(\mu\text{-}R_2SbCH_2SbR_2)]$ (R = Me or Ph) were made in modest yield from $Mn_2(CO)_{10}$ and the ligands in toluene in the presence of $[\{(Cp)Fe(CO)_2\}_2]$ [243] whilst photolysis of a mixture of $Mn_2(CO)_{10}$ and the ligand in toluene gives $[Mn_2(CO)_8(\mu\text{-}Me_2SbCH_2SbMe_2)]$ and $[Mn_2(CO)_6(\mu\text{-}Ph_2SbCH_2SbPh_2)_2]$ respectively [244]. The latter has structure shown in Fig. 24. Carbonyl groups are less easily displaced from rhenium carbonyl and even photolysis gives only *ax*-$[Re_2(CO)_9(\eta^1\text{-}R_2SbCH_2SbR_2)]$ [244]. Photolysis of $[(MeC_5H_4)Mn(CO)_3]$ in thf, followed by addition of the appropriate ligand gave $[(MeC_5H_4)Mn(CO)_2(\eta^1\text{-}R_2SbYSbR_2)]$ and $[\{(MeC_5H_4)Mn(CO)_2\}_2(\mu\text{-}R_2SbYSbR_2)]$ (Y = CH_2, O, S) [245]. Reaction of $Ph_2SbCH_2SbPh_2$ with $[Mn(CO)_5X]$ (X = Cl, Br, I) gave *cis*-$[Mn(CO)_4(\eta^1\text{-}Ph_2SbCH_2SbPh_2)X]$ [243].

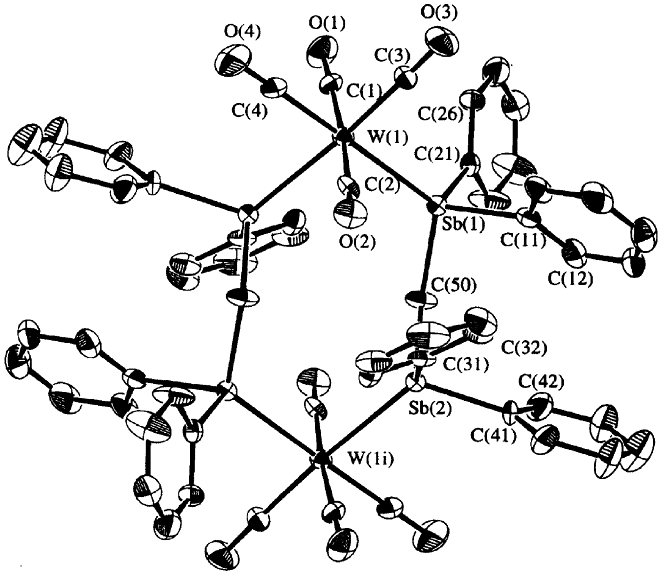


Fig. 22. Structure of $[(CO)_4W(Ph_2SbCH_2SbPh_2)_2W(CO)_4]$ from ref. [27] by permission of the Royal Society of Chemistry.

Direct reaction of $Fe(CO)_5$ with $Ph_2SbCH_2SbPh_2$ using various catalysts gives poor yields of $[Fe(CO)_4(\eta^1\text{-}$

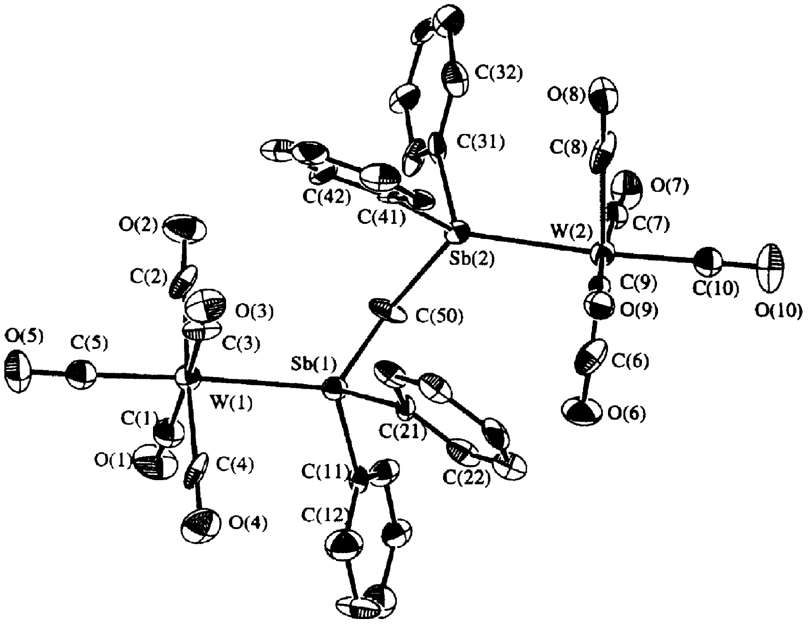


Fig. 21. Structure of $[(CO)_5W(Ph_2SbCH_2SbPh_2)W(CO)_5]$ from ref. [27] by permission of the Royal Society of Chemistry.

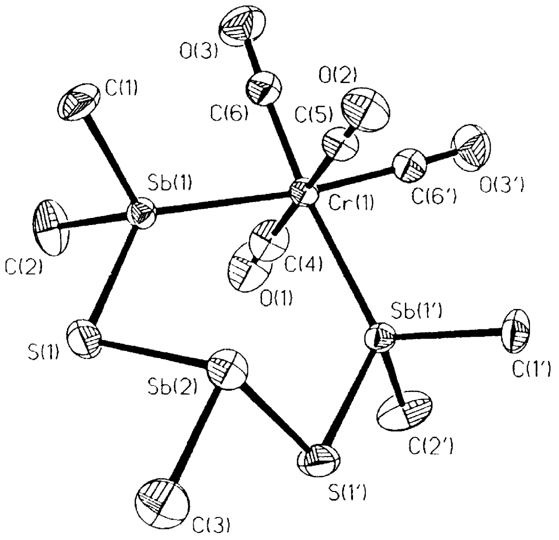


Fig. 23. Structure of [$Cr(CO)_4\{MeSb(SSbMe_2)_2\}$] from ref. [242] by permission of Wiley-VCH.

$Ph_2SbCH_2SbPh_2$)] and the complex is best made from $Fe_2(CO)_9$/thf and the ligand [243]. The structure reveals an axially substituted trigonal bipyramidal molecule. Attempts to attach a second-$Fe(CO)_4$ gave very unstable products, but with the stronger donor methyl ligand the product is [$(CO)_4Fe(\mu\text{-}Me_2SbCH_2SbMe_2)Fe(CO)_4$] [243]. The dimers [$\{P(OPh)_3\}_2(CO)_2Fe(\mu\text{-}Ph_2SbYSbPh_2)Fe(CO)_2\{P(OPh)_3\}_2$] (Y = CH_2, O, S) are also known [245].

The combination of $Ph_2SbCH_2SbPh_2$, [$Ru(dmf)_6$] [CF_3SO_3]$_2$, and LiX (X = Cl or Br) in refluxing ethanol gave pink or brown *trans*-[$RuX_2(\eta^1\text{-}Ph_2SbCH_2SbPh_2)_4$], whilst [$OsCl_2(dmso)_4$] formed yellow *trans*-[$OsCl_2(\eta^1\text{-}Ph_2SbCH_2SbPh_2)_4$] [246]. However the complexes isolated from related systems had a different stoichiometry [$RuI_2(Ph_2SbCH_2SbPh_2)_3$] and [$OsBr_2(Ph_2SbCH_2SbPh_2)_3$], and the structure of the former showed it to contain the first example of a chelating distibinomethane ligand (Fig. 25) [246]. As can be seen the complex contains two monodentate and one chelate distibine, the latter in a strained 4-membered ring, <Sb–C–Sb = 93.5° (compared with ~118° in the η^1-coordinated ligands), and the Ru–Sb is also longer in the ring (2.611 Å (av)) versus 2.581 Å (av)). The presence of the two different coordination modes of the ligands is also evident in the ^1H or ^{13}C NMR spectra, where the ring CH_2 resonances are substantially to high frequency of that in the η^1-coordinated ligands [246].

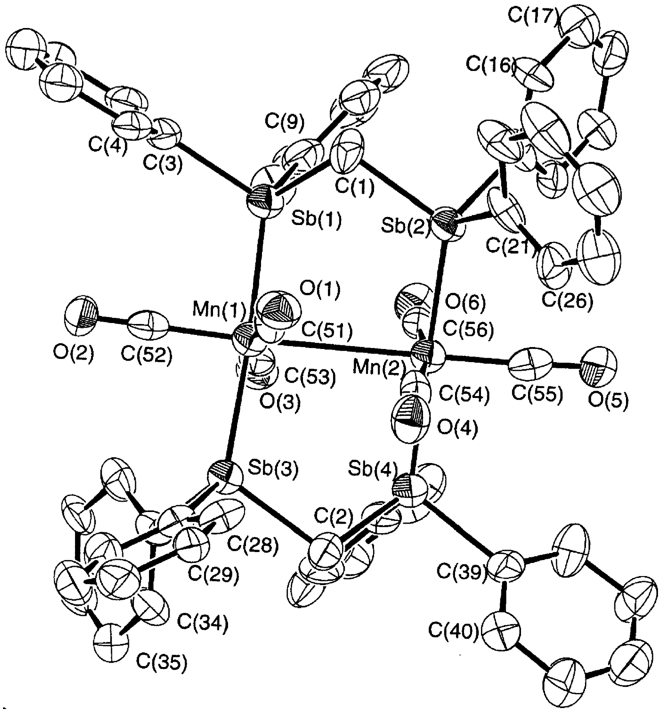


Fig. 24. Structure of [$Mn_2(CO)_6(Ph_2SbCH_2SbPh_2)_2$] from ref. [244] by permission of Elsevier S.A.

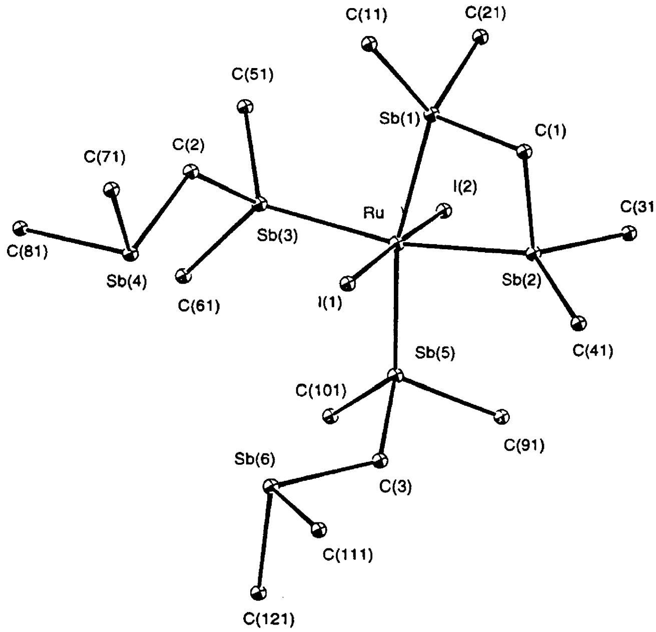


Fig. 25. Core geometry of [$RuI_2(Ph_2SbCH_2SbPh_2)_3$] with phenyl groups omitted, from ref. [246] by permission of the Royal Society of Chemistry.

Dicobalt octacarbonyl and $R_2SbCH_2SbR_2$ form unstable [$Co_2(CO)_6(\mu\text{-}R_2SbCH_2SbR_2)$] [243]. Dimeric [$\{Rh(CO)Cl\}_2(\mu\text{-}R_2SbCH_2SbR_2)_2$] are also formed on reaction of $R_2SbCH_2SbR_2$ with [$\{Rh(CO)_2Cl\}_2$] [246]. The phosphino(stibino)methanes $R_2PCH_2SbR'_2$ (R = ^{i}Pr R′ = ^{i}Pr, ^{t}Bu; R = Cy, R′ = ^{t}Bu) cleave [$\{Rh(COD)Cl\}_2$] to form [$Rh(COD)Cl(\eta^1\text{-}R_2PCH_2SbR'_2)$] with the ligands coordinated only via the phosphorus; treatment with a large anion (Y = BPh_4^- or PF_6^-) converts them to chelate complexes [$Rh(COD)(R_2PCH_2SbR'_2)$]Y [247]. The cations react with CF_3CO_2H to give hydrido-dimers [$Rh_2(R_2PCH_2SbR'_2)_2H_2(\mu\text{-}H)(\mu\text{-}CF_3CO_2)_2$]Y, and with CH_2N_2 insert a methylene group into the Rh–Sb bond to give Sb-ylide ligands [247,248].

Rhodium(III) halides and $Ph_2SbCH_2SbPh_2$ were reported some years ago to give mononuclear non-electrolytes [$RhX_3(Ph_2SbCH_2SbPh_2)_2$] of unknown structure [1]. Re-examination by ^1H and $^{13}C\{^1H\}$ NMR shows that similar to the Ru(II) complex above they contain both chelated and mon-

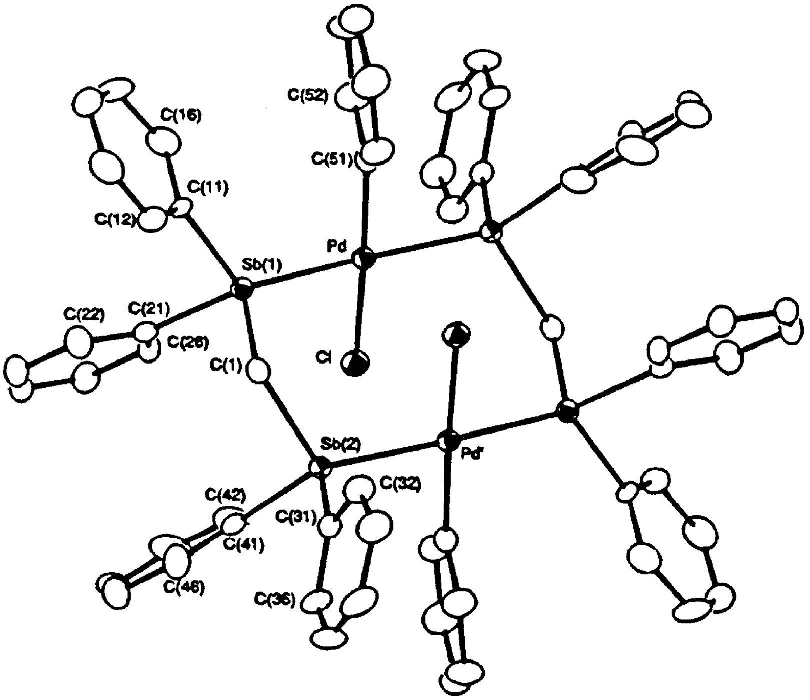


Fig. 26. Structure of [{PdCl(σ-Ph)($Ph_2SbCH_2SbPh_2$)}$_2$] from ref. [249] by permission of the American Chemical Society.

odentate distibine groups, the major isomer being the meridional form, although for X = Br or I there is evidence for a second minor isomer presumably with a facial geometry [246].

Excess tetracarbonylnickel and $R_2SbCH_2SbR_2$ produce a waxy solids [$Ni_2(CO)_6(R_2SbCH_2SbR_2)$] which have IR and $^{13}C\{^1H\}$ NMR spectra consistent with the ligand bridging two tricarbonylnickel moieties [243]. On standing in solution these partially decompose forming $Ni(CO)_4$, some black solid and [$Ni(CO)_3(\eta^1\text{-}R_2SbCH_2SbR_2)$]. Palladium(II) and platinum(II) halides form two types of complex with $Ph_2SbCH_2SbPh_2$, mononuclear [$MX_2(Ph_2SbCH_2SbPh_2)_2$] and dimers [$M_2X_4(Ph_2SbCH_2SbPh_2)_2$] [1]. The [$MX_2(Ph_2SbCH_2SbPh_2)_2$] are unstable in solution decomposing into the dimers (and other products) on standing, but multinuclear NMR data on freshly prepared solutions shows a mixture of *cis*- and *trans*-isomers with η^1-$Ph_2SbCH_2SbPh_2$ for M = Pt, and single isomers for M = Pd [246]. The [$PdCl_2(Ph_2SbCH_2SbPh_2)_2$] is very prone to Sb–Ph bond cleavage in solution, cleanly forming the structurally characterised σ-Ph complex [{PdCl(σ-Ph)($Ph_2SbCH_2SbPh_2$)}$_2$] (Fig. 26); the process being promoted photochemically [249]. The decomposition is minimal with the bromide or iodide systems and does not occur for the platinum systems.

The structures of the dimers [$M_2X_4(Ph_2SbCH_2SbPh_2)_2$] show them to be distibine-bridged, but whilst [$Pd_2I_4(Ph_2SbCH_2SbPh_2)_2$] has *trans*-geometry at each Pd, the [$Pd_2Br_4(Ph_2SbCH_2SbPh_2)_2$], [$Pt_2Cl_4(Ph_2SbCH_2SbPh_2)_2$] and [$Pt_2Br_4(Ph_2SbCH_2SbPh_2)_2$] all have the *cis–trans*-dimer structure shown in Fig. 27, and multinuclear NMR studies suggest these are the major (only) form in solution [246]. The reasons underlying the preference for this structure are unclear, none of the very many $Ph_2PCH_2PPh_2$ [240] compounds has been shown to have this structure, but very recently both *trans–trans*- and *cis–trans*-isomers of [$Pt_2Cl_4(Ph_2AsCH_2AsPh_2)_2$] have been structurally characterised [250]. The [$MCl_2(Me_2SbCH_2SbMe_2)$] (M = Pd or Pt) show dimer ions in the FAB MS, but were too poorly soluble in common solvents for any solution measurements, a property

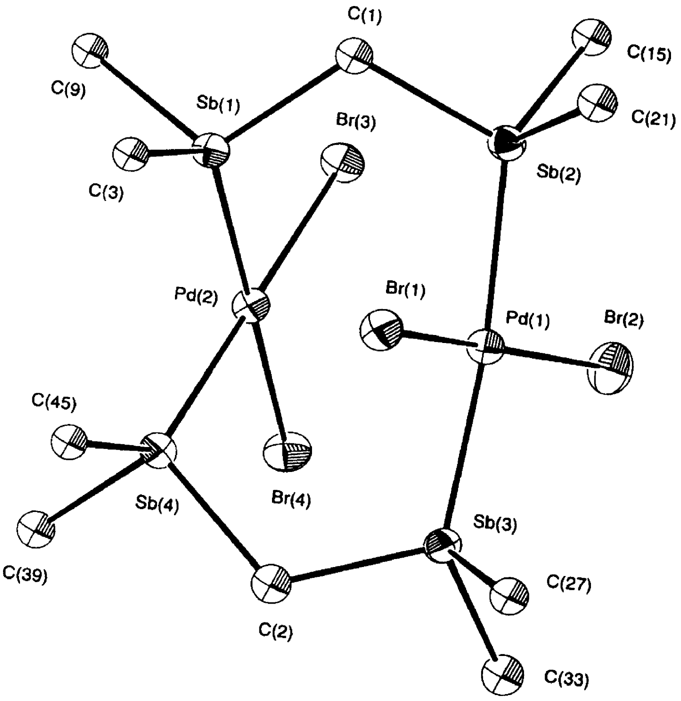


Fig. 27. Structure of [{$PdBr_2(Ph_2SbCH_2SbPh_2)$}$_2$] with phenyl groups omitted from ref. [246] by permission of the Royal Society of Chemistry.

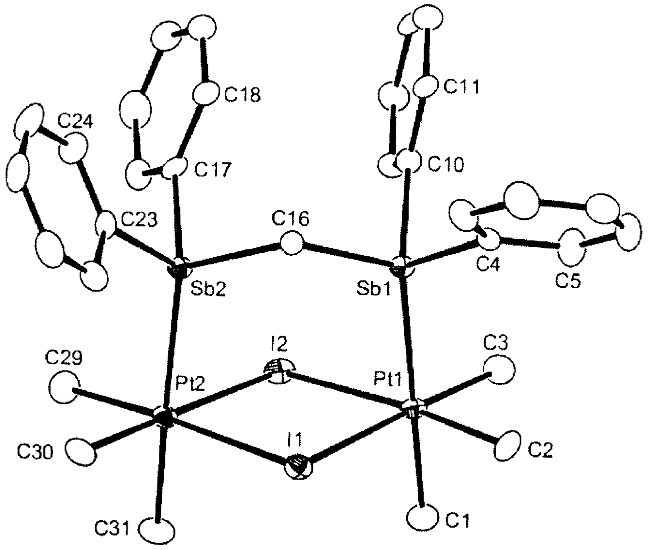


Fig. 28. Structure of [$(Me_3PtI)_2(Ph_2SbCH_2SbPh_2)$] from ref. [198].

shared by $Me_2PCH_2PMe_2$ and $Me_2AsCH_2AsMe_2$ analogues [251], and their structures are unclear [246].

In contrast to longer backboned ligands (q.v.) the $R_2SbCH_2SbR_2$ react with $[PtMe_3I]_4$ to form dimers of the type [$\{Me_3Pt\}_2(\mu\text{-}I)_2(\mu\text{-}R_2SbCH_2SbR_2)$] shown in Fig. 28 [198].

Copper(I), silver(I) and gold(I) form complexes [$M(R_2SbCH_2SbR_2)$]Y (R = Me or Ph, Y = BF_4, PF_6) which are labile in solution and presumably ligand bridged oligomers in the solid state [246]. A red-brown [$(AuCl)_2(Ph_2SbCH_2SbPh_2)$] was made from [AuCl(tetrahydrothiophen)] and $Ph_2SbCH_2SbPh_2$, and was the unexpected product of reaction of [$PdCl_2(Ph_2SbCH_2SbPh_2)_2$] with [AuCl(tetrahydrothiophen)] [251].

7.2. Other distibines

Although distibines with long alkyl backbones have been prepared [1] there is no study of their complexes, and since neither C_2 distibino-alkanes, $R_2SbCH_2CH_2SbR_2$, or alkenes, *cis*-$R_2SbCH=CHSbR_2$, have been prepared [1,2], the ligands capable of chelation are *o*-$C_6H_4(SbR_2)_2$, $R_2Sb(CH_2)_3SbR_2$ and *o*-$C_6H_4(CH_2SbR_2)_2$ which afford 5, 6 or 7 membered rings, respectively. Ligands incapable of chelation are the *m*- or *p*-$C_6H_4(SbR_2)_2$ and *m*- or *p*-$C_6H_4(CH_2SbR_2)_2$ for which a few examples of monodentate or bridging bidentate behaviour are reported.

The complexes of $R_2Sb(CH_2)_3SbR_2$ (R = Me or Ph) with group 6 carbonyls have been reinvestigated (some were reported in the 1970's but with little data). The [$M(CO)_4\{R_2Sb(CH_2)_3SbR_2\}$] (M = Cr, Mo, W) are best made from [$M(CO)_4(L\text{–}L)$] (L–L = norbornadiene or (piperidine)$_2$) [31]. They were fully characterised by IR, ^1H, $^{13}C\{^1H\}$ NMR and APCI MS and comparison of the IR and NMR data with those in corresponding group 16 ligands suggested that the distibines are better donors towards these low valent metal centres than dithio- or diseleno-ethers and similar to ditelluroethers. The *o*-$C_6H_4(CH_2SbMe_2)_2$ formed similar complexes [$M(CO)_4\{o\text{-}C_6H_4(CH_2SbMe_2)_2\}$] (M = Mo, W) [16]. The *p*-$C_6H_4(CH_2SbMe_2)_2$ reacted with excess [$W(CO)_5(thf)$] to form the ligand bridged dimer [$(CO)_5W\{p\text{-}C_6H_4(CH_2SbMe_2)_2\}W(CO)_5$], but curiously the *m*-$C_6H_4(CH_2SbMe_2)_2$ only attached one tungsten centre on reaction with excess of [$W(CO)_5(thf)$] to form [$W(CO)_5\{\eta^1\text{-}m\text{-}C_6H_4(CH_2SbMe_2)_2\}$] [16].

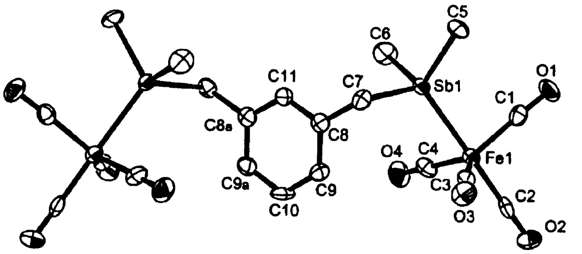
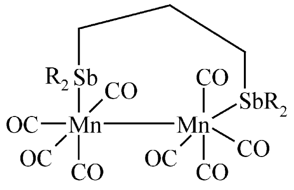


Fig. 29. Structure of [$\{Fe(CO)_4\}_2\{m\text{-}C_6H_4(CH_2SbMe_2)_2\}$] from ref. [16] by permission of the Royal Society of Chemistry.

Photolysis of a mixture of [$Mn_2(CO)_{10}$] with $Ph_2Sb(CH_2)_3SbPh_2$ in toluene, or reaction in the presence of [$\{CpFe(CO)_2\}_2$], gave [$Mn_2(CO)_8\{Ph_2Sb(CH_2)_3SbPh_2\}$] which was assigned structure (VIII) on the basis of its IR spectrum [35]. The *fac*-[$Mn(CO)_3Cl\{R_2Sb(CH_2)_3SbR_2\}$] were formed from $Mn(CO)_5Cl$ and the distibines in $CHCl_3$, and are much less stable than diphosphine or diarsine analogues, decomposing quite rapidly in solution [252]. The reaction of $Fe_2(CO)_9$ in thf (essentially "$Fe(CO)_4$(thf)") with $R_2Sb(CH_2)_3SbR_2$, or *o*-, *m*-, or *p*-$C_6H_4(CH_2SbMe_2)_2$ gave red-brown oils or waxy solids [$(CO)_4Fe(\mu\text{-distibine})Fe(CO)_4$], identified by IR spectroscopy and APCI MS as ligand bridged dimers with the antimony in axial sites on trigonal bipyramidal iron centres, and confirmed in the case of the *m*-$C_6H_4(CH_2SbMe_2)_2$ complex by an X-ray structure (Fig. 29) [16,31].



(VIII)

The [$RuX_2\{Ph_2Sb(CH_2)_3SbPh_2\}_2$] (X = Cl, Br or I) were obtained from [$Ru(dmf)_6$][CF_3SO_3]$_2$, LiX and the ligand in ethanol as pale pink-brown powders, very poorly soluble in most organic solvents [28]. They are easily oxidised by HNO_3/HBF_4 to soluble intensely coloured cations [$RuX_2\{Ph_2Sb(CH_2)_3SbPh_2\}_2$]$BF_4$, and cyclic voltammetry studies on these reveal reversible Ru(II)/Ru(III) couples at somewhat more positive potentials than diarsine or diphosphine analogues. Crystals of [$RuBr_2\{Ph_2Sb(CH_2)_3SbPh_2\}_2$] were obtained by decomposition of a solution of the Ru(III) complex and revealed a *trans*-octahedral geometry [28]. The orange osmium(II) analogue [$OsCl_2\{Ph_2Sb(CH_2)_3SbPh_2\}_2$] was made from [$OsCl_2(dmso)_4$] and has an identical structure [253].

Cobalt carbonyl–stibine complexes are often unstable and that is true of the complexes formed from $[Co_2(CO)_8]$ and $R_2Sb(CH_2)_3SbR_2$, both of which decomposed in a few days in the solid state and rapidly in solution. For R = Ph the complex formed, $[Co_2(CO)_6\{Ph_2Sb(CH_2)_3SbPh_2\}]_n$, appears to be oligomeric with unbridged hexacarbonyldicobalt units linked by distibine molecules, whilst for R = Me, the product was $[Co_2(CO)_4\{Me_2Sb(CH_2)_3SbMe_2\}_3][Co(CO)_4]_2$ containing 5-coordinate cobalt cations linked by a bridging distibine [31]. Rare cobalt(III) distibine cations *trans*-$[CoX_2\{o\text{-}C_6H_4(CH_2SbMe_2)_2\}_2]BPh_4$ were formed by air-oxidation of CoX_2 (X = Br, I, ≠Cl) $NaBPh_4$ and *o*-$C_6H_4(CH_2SbMe_2)_2$ in nitromethane [254]. The complexes are unstable in solution and decompose slowly in the solid state, but were identified by comparison of their spectroscopic properties with those of the more robust $[CoX_2\{o\text{-}C_6H_4(SbMe_2)_2\}_2]^+$ reported some years ago [1]. The formation of complexes with the small hard Co(III) cation with 7-membered chelate rings in the xylyl distibine was unexpected [254]. The orange $[Rh(CO)\{Ph_2Sb(CH_2)_3SbPh_2\}_2][Rh(CO)_2Cl_2]$ is formed from $[\{Rh(CO)_2Cl\}_2]$ and the ligand, and converted by excess ligand into $[Rh(CO)\{Ph_2Sb(CH_2)_3SbPh_2\}_2]Cl$ [147]. *trans*-$[RhX_2(L\text{-}L)_2]BF_4$ (L-L = $Ph_2Sb(CH_2)_3SbPh_2$, *o*-$C_6H_4(SbMe_2$, X = Cl, Br, I) were formed by reaction of $RhX_3 \cdot nH_2O$ or $[Rh(H_2O)_6]^{3+}$/LiX and the distibines in ethanol [255]. In contrast to many similar reactions with diphosphines or diarsines which yield a mixture of *cis* and *trans* isomers, only *trans* isomers were observed with the distibines, and attempts to convert these to the *cis* via the carbonates caused decomposition. The X-ray structure of *trans*-$[RhCl_2\{Ph_2Sb(CH_2)_3SbPh_2\}_2]ClO_4$ was reported, and ^{103}Rh NMR data recorded; the latter show δ(Rh) to high frequency of phosphorus or arsenic analogues, and a low frequency shift with halide Cl → Br → I. The $[RhCl_2\{o\text{-}C_6H_4(CH_2SbMe_2)_2\}_2]BF_4$ has also been characterised [254].

Substituted nickel carbonyl complexes have been made for various distibines, mostly to establish the electronic properties of the ligands via the a_1 IR stretch of $-Ni(CO)_3$ groups and the ^{13}C NMR resonance of the same, which can be compared with similar data on a wide range of group 15 ligands. The stibine complexes are oils or waxy solids, which decompose in a few hours–days depositing elemental nickel. The complexes identified by a combination of IR, ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy are $[(CO)_3Ni(\mu\text{-distibine})Ni(CO)_3]$ (distibine = $R_2Sb(CH_2)_3SbR_2$ R = Me or Ph), $[(CO)_3Ni(\eta^1\text{-distibine})]$ (distibine = *m*- or *p*-$C_6H_4(CH_2SbMe_2)_2$, $Me_2Sb(CH_2)_3SbMe_2$), whilst *m*- or *p*-$C_6H_4(SbMe_2)_2$ give inseparable mixtures of $[(CO)_3Ni(\mu\text{-distibine})Ni(CO)_3]$, $[(CO)_3Ni(\eta^1\text{-distibine})]$, and some dicarbonyl species, probably $[(CO)_2Ni(\mu\text{-distibine})_2Ni(CO)_2]$, since they cannot chelate [16,31]. Only *o*-$C_6H_4(CH_2SbMe_2)_2$ cleanly forms a dicarbonyl monomer in $[Ni(CO)_2\{o\text{-}C_6H_4(CH_2SbMe_2)_2\}]$ [16].

The reaction of "$NiXClO_4$" with *o*-$C_6H_4(CH_2SbMe_2)_2$ in ^{n}BuOH gave deep blue (X = Br) or dark green (X = I) complexes $[NiX\{o\text{-}C_6H_4(CH_2SbMe_2)_2\}_2]ClO_4$, with UV-vis spectra consistent with low-spin trigonal bipyramidal Ni(II) [254], and the structure was confirmed by an X-ray study of the iodide (Fig. 30).

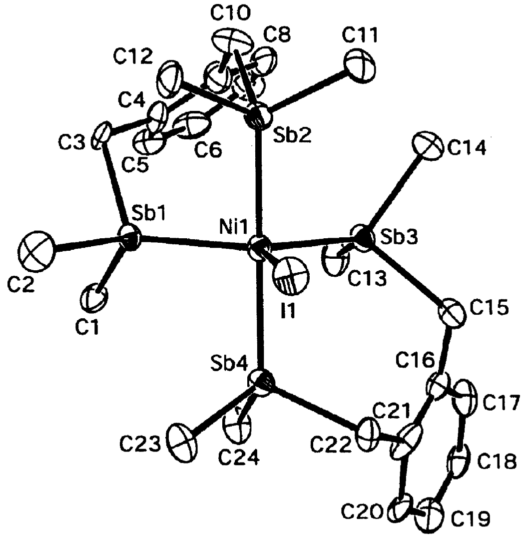


Fig. 30. Structure of the cation $[NiI\{o\text{-}C_6H_4(CH_2SbMe_2)_2\}_2]^+$ from ref. [254] by permission of the Royal Society of Chemistry.

The formation of Ni(II) complexes of the xylyl distibine was unexpected and clearly shows that the ligand, despite forming a 7-membered chelate ring is pre-organised for chelation; the "flexibility" is evident in that the chelate bite in the iodide, d(Sb· · ·Sb), was ~3.46 Å, whereas in the Cu(I) complex (below) it is ~4 Å, the difference being accommodated by different conformations of the xylyl backbone [254].

The *o*-$C_6H_4(CH_2SbMe_2)_2$ forms only 1:1 complexes with $PtCl_2$ or $PdCl_2$, which have planar geometries, but in the presence of $TlPF_6$ and 2 equiv. of ligand, the planar bis(ligand) complexes $[M\{o\text{-}C_6H_4(CH_2SbMe_2)_2\}_2][PF_6]_2$ (M = Pd or Pt) are formed; both have been characterised by X-ray studies (Fig. 31) [254]. Palladium(II) complexes of chiral distibines or an Sb,P chelate based upon the binaphthyl backbone (Section 2) have been briefly described [20,21]. Platinum(IV) halide complexes of stibine ligands have been described but decompose very rapidly in solution with halogenation of the stibine[1]. In marked contrast, $[PtMe_3I(\text{distibine})]$ (distibine = *o*-$C_6H_4(CH_2SbMe_2)_2$,

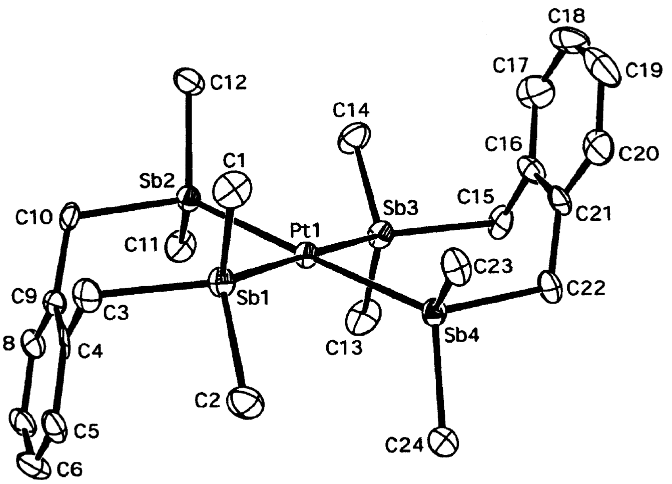


Fig. 31. Structure of $[Pt\{o\text{-}C_6H_4(CH_2SbMe_2)_2\}_2]^{2+}$ from ref. [254] by permission of the Royal Society of Chemistry.

$R_2Sb(CH_2)_3SbR_2$), made from the ligands and $[PtMe_3I]_4$ are stable both in the solid state or in solution, although on moderate heating they decompose predominantly by reductive elimination of ethane [198]. All three complexes were characterised by X-ray crystal structures and multinuclear NMR spectroscopy. The Pt(II) analogues $[PtMe_2(\text{distibine})]$ (distibine = $R_2Sb(CH)_3SbR_2$, R = Me or Ph, $o\text{-}C_6H_4(CH_2SbMe_2)_2$) and the ligand bridged dimers $[Me_2Pt(R_2SbCH_2SbR_2)_2PtMe_2]$ were made from $[PtMe_2(SMe_2)_2]$ and the distibines in benzene solution [198].

Pseudo-tetrahedral copper(I) complexes $[Cu(\text{distibine})_2]BF_4$ (distibine = $o\text{-}C_6H_4(CH_2SbMe_2)_2$, $o\text{-}C_6H_4(SbMe_2)_2$, $R_2Sb(CH_2)_3SbR_2$) are obtained from $[Cu(MeCN)_4]BF_4$ and the ligand in chlorocarbons and are air-stable colourless solids [199,200]. Their pseudo-tetrahedral structure follows from the presence of sharp ^{63}Cu NMR resonances which show the presence of near cubic symmetry, and was confirmed for $[Cu\{o\text{-}C_6H_4(CH_2SbMe_2)_2\}_2]BF_4$ by an X-ray structure [254]. The silver(I) complexes $[Ag(\text{distibine})_2]Y$ (distibine = $o\text{-}C_6H_4(CH_2SbMe_2)_2$, $R_2Sb(CH_2)_3SbR_2$; Y = BF_4 or CF_3SO_3) made directly from the silver(I) salt and the ligands in dichloromethane, exhibit varying degrees of light sensitivity, the xylyl ligand complex being particularly sensitive [200,254].

The reaction of $o\text{-}C_6H_4(CH_2SbMe_2)_2$ with 2 equiv. of [AuCl(tht)] (tht = tetrahydrothiophen) gives yellow $[\{o\text{-}C_6H_4(CH_2SbMe_2)_2\}(AuCl)_2]$ but this turns black in a few hours even in a freezer in the dark [254].

The hybrid ligands $Ph_2SbCH_2CH(Me)ZH$ (Z = O or S) eliminate propane on reaction with Ga^iPr_3 or In^iPr_3 to form $[M^iPr_2(Ph_2SbCH_2CH(Me)Z)]$, formulated as monomers on the basis of their ^1H NMR spectra [256].

8. Polydentates

Only one tritertiary stibine has been characterised, $MeC(CH_2SbPh_2)_3$ and a selection of its complexes have been described [4]. The ligand behaves as a tridentate chelate in *fac*-$[M(CO)_3\{MeC(CH_2SbPh_2\}_3)]$ (M = Cr, Mo, W) made directly from the ligand and $[M(CO)_6]$ in refluxing ethanol in the presence of $NaBH_4$. The structure of the molybdenum complex was determined (Fig. 32). The ligand did not react with Co(II) or Ni(II) salts, but with $[Cu(MeCN)_4]BF_4$ it formed the white $[Cu\{MeC(CH_2SbPh_2)_3\}(MeCN)]BF_4$ probably with a tetrahedral $CuNSb_3$ core, and with $RhCl_3{\cdot}3H_2O$ gave the rhodium(III) complex *fac*-$[Rh\{MeC(CH_2SbPh_2)_3\}Cl_3]$. In contrast, the ligand is bidentate in $[M\{MeC(CH_2SbPh_2)_3\}Cl_2]$ (M = Pd or Pt) on the basis of NMR studies, and although the VTNMR data indicated the absence of exchange between coordinated and 'free' $-SbPh_2$ groups, attempts to coordinate an AuCl group to the free arm was unsuccessful. This contrasts with the behaviour of the phosphine or arsine analogues, where $[MCl_2\{MeC(CH_2EPh_2)_3\}AuCl]$ are readily formed [251].

9. Bismuthine complexes

The number of bismuthine complexes remains small. Of the papers surveyed for this article approximately half of those mentioning bismuthines reported the failure to isolate complexes from systems successfully incorporating other group 15 ligands. In several more, $BiPh_3$ appeared in the list of ligands "complexed" along with its lighter analogues, but with little or no data provided to substantiate the formation of a bismuthine complex. Whilst the new complexes described below show that

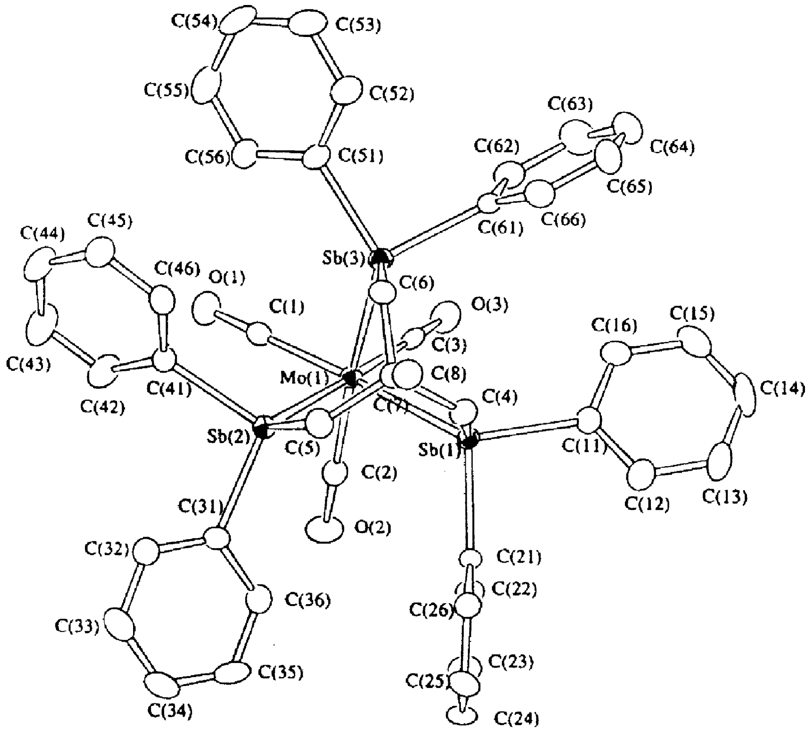


Fig. 32. Structure of $[Mo(CO)_3\{MeC(CH_2SbPh_2)_2\}]$ from ref. [4] by permission of the American Chemical Society.

bismuthine complexes can be made for at least a limited range of systems, it is clearly necessary for new compounds to be thoroughly characterised, assumed identification by “analogy” with lighter analogues is unreliable.

Included in the systems investigated for $BiPh_3$ which failed to give complexes, in almost all cases using routes successful with $SbPh_3$ were reactions with $Ni(CO)_4$, $Fe(CO)_5$, $Fe(CO)_4(thf)$, $Co_2(CO)_8$ and $Mn_2(CO)_{10}$ [24]. The ES^+ mass spectra obtained from MeCN solutions of $[Cu(MeCN)_4]^+$ or $AgNO_3$ containing $BiPh_3$ gave spectra mostly indicative of decomposition products (some unidentified) [201]. Attempts to make Au(I)–BiR_3 species using a range of gold reagents and $BiMe_3$, $BiPh_3$, $BiMePh_2$ and Bi(*o*-tolyl)$_3$ failed; in all cases the bismuthine transferred R groups to the gold [257].

Slightly more successful were the spectroscopic identification in solution of $[(C_5H_5)Mo(CO)(BiPh_3)_2]BF_4$ [57] and $[Fe(C_9H_7)(CO)_2(BiPh_3)]BF_4$ [77]. Although neither complex could be isolated, the trends in the spectroscopic data relative to characterised analogues with lighter group 15 ligands support the formulations.

Three examples of Cu thione/$BiPh_3$ mixed ligand complexes have been reported, however no evidence for Cu–Bi bonding was presented [206].

The previously known $[M(CO)_5(BiPh_3)]$ (M = Cr, Mo W) were re-examined in detail [32] and the structures of M = Mo and W determined ($[Cr(CO)_5(BiPh_3)]$ was structurally characterised in 1979 [258]). The complexes were prepared from $[M(CO)_5(thf)]$ and $BiPh_3$, and appear air-stable in the solid state, although solutions in common solvents deposit black solids in a few hours. The points of interest are the $^1J(^{183}W–^{13}C)$ coupling constant (183 Hz) on the resonance of the carbonyl group *trans* to $BiPh_3$ in $[W(CO)_5(BiPh_3)]$ which places $BiPh_3$ very low in the *trans* influence series, and the opening of the C–Bi–C angles in the ligand upon coordination (Section 4).

The dibismuthine *p*-$C_6H_4(BiPh_2)_2$ was succesfully complexed with Cr and W pentacarbonyl residues, but all attempts to isolate the Mo analogue resulted in rapid decomposition even at low temperatures [24]. The reaction of $[W(CO)_5(thf)]$ with one or 0.5 molar equivalents of *p*-$C_6H_4(BiPh_2)_2$ gave yellow $[W(CO)_5\{p\text{-}C_6H_4(BiPh_2)_2\}]$ or $[W(CO)_5\{p\text{-}C_6H_4(BiPh_2)_2\}W(CO)_5]$ respectively, which were characterised by analysis, IR and $^{13}C\{^1H\}$ NMR spectroscopy. Similar reactions using $[Cr(CO)_5(thf)]$ gave the greenish-yellow $[Cr(CO)_5\{p\text{-}C_6H_4(BiPh_2)_2\}Cr(CO)_5]$ and yellow $[Cr(CO)_5\{p\text{-}C_6H_4(BiPh_2)_2\}]$. Although stable in the solid state, the 2:1 chromium complex decomposes rapidly in solution to the 1:1 complex, $Cr(CO)_6$ and unidentified products.

The reaction of $[Fe(C_5H_5)(CO)_2(thf)]BF_4$ with *p*-$C_6H_4(BiPh_2)_2$ in CH_2Cl_2 gave orange crystals identified by an X-ray crystal structure as the known complex $[Fe(C_5H_5)(CO)_2(BiPh_3)]BF_4$ which must result from Bi–C bond fission in the dibismuthine [24].

A completely different mode of coordination of $BiPh_3$ was identified in some half-sandwich ruthenium complexes. Whilst treatment of $[Ru(C_5H_5)(MeCN)_3]PF_6$ with PPh_3, $AsPh_3$ or $SbPh_3$ (L) gave $[Ru(C_5H_5)(MeCN)_2\ L]^+$ with the ligands functioning a monodentates coordinated through the group 15 atom, the product using $BiPh_3$ was a mixture of compounds with the ligand coordinated via an η^6-phenyl group [97]. The 1:1 complex $[Ru(C_5H_5)(BiPh_3)]^+$ was characterised spectroscopically in solution, but a 2:1 Ru:Bi species $[Ru_2(C_5H_5)_2(BiPh_3)][PF_6]_2$ was isolated as a yellow solid and its X-ray structure (Fig. 33) revealed two $Ru(C_5H_5)$ moities bridged by the bismuthine, each Ru being coordinated η^6 to a different phenyl group.

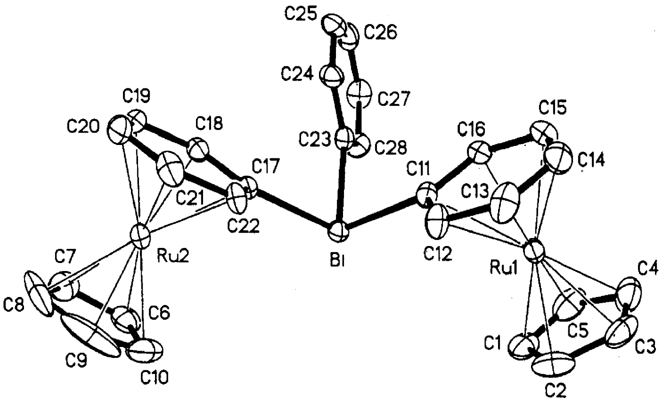


Fig. 33. Structure of $[Ru_2(\eta^5\text{-}C_5H_5)_2(\eta^6,\eta^6\text{-}Ph_2BiPh)][PF_6]_2$ from ref. [97] by permission of Elsevier S.A.

The first main group bismuthine complexes have been characterised recently [259]. The combination of R_3Ga (R = Me, Et, ^{t}Bu) with BiR'_3 (R′ = ^{i}Pr, $SiMe_3$) produced solid or liquid adducts $[R_3Ga(BiR'_3)]$ which NMR studies show are extensively dissociated in solution. Structures of $[Et_3Ga\{Bi(SiMe_3)_3\}]$ and $[^tBu_3Ga(Bi^iPr_3)]$ (Fig. 34) were determined and show very long Ga–Bi bonds (2.966(1), 3.135(1) Å, respectively) which are consistent with the weakness of the adducts. Whilst distibines R_4Sb_2 react with Me_3Ga or Me_3In to give heterocycles $[\{Me_2Ga(In)SbR_2\}_3]$, the dibismuthine Et_4Bi_2 gives simple adducts, $[^tBu_3Al(BiEt_3)]$ and $[^tBu_3Ga(BiEt_3)]$, on reaction with $^tBu_3Al$ or $^tBu_3Ga$, eliminating elemental bismuth in the process [260].

The hybrid ligand $Ph_2BiCH_2CHMeOH$ reacts with $^iPr_3Ga$ or $^iPr_3In$ with elimination of propane, forming $[^iPr_2Ga(In)(Ph_2BiCH_2CHMeO)]$ which are Bi, O chelates characterised, by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy [256].

10. Applications

The vast transition metal and organometallic chemistry supported by phosphine, and to a lesser extent arsine ligands, and the widespread use of such ligands in catalyst systems has up to now found few analogues in stibine systems. The search for new synthons and more specific catalysts systems continues unabated, and the quite different chemistry in platinum metal stibine systems developed by Werner and co-workers, surely will prompt much further effort in this area. The first chiral distibines have recently been obtained, and their catalytic applications are expected to follow. The very recent reports of the first well characterised stibine and bismuthine complexes of *p*-block metals, have resulted from the need for routes to III–V semi-conductors, and since the band gaps are dependent upon the element combi-

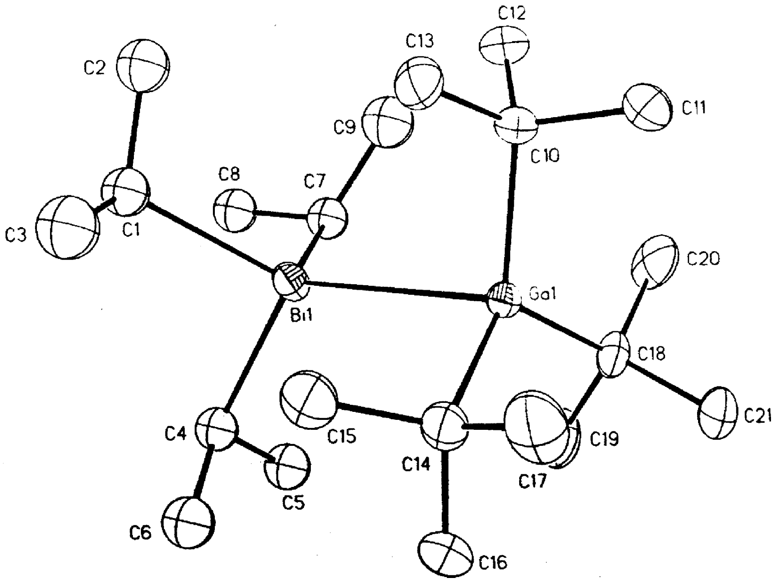


Fig. 34. Structure of [$^{t}Bu_3Ga(Bi^{i}Pr_3)$] from ref. [259] by permission of the American Chemical Society.

nation(s) present, this area is also expected to be very active in the future.

11. Conclusions

The results detailed in previous sections show that stibine chemistry has come of age in the last few years, and the profoundly different electronic properties of these ligands compared with lighter analogues, should result in much new research focusing on stibines and distibines in their own right, rather than as small components of work on group 15 ligands in general. The synthesis of new di- and poly-stibine ligands remains synthetically challenging, but here too, the quite different ligand properties expected compared to lighter analogues, will promote more effort. Incorporation of stibine donors into macrocycles is now also a feasible target, although the reactivity of the Sb–C bond will make the development of high yield routes very difficult. The search for bridging stibine ligand systems with metals other than Rh is also very timely, although the success will likely be serendipitous in the first few examples, since present understanding of the chemistry does not indicate clear synthetic strategies. The chemistry of stibines with early transition metal centres in positive oxidation states remains largely unexplored. The soft–hard ligand combination in such systems, probably requires that the strongest binding stibines will be required, those with alkyl substituents, small ring size chelates in this context a high yielding synthesis for $o\text{-}C_6H_4(SbR_2)_2$, would be extremely useful. Although it is difficult to predict chemistry in this area, the very different electronic properties of stibines compared with their lighter analogues, are likely to be particularly evident in such demanding systems.

Bismuthine complex chemistry will no doubt remain rather limited, but the characterisation of the first *p*-block examples, shows that in appropriate systems and with the carefully considered approaches, complexes can be formed. One should not take the poorly coordinating $BiPh_3$ as the archetypal bismuthine, and much work remains to be done with trialkyl bismuthines. Currently almost nothing is known about dibismuthine ligands and both polydentates and macrocycles are unknown.

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