Extreme Symbiosis: the Facile One-step Synthesis of the Paramagnetic Cobalt(III) Complex of Triphenylantimony, $CoI_3(SbPh_3)_2$, from the Reaction of Triphenylantimonydiiodine with Unactivated Coarse Grain Cobalt Metal Powder

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Triphenylantimony diiodine (2 equiv.) reacts with unactivated cobalt powder to yield the unexpected cobalt(III) complex $CoI_3(SbPh_3)_2$; this five coordinate species represents a rare example of a paramagnetic cobalt(III) complex.

In contrast to the large number of known complexes containing tertiary phosphine and arsine ligands, those containing tertiary stibines as ligands are much rarer.[1] Previous work has concentrated on complexes containing carbonyl ligands in which the metal is in a low oxidation state, thus facilitating the binding of the tertiary stibine. Even with these factors, it is only with 'soft' metals that a comprehensive range of complexes of stibines has been recognised.[1,2] The inferior coordinating ability of tertiary stibines, compared to the respective phosphines and arsines, has been shown from ^{13}C NMR,[3] IR[4] photoelectron spectroscopy,[5] gas phase proton affinities[6] and ligand displacement reaction studies.[7]

Perceived wisdom indicates that a tertiary stibine would not form a complex with a 'hard', high-oxidation metal, unless in the presence of carbonyl or other organometallic coligands. Thus, the relatively hard cobalt(II) centre is complexed with H_2dmg (dimethylglyoxime) to form $[Co(dmgH)_2(Ph_3Sb)]$[8]; and with such ligands even cobalt(III) complexes may be isolated, *viz*. $[Co(dmgH)_2(SnPh_3)(Ph_3Sb)]$,[9] $[Co(dmgH)_2Cl(Ph_3Sb)]$,[10] $[Co(dmgH)_2(N_3)(Ph_3Sb)]$[11] and $[Co(dmgH)_2(O_2Sr)(Ph_3Sb)]$.[12]

However, no cobalt(III) complex containing only halide and tertiary stibine ligands has previously been reported, and it is notable that apart from the complex $[Ph_3SbI][CoI_3(SbPh_3)]$[13] prepared here, *viz*. the reaction of cobalt powder with triphenylantimony diiodine, all previously known cobalt(II) or cobalt(III) complexes contained chelating tertiary stibine ligands,[9–12] there were no examples with only monodentate coligands. The only example of a crystallographically characterised cobalt(III) complex containing antimony donor atoms is $[Co(dmgH)_2Cl(Ph_3Sb)]$. The *d*(Co–Sb) in this complex is 2.55(5) Å which compares favourably with the present complex $CoI_3(SbPh_3)_2$ [*d*(Co–Sb) 2.536(3) and 2.589(3) Å]. the magnetic properties of the former complex were not investigated.

The results presented here are an extension of our reports of the reactions of R_3PX_2 (X = Br, I) species with coarse grain, unactivated metal powders, which yield known transition metal complexes, novel isomers of known complexes, complexes with the metal in a high oxidation state, and previously unknown metal complexes.[13] Since these reactions mostly proceed at room temperature and pressure, this novel synthetic technique clearly has great potential.

We have recently reported[14] the reaction of a number of diiodotriorganophosphorus compounds, R_3PI_2 ($R \neq Me$) and Ph_3SbI_2 with cobalt metal powder to produce the ionic complexes $[R_3PI][CoI_3(PR_3)I]$ and $[Ph_3SbI][CoI_3(SbPh_3)]$, **I**, respectively. In all cases the products are formed in quantitative yield, *e.g.* eqn. (1).

$$2Ph_3SbI_2 + Co \xrightarrow[Et_2O]{7\,d,\,60\,°C} \underset{\textbf{I}}{[Ph_3SbI][CoI_3(SbPh_3)]} \tag{1}$$

We report here that we have repeated this reaction to produce pale-green **I**, and allowed the reaction vessel and contents to stand for *ca*. 2 weeks. Examination of the vessel revealed that **I** had redissolved to form a dark-green solution. Standing in the refrigerator produced a large crop of dark-green/black crystals. After isolation and drying, elemental analyses revealed these to have the empirical formula $CoI_3(SbPh_3)_2$, **II**.† From these air-stable crystals one was selected suitable for study by single crystal X-ray diffraction methods, and the X-ray crystal structure‡ is revealed in Fig. 1. The $CoI_3(SbPh_3)_2$ complex is a simple monomeric trigonal bipyramidal species containing axial triphenylantimony ligands and represents the sole example fo this type, *i.e.* a cobalt(III) centre coordinated by soft triphenylantimony and iodide ligands. Moreover, this trigonal bipyramidal geometry for cobalt(III) is extremely rare, there being only two other crystallographically confirmed examples, *viz* $CoCl_3(PEt_3)$[15] and $CoI_3(PMe_3)_2$,[14] the latter being produced by us *via* the same synthetic method as used to produce **II**, eqn. (2).

$$2Me_3PI_2 + Co \xrightarrow[Et_2O]{5\,d,\,60\,°C} CoI_3(PME_3)_2 + \tfrac{1}{2}I_2 \tag{2}$$

Eqn. (2) represents a one-step synthesis of a cobalt(III) species from cobalt(0). Hence the diversity of the new synthetic method[14] is further illustrated here by the initial production of **I**, a cobalt(II) species from cobalt(0), and the subsequent autoxidation of **I** to **II**, a cobalt(III) species.† This essentially occurs as postulated in eqn. (3):

$$\underset{\textbf{I}}{[Ph_3SbI][Co(SbPh_3)I_3]} \rightarrow \underset{\textbf{II}}{CoI_3(SbPh_3)_2} + \tfrac{1}{2}I_2 \tag{3}$$

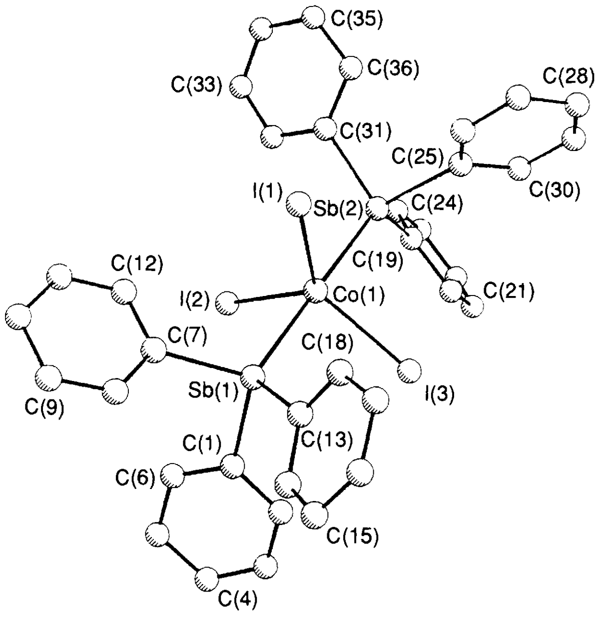

Fig. 1 Selected bond lengths (Å) and angles (°) for $CoI_3(Ph_3Sb)_2$: I(1)–Co(1) 2.563(3), I(2)–Co(1) 2.564(3), I(3)–Co(1) 2.563(3), Sb(1)–Co(1) 2.536(3), Sb(2)–Co(1) 2.589(3), Sb(1)–C(1) 2.11(2), Sb(2)–C(19) 2.12(2); Co(1)–Sb(1)–C(1) 116.0(4), C(1)–Sb(1)–C(7) 101.0(7), Co(1)–Sb(2)–C(19) 119.6(5), C(19)–Sb(2)–C(25) 100.2(7), I(1)–Co(1)–I(2) 117.6(1), I(1)–Co(1)–I(3) 122.5(1), I(1)–Co(1)–S(1) 88.43(8), I(1)–Co(1)–Sb(2) 91.79(8), I(2)–Co(1)–I(3) 119.3(1), I(2)–Co(1)–Sb(1) 86.83(9), I(2)–Co(1)–Sb(2) 94.05(9), Sb(1)–Co(1)–Sb(2) 178.9(1).

During the conversion of **I** into **II** plus diiodine we removed a sample of the diethyl ether above the precipitated **II** and measured its electronic spectrum. No bands were seen assignable to **II** (it is very insoluble in Et_2O), but bands were exhibited at 701, 636 and 619 cm^{-1} assignable to the tetrahedral anion of **I**,[13] and t 470.5 cm^{-1}, assignable to I_2 in Et_2O.

As well as being five-coordinate, **II** is also unusual in being paramagnetic, exhibiting room temperature magnetic moment of 4.4 μ_B. This indictes that, the triphenylantimony and iodide ligands are weak-field ligands in this complex and the electron occupancy is $(d_{z^2})^1$ $(d_{xy}, d_{x^2-y^2})^2$ $(d_{xz}, d_{yz})^3$ giving four unpaired electrons. This is a surprising result since it might have been thought that a complex of this structure would be diamagnetic or paramagnetic with two unpaired electrons, in accord with other reported complexes of cobalt(III) with this geometry containing tertiary phosphine ligands.[16] However, the experimental value is lower than expected for a system with four unpaired electrons, and this may indicate that a spin-equilibrium system exists. We are currently instigating a variable temperature magnetic study of this complex, the results of which will form the basis of a forthcoming publication.

Complex **II** is surprisingly stable and can be exposed to air for months without signs of decomposition. It represents an extreme example of so-called symbiosis, a species defying the normal HSAB principle. The isolation of **II** further indicates the power of the new synthetic route to metal complexes from unactivated metals, which is producing species previously not thought to be capable of existence.

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Footnotes

† *Selected data*: $CoI_3(Ph_3Sb)_2$, black crystals decomp. >200 °C, correct elemental analysis (C,H,I). Its IR data exhibited bands assignable to the metal sensitive modes of metal phenyls ν/cm^{-1}: 1061q, 448y, 270t. Low frequency Raman spectrum ν/cm^{-1}: 214 (x), 180, ν(Co–Sb), 123, ν(Co–I), and a band at 93 cm^{-1} which we cannot readily assign. Attempts to record the VIS spectrum of $CoI_3(Ph_3Sb)_2$ failed due to its insolubility in a range of organic solvents; only acetone appeared to dissolve the complex but the spectrum obtained showed a main band at 707 nm (together with shoulders at 630 and 750 nm), ε = 444 $dm^3\ mol^{-1}\ cm^{-1}$, indicative of a tetrahedral cobalt(II) species. Clearly the complex had decomposed.

‡ *Crystal data* for $C_{36}H_{30}CoI_3Sb_2$, M_r = 1145.78, monoclinic space group $P2_1/c$ (No. 14), a = 12.586(7), b = 14.476(7), c = 19.196(9) Å, V = 3690(6) $Å^3$, β — 101.29(4)°, Z = 4, D_c = 2.062 Mg m^{-3}, Mo-Kα radiation (λ = 0.71069 Å), crystal dimensions 0.2 × 0.2 × 0.15 mm. Rigaku AFC6S diffractometer yielding 3678 observed [$I > 300\sigma(I)$]. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealised positions (C–H = 0.95 Å). The final cycle of full-matrix least-square refinement was based on 3678 observed reflections and 379 variable parameters and converged to give final residuals R = 0.057, R' = 0.070. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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