Unusual Behaviour of Triphenylstibine Complexes of Zerovalent Platinum

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The novel triphenylstibine complexes PtL_2, PtL_3, and $(PtL_3)_nN_2$ (L = $SbPh_3$) have been synthesised; the binary compounds are unusually unreactive even towards cold mineral acids.

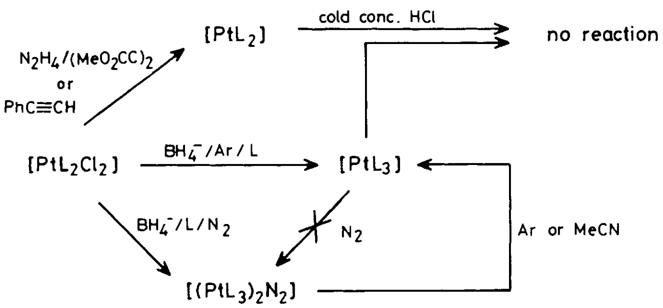
The chemistry of zerovalent platinum supported solely by tertiary phosphine ligands is extensive: compounds which are formally complexes of 14 electrons (PtL_2), 16 electrons (PtL_3), and 18 electrons (PtL_4) are well characterized.[1—4] Analogous arsine complexes have been less studied, and for the bulky stibine ligands only mixed compounds such as $[Pt(PPh_3)_2(SbAr_3)_2]$ (Ar = Ph or p-MeC_6H_4) have been described.[5] Previous attempts to prepare binary stibine complexes of platinum failed.[5]

We found that $[PtCl_2(SbPh_3)_2]$ was rapidly precipitated and in almost quantitative yield when a hot ethanolic solution of $SbPh_3$ was added to a cold solution of H_2PtCl_6 also in ethanol. Filtration and washings with ethanol and ether afforded the complex in analytically pure form.

Rapid addition of a solution of sodium borohydride in ethanol to a suspension of $[PtCl_2(SbPh_3)_2]$ in the same solvent under dry nitrogen caused precipitation of a black substance. However, when the addition was carried out dropwise the colour of the suspended material changed only slightly, and after work-up as before a complex formulated as $[\{Pt(SbPh_3)_3\}_nN_2]$ (n = 1 or 2) was obtained in 88% yield. The presence of a co-ordinated molecule of dinitrogen was evidenced by C, H, and N analysis and by i.r. spectroscopy which showed no Pt–Cl stretching bands, but a strong band at 270 cm^{-1} (ν_{Pt-Sb}) and a new, medium intensity band at 1750 cm^{-1} (ν_{N-N}). Similarly low frequencies for co-ordinated dinitrogen molecules have been found in systems where the $M–N_2$ bonding is highly delocalised, such as bridging dinitrogen complexes.[6] Unfortunately, the microanalytical data for the present compound do not permit a distinction between the two possible formulations. However, the existence of a bimetallic nickel phosphine complex containing a bridging dinitrogen molecule[7,8] reinforces the formulation of the present compound as $[\{Pt(SbPh_3)_3\}_2N_2]$.

When the reduction of $[PtCl_2(SbPh_3)_2]$ was carried out as before but under argon, the complex $[Pt(SbPh_3)_3]$ was obtained (no i.r. bands at 1750 cm^{-1}). A solid with the physical properties of $[Pt(SbPh_3)_3]$ was also obtained after a solution of the dinitrogen complex was purged with argon, and after an unsuccessful attempt to replace the co-ordinated dinitrogen by acetonitrile. In all cases the dinitrogen complex could not be re-formed by purging the solution of $[Pt(SbPh_3)_3]$ with nitrogen.

The new complexes are remarkably unreactive towards reagents which react quickly with zerovalent platinum phosphine compounds. For instance, $[PtCl_2(PPh_3)_2]$ is reduced by hydrazine hydrate in the presence of the phosphine and an acetylene to give $[Pt(PPh_3)_2(acetylene)]$, and the acetylene is labile.[9] Under the same experimental conditions $[PtCl_2(SbPh_3)_2]$ gave a creamy solid which seemed to decompose, but which gave analytical data corresponding to $[Pt(SbPh_3)_2]$. It is known that $[Pt(PPh_3)_3]$ in benzene reacts



L = SbPh$_3$

with CO_2 from air producing carbonate complexes,[10,11] but [Pt(SbPh$_3$)$_3$] was unchanged under the same conditions. Moreover, neither [Pt(SbPh$_3$)$_2$] nor [Pt(SbPh$_3$)$_3$] reacted with cold aqueous HCl, whereas [Pt(PPh$_3$)$_3$] rapidly forms the hydride complex [Pt(H)Cl(PPh$_3$)$_2$].[12,13] When hot concentrated HCl reacted with the binary triphenylstibine complexes only solutions which seemed to contain chloroplatinic acid were recovered. It is of interest that so far the complex [Pt(SbPh$_3$)$_4$] has not been observed, whereas the triphenylphosphine analogue is easily prepared by reduction procedures similar to those used in this work. It is also noteworthy that the zerovalent triphenylphosphine complexes are very soluble in aromatic solvents, but solubility decreases on changing these ligands to arsines and stibines.[14]

The reason for the lack of reactivity of the present compounds is difficult to ascertain; the formally 14-electron complex [Pt(SbPh$_3$)$_2$] is the most intriguing in this respect. Neither steric nor electronic factors alone can account for the apparent unreactivity towards HCl, since [PtCl$_2$(SbPh$_3$)$_2$] is formed easily from chloroplatinic acid as already mentioned. The lability of [Pt(PPh$_3$)$_n$] (n = 3 or 4) in solution is crucial for the majority of the reactions of these complexes. In this context the complexes [Pt(SbPh$_3$)$_n$] (n = 2 or 3) are still unusual, for they can be regarded as the products of the dissociation of the hypothetical [Pt(SbPh$_3$)$_4$] and therefore they should be in principle very reactive.

It is intriguing that SbPh$_3$ is able to stabilize a bond between platinum and dinitrogen, whereas PPh$_3$ and AsPh$_3$ do not.[14] Although [{Pt(SbPh$_3$)$_3$}$_2$N$_2$] does decompose over a period of weeks, the platinum–dinitrogen bond appears quite strong. This was evidenced by a preliminary thermogravimetric analysis on a freshly prepared sample, which suggested that evolution of N_2 occurred only above 110 °C.

To our knowledge the complex formulated as [{Pt(SbPh$_3$)$_3$}$_2$N$_2$] is the first example of a dinitrogen complex of platinum. Previous studies on this class of compounds have only been made on solid matrices at temperatures slightly above that of liquid helium.[15]

We thank the Brazilian Government (CNPq) and COPENE S/A for financial support.

Received, 6th April 1987; Com. 442

References

1 L. Malatesta and C. Cariello, *J. Chem. Soc.*, 1958, 2323.
2 L. Malatesta and R. Ugo, *J. Chem. Soc.*, 1963, 2080.
3 R. Ugo, F. Cariati, and G. La Monica, *Chem. Commun.*, 1966, 868.
4 R. Ugo, F. Cariati, and G. La Monica, *Inorg. Synth.*, 1968, **11**, 105.
5 P.E. Garrou and G. E. Hartwell, *Inorg. Chem.*, 1976, **15**, 730.
6 M. Moercer, R. H. Crabtree, and R. L. Richards, *Chem. Commun.*, 1973, 808.
7 M. Aresta, C. F. Nobile, and A. Sacco, *Inorg. Chim. Acta*, 1975, **12**, 167.
8 P. W. Jolly, K. Jonas, C. Kruger, and Y. H. Tsay, *J. Organomet. Chem.*, 1971, **33**, 109.
9 F. R. Hartley, *Chem. Rev.*, 1969, **69**, 799.
10 C. J. Nyman, C. E. Wymore, and G. Wilkinson, *J. Chem. Soc. A*, 1968, 561.
11 P. J. Hayward, D. M. Blake, and C. J. Nyman, *Chem. Commun.*, 1969, 987.
12 J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1962, 5075.
13 L. Malatesta and R. Ugo, *J. Chem. Soc.*, 1963, 2080.
14. R. S. Barbiéri, S. I. Klein, and A. C. Massabni, unpublished results.
15 G. A. Ozin and W. E. Klotzbücher, *J. Am. Chem. Soc.*, 1975, **97**, 3965.