Inorganica Chimica Acta, 65 (1982) L161–L162

An NMR Study of the Insertion of Tin(II) Halides into a Platinum–Platinum Bond

ROBIN J. GOODFELLOW* and IAN R. HERBERT

Department of Inorganic Chemistry, The University, Bristol BS8 1TS, U.K

Received April 23, 1982

Although tin(II) chloride commonly inserts into metal–metal bonds, *e.g.* with $Mn_2(CO)_{10}$, $Fe_2(\eta\text{-}C_5H_5)_2(CO)_4$, $Co_2(CO)_8$ and $Ni_2(\eta\text{-}C_5H_5)_2(CO)_2$ [1], it does not do so with $M_2Cl_2(dppm)_2$ (M = Pd or Pt, dppm = bis(diphenylphosphino)methane) but rather gives terminal $SnCl_3$ derivatives [2]. To investigate whether this is a general distinction of Pt–Pt bonds, we have studied the reactions of tin(II) halides with the anions $[Pt_2X_4)CO)_2]^{2-}$ X = Cl or Br [3].

When $[NBu^n_4]_2[Pt_2Cl_4(CO)_2]$, dissolved in dichloromethane, is stirred over $SnCl_2$, the latter dissolves to give a yellow-green solution. The ^{195}Pt NMR spectrum shows conversion of the resonance of the starting material (δ(Pt), 398 p.p.m. to high frequency of $\Xi(^{195}Pt)$ = 21.4 MHz) to one at 368 p.p.m. which has two pairs of satellites, typical of coupling to tin isotopes [$^1J(^{195}Pt^{119}Sn)$, 15264; $^1J(^{195}Pt^{117}Sn)$, 14580 Hz]. Using the less soluble tetrapropylammonium salt, pale yellow crystals were isolated which analysed satisfactorily (C, H, N and Cl) for $[NPr^n_4]_2[Pt_2SnCl_6(CO)_2]$. Similar results were obtained for the bromo-analogue. The change in platinum chemical shift on reaction with $SnCl_2$ is much less than that previously observed when $SnCl_2$ inserts into a Pt–Cl bond to form a Pt–$SnCl_3$ group [4]. That a terminal $SnCl_3$ group is not formed in the present case is confirmed by the ^{119}Sn spectra (*e.g.* Fig. 1) which show equal coupling to two platinum centres.

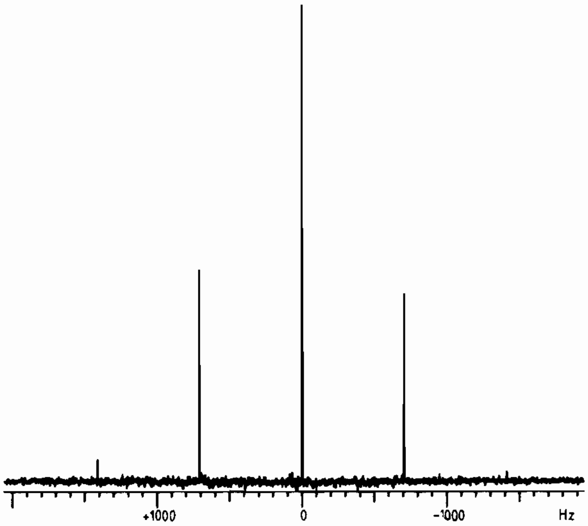

Fig. 1. 33.4 MHz ^{119}Sn NMR spectrum of $[NBu^n_4]_2[Pt_2Br_4(CO)_2]$ + $SnBr_2$.

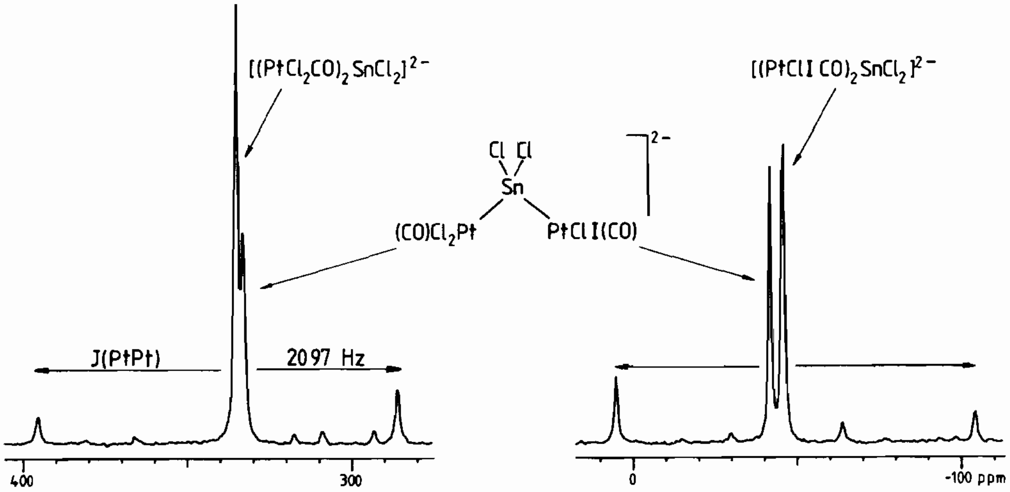

Fig. 2. 19.2 MHz ^{195}Pt NMR spectrum of '$Pt_2Cl_3I(CO)_2]^{2-}$' + $SnCl_2$.

---

*Author to whom correspondence should be addressed.

0020-1693/82/0000-0000/$02.75

We have obtained information on the Pt–Pt bond in $[Pt_2X_4(CO)_2]^{2-}$ by ^{195}Pt NMR measurements on asymmetric mixed halide species of the type $[Pt_2XY_3(CO)_2]^{2-}$ formed in solution [5]. To apply this approach to the derivatives with SnX_2, we prepared '$Pt_2Cl_3I(CO)_2^{2-}$' {*i.e.* a mixture of $Pt_2Cl_4(CO)_2]^{2-}$, $[Pt_2Cl_3I(CO)_2]^{2-}$, and $[Pt_2Cl_2I_2(CO)_2]^{2-}$} by adding 1 equivalent of sodium iodide to $[NBu^n_4]_2[Pt_2Cl_4(CO)_2]$ in acetone and removing the solvent. After reaction with $SnCl_2$, the ^{195}Pt NMR spectrum shows features that can be assigned to $[\{PtCl_2(CO)\}_2SnCl_2]^{2-}$ (I), $[\{PtCl_2(CO)\}SnCl_2\{PtClI(CO)\}]^{2-}$ (II), and $[\{PtClI(CO)\}SnCl_2]^{2-}$ (III) (Fig. 2)*. The Pt–Pt coupling constant in II (2097 Hz) is under half that in $[Pt_2Cl_3I(CO)_2]^{2-}$ [5]. The ^{195}Pt chemical shift of the '$PtCl_2CO$' end of II is 2 p.p.m. to low frequency of that of I whereas the equivalent end of $[Pt_2Cl_3I(CO)_2]^{2-}$ occurs 264 p.p.m. to high frequency of that of $[Pt_2Cl_4(CO)_2]^{2-}$ and a similar comparison arises for the '$PtClI(CO)$' ends [5]. Further, the CO stretching vibrations of $[Pt_2Cl_4(CO)_2]$ are separated by 26 cm^{-1} but in its $SnCl_2$ derivative they have coalesced into a single band (at 2071 cm^{-1}) indicating a decrease in the interaction between the Pt centres. From this evidence, we conclude that there is no significant Pt–Pt bond remaining after the reaction with $SnCl_2$ and hence that the products can be fairly represented as $[(CO)Cl_2Pt-(SnCl_2)-PtCl_2(CO)]^{2-}$. In view of the high *trans* influence of tin as a ligand [6], we expect that CO will be *cis* to the Pt–Sn bond and the complexity of the IR spectra in the combined Pt–X plus Sn–X stretching region supports this configuration.

Conclusions

The formation of I demonstrates that $SnCl_2$ will insert into a Pt–Pt bond. Since the M–M bond of $M_2Cl_2(dppm)_2$ (M = Pd Or Pt) is attacked by ligands such as SO_2 or CO [7], it seems likely that the failure of $SnCl_2$ to insert into it is associated with the strain that the greater span of the $\overset{\mathrm{Sn}}{\mathrm{M}\diagup\ \diagdown\mathrm{M}}$ unit puts on the dppm bridging ligands.

Acknowledgements

We thank the S.E.R.C. for funds for the purchase of equipment and Bristol University for a postgraduate scholarship (to I.R.H.).

References

1 J. Hoyano, D. J. Patmore and W. A. G. Graham, *Inorg. Nucl. Chem. Lett.*, *4*, 201 (1968);
F. Bonati and G. Wilkinson, *J Chem. Soc*, 1979 (1964);
D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, *5*, 1405 (1966),
F. Bonati, S. Cenini, D. Morelli and R. Ugo, *J. Chem. Soc (A)*, 1052 (1966).
2 M. M. Olmstead, L. S. Benner, H. Hope and A. L. Balch, *Inorg Chim. Acta*, *32*, 193 (1979),
M. C. Grossel, J. Batson, R. P. Moulding and K. R. Seddon, 'International Conference on the Chemistry of the Platinum Group Metals, Bristol (1981), Abstract E10.
3 P. L. Goggin and R. J. Goodfellow, *J. Chem. Soc., Dalton Trans.*, 2355 (1973).
4 P. S. Pregosin and S. N. Sze, *Helv Chim. Acta*, *61*, 1848 (1978).
5 N. M. Boag, P. L. Goggin, R. J. Goodfellow and I. R. Herbert, to be published.
6 R. V. Lindsay, G. W. Parshall and U G. Stolberg, *J. Am. Chem. Soc*, *87*, 658 (1965).
7 L. S. Benner, M. M. Olmstead, H. Hope and A. L. Balch *J. Organomet. Chem.*, *153*, C31 (1978).

---

*We have found that there is a preference for the heavier halide to be bonded to platinum rather than tin in complexes containing two different halides.