Nuclear Magnetic Resonance Studies of the Addition of Hydrogen Halides to *trans*-Cyanohydridobis(triethylphosphine)platinum(II) and Hydridotris(triethylphosphine)platinum(II) Tetraphenylborate

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The complexes $[Pt(CN)H_2X(PEt_3)_2]$ (X = Cl, Br, or I) have been identified by ^1H and ^{31}P n.m.r. spectroscopy at −80 °C as the initial products from the reaction of *trans*-$[Pt(CN)H(PEt_3)_2]$ and HX. Similarly, $[PtH(PEt_3)_3]^+$ and HCl yield $[PtClH_2(PEt_3)_3]^+$. In this case deuterium substitution indicates *trans* addition, but with the cyanide no distinction of *cis* or *trans* addition is possible. The platinum(IV) cyanides do not disproportionate and on warming to room temperature yield the mixed complexes *trans*-$[Pt(CN)X(PEt_3)_2]$.

IN previous papers we have reported the formation of six-co-ordinate hydride complexes by the addition of HX (X = Cl, Br, or I) to platinum(II) substrates.[1,2] While addition of HY to *trans*-$[PtX_2(PEt_3)_2]$ (Y = Cl, Br, I $\neq$ X) was found to be initially *trans* with subsequent rearrangement to put the hydride *trans* to the lightest halogen present, it was not possible to discover whether addition of DY to *trans*-$[PtH(X)(PEt_3)_2]$ was stereospecific since even at −90 °C the first ^1H n.m.r. spectrum obtained showed H *trans* to both X and Y. Addition of HY to *trans*-$[PtH(X)(PEt_3)_2]$ is further complicated by the rapid disproportionation of the original product, *cis-cis-trans*-$[PtH_2X(Y)(PEt_3)_2]$ to give *cis-cis-trans*-$[PtH_2X_2(PEt_3)_2]$ and *cis-cis-trans*-$[PtH_2Y_2(PEt_3)_2]$. Where Y = $[HS]^-$ or $[HSe]^-$, low-temperature ^{31}P n.m.r. studies revealed an equilibrium of these six-co-ordinate dihydrides with *trans*-$[PtH(X)(PEt_3)_2]$ and *trans*-$[PtH(Y)(PEt_3)_2]$. It appeared therefore that to obtain more information about the stereochemistry of the addition of HY to *trans*-$[PtH(Y)(PEt_3)_2]$ it would be necessary to study a system which did not disproportionate and this in turn requires a choice of X such that the dissociation (1) is unlikely to occur.

$$[PtH_2X(Y)(PEt_3)_2] \rightleftharpoons [PtH(Y)(PEt_3)_2] + HX \quad (1)$$

Two ligands that fulfil this requirement for X are $[CN]^-$ and PEt_3. Cyanide is one of the strongest ligands to platinum; for example it will displace even phosphine ligands to form complexes,[3] and dissociation of the Pt–CN bond might well be unfavourable. This is probably the reason why disproportionation of *trans*-$[Pt(CN)_2(PEt_3)_2]$ and $[PtX_2(PEt_3)_2]$ to form mixed halide–cyanide species does not occur. Similarly, $[PtH_2X(PEt_3)_3]^+$ would be required to eliminate the phosphonium ion $[PHEt_3]^+$ in order to disproportionate.

RESULTS AND DISCUSSION

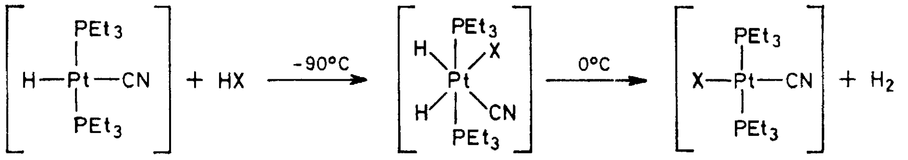
Equimolar proportions of *trans*-$[Pt(CN)H(PEt_3)_2]$ and HX with CD_2Cl_2 as solvent were sealed in a 5-mm n.m.r. tube and the reaction followed from −90 °C by ^1H and ^{31}P n.m.r. spectroscopy. In all cases the main reaction involved formation of *cis-cis-trans*-$[Pt(CN)H_2X(PEt_3)_2]$ at −90 °C and subsequent elimination of dihydrogen at *ca.* 0 °C to yield *trans*-$[Pt(CN)X(PEt_3)_2]$. For X = Cl an identical reaction was observed in toluene. The n.m.r. data are given in Tables 1 and 2.

TABLE 1

Phosphorus-31 and ^{195}Pt n.m.r. parameters for platinum cyanide complexes

	trans-$[Pt(CN)X(PEt_3)_2]$			*cis-cis-trans*-$[Pt(CN)H_2X(PEt_3)_2]$		
X	δ(P) [a,b]	δ(Pt) [a,b]	^1J(Pt–P)/Hz	δ(P) [a,c]	δ(Pt) [a,c]	^1J(Pt–P)/Hz
H	19.21		2 500			
CN	13.64	−31.5	2 160			
Cl	16.41	373.7	2 250	8.25	265.4	1 677
Br	13.89	233.2	2 224	6.39	60.1	1 665
I	9.72	−23.9	2 195	2.09	−288.8	1 657

[a] Chemical shifts in p.p.m., positive to high frequency of 85% H_3PO_4 (^{31}P) or 0.5 mol dm^{-3} $[PtCl(H)(PEt_3)_2]$ in CH_2Cl_2 (^{195}Pt) external reference. Measured in CD_2Cl_2 (^{31}P) or $CDCl_3$ (^{195}Pt). [b] At 28 °C. [c] At −60 °C.



(2)

In the ^1H n.m.r. spectrum, assignment of the two hydride resonances as either *trans* to CN or *trans* to X

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[1] D. W. W. Anderson, E. A. V. Ebsworth, and D. W. H. Rankin, *J.C.S. Dalton*, 1973, 954.

[2] E. A. V. Ebsworth, D. W. H. Rankin, I. M. Blacklaws, and H. E. Robertson, *J.C.S. Dalton*, 1978, 753.

[3] F. Canati, R. Ugo, and F. Bonati, *Inorg. Chem.*, 1966, **5**, 1128.

was made on the assumption that, as with the mixed-halogen complexes $[PtH(X)Y_2(PEt_3)_2]$ and $[PtH_2X(Y)(PEt_3)_2]$, the chemical shift of the PtH protons within a group of similar complexes is determined mainly by the halogen in the *trans* position.[1] The geometry of the complexes is determined by the magnitude and multiplicity of the couplings.

TABLE 2

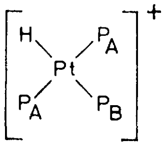
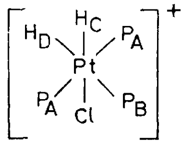
Hydrogen-1 n.m.r. parameters for platinum cyanide complexes

Complex	δ(H) * (*trans* CN)	^1J(Pt–H) Hz	^2J(P–H) Hz	δ(H) (*trans* X)	^1J(Pt–H) Hz	^2J(P–H) Hz
trans-$[Pt(CN)H(PEt_3)_2]$	−7.75	827	15.5			
cis-cis-trans-$[Pt(CN)H_2X(PEt_3)_2]$						
X = Cl	−12.31	706	8.0	−18.40	1 225	6.5
Br	−12.61	695	8.5	−17.35	1 210	6.5
I	−13.30	661	8.5	−15.85	1 232	6.0

* Chemical shifts in p.p.m., positive to high frequency of $SiMe_4$ internal reference. A coupling ^2J(H–H′) was not resolved.

TABLE 3

N.m.r. parameters for $[PtH(PEt_3)_3][BPh_4]$ and $[PtClH_2(PEt_3)_3][BPh_4]$

		δ(P)	^1J(Pt–P) Hz	$J(P_A–P_B)$ Hz	δ(H)	^1J(Pt–H) Hz	^2J(P–H) Hz
	P_A	15.59	2 459	21	−5.90	799	17(t)
	P_B	12.80	2 000				159(d)
	P_A	4.43	1 632	19	H_C −17.15	1 107	7(q)
	P_B	−17.68	1 340		H_D −10.07	710	215(d)

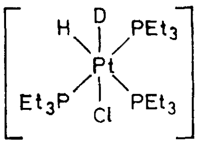
Measured in CD_2Cl_2 at −80 °C, see also footnotes to Tables 1 and 2. t = Triplet, d = doublet, q = quartet. The couplings $^2J(P_A–H_D)$ and $^2J(H_C–H_C)$ were not resolved.

For X = Cl the reaction yielded only the complexes shown in (2); when X = Br small amounts of *trans*-$[Pt(CN)_2(PEt_3)_2]$ were formed, and when X = I small amounts of *cis-cis-trans*-$[PtH_2I_2(PEt_3)_2]$, *trans*-$[PtI_2(PEt_3)_2]$, and *trans*-$[Pt(CN)_2(PEt_3)_2]$ were detected and identified by their phosphorus chemical shift and ^1J(Pt–P) coupling.

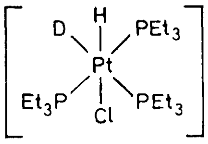
It was therefore possible to use the reaction of HCl with *trans*-$[Pt(CN)H(PEt_3)_2]$ on a preparative scale to produce the mixed complex, *trans*-$[PtCl(CN)(PEt_3)_2]$. Metathetical reactions with NaBr and NaI were used to convert this into the corresponding bromide and iodide. None of these three complexes showed any tendency to disproportionate in solution, nor did mixtures of *trans*-$[Pt(CN)_2(PEt_3)_2]$ [4] and $[PtX_2(PEt_3)_2]$ show any equilibration to give the mixed complexes. We have also investigated the interaction between HCN and *trans*-$[PtCl(H)(PEt_3)_2]$, *trans*-$[Pt(CN)H(PEt_3)_2]$, and *trans*-$[Pt(CN)_2(PEt_3)_2]$; only in the first case, where small quantities of *trans*-$[Pt(CN)H(PEt_3)_2]$ and *trans*-$[PtCl(CN)(PEt_3)_2]$ were formed, was any reaction detected.

These platinum cyanide complexes therefore appear very stable to disproportionation, either through elimination and re-addition of HCN or through halide–cyanide exchange. However, the addition of DCl to *trans*-$[Pt(CN)H(PEt_3)_2]$ at −90 °C gave a ^1H n.m.r. spectrum with H *trans* to both Cl and CN. This implies a rapid H–D scrambling even at so low a temperature, and it was not possible to discover if the initial addition was *cis* or *trans*.

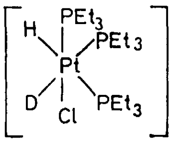
The addition of HCl to the cation $[PtH(PEt_3)_3]^+$ (ref. 5) was also followed from low temperatures by n.m.r. spectroscopy. In CD_2Cl_2 solution the first product observed at −80 °C was $[PtClH_2(PEt_3)_3]^+$ and the n.m.r. data for this cation and the starting material are given in Table 3. The structure of the addition complex is of the type (A)–(B) below.



(A)



(B)



(C)

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[4] P. L. Goggin and R. J. Goodfellow, *J. Chem. Soc.* (*A*), 1966, 1462.

[5] M. J. Church and M. J. Mays, *J. Chem. Soc.* (*A*), 1968, 1186.

The hydride *trans* to the unique triethylphosphine is characterised by the large ^2J(PH) coupling of 215 Hz. Addition of DCl to the cation gave a ^{1}H n.m.r. spectrum at −80 °C showing that the only complex present had hydride *trans* to PEt_3, *i.e.* structure (A) but not (B) was present. In addition an off-resonance ^{31}P n.m.r. spectrum with ^{1}H decoupling only in the ethyl region showed the unique phosphorus resonance to be clearly split into a wide doublet. It seems therefore that in this system addition of DCl is *trans* and that H–D scrambling does not occur. Decomposition of $[PtClH_2(PEt_3)_3]^+$ started above −60 °C with the slow formation of some *cis-cis-trans*-$[PtCl_2H_2(PEt_3)_2]$. At room temperature $[PtCl(PEt_3)_3]^+$, $[PtH(PEt_3)_3]^+$, $[PtCl_2H_2(PEt_3)_2]$, *cis*-$[PtCl_2(PEt_3)_2]$, and $[PHEt_3]^+$ were also present in solution and identified by ^{31}P n.m.r. Decomposition of $[PtCl(D)H(PEt_3)_3]^+$ was similar except that both $[PHEt_3]^+$ and $[PDEt_3]^+$ were formed.

The contrast between these two results is striking. The addition of DCl to $[PtH(PEt_3)_3]^-$ is clearly stereospecific. It is not so clear why the product of the addition of DCl to *trans*-$[Pt(CN)H(PEt_3)_2]$ should give a product with H and D randomly arranged. Perhaps in this system addition is not stereospecific; in view of our results here with $[PtH(PEt_3)_3]^+$ and previously with HX and *trans*-$[PtY_2(PEt_3)_2]$ this conclusion would be surprising. Perhaps there is intramolecular interchange of H *trans* to CN and H *trans* to Cl in $[PtCl(CN)H_2(PEt_3)_2]$; if so, such interchange must be slow on an n.m.r. time scale since we observe separate resonances for the protons in the two sites. Perhaps there is *trans* addition followed by *cis* elimination. If rapid re-addition occurred the net result would be H–D scrambling. There seems no obvious reason why such a process should occur readily with the cyanide adduct but not with the cation. It is true that CN has a larger *trans*-labilising influence than PEt_3; on the other hand we have observed similar scrambling in *cis-cis-trans*-$[PtD(H)X(Y)(PEt_3)_2]$, where X and Y are halides and are expected to have smaller *trans* effects than PEt_3. It is possible that the positive charge reduces any tendency to elimination for the six-co-ordinate cation. If this interpretation is correct it seems likely that the initial addition of HX to all the platinum(II) species we have studied is initially *trans*; the subsequent elimination must be equally likely to involve either *cis* or *trans* groups. It is possible that one or both of these reactions may occur through a two-stage ionic mechanism, but we believe that these results and those previously reported [1] are most simply explained in terms of a concerted addition.

EXPERIMENTAL

N.m.r. and i.r. measurements were made as in ref. 6. The complexes *trans*-$[PtH(X)(PEt_3)_2]$ (X = Cl or CN) and *trans*-$[Pt(CN)_2(PEt_3)_2]$ were made by literature methods.[4,7] Quantities of HX gas were measured using a standard Pyrex glass vacuum line and condensed on to a frozen solution of the platinum substrate at −196 °C. Reactions in n.m.r. tubes were sealed and stored at this temperature.

The complex *trans*-$[PtCl(CN)(PEt_3)_2]$ [8] was prepared from *trans*-$[Pt(CN)H(PEt_3)_2]$ (1.0 mmol) and HCl (1.1 mmol) in CH_2Cl_2 (5 cm^3). The reaction was complete within 5 min of reaching room temperature and the solvent was removed *in vacuo* to yield a pale yellow solid. Recrystallisation from acetone yielded the pure product, m.p. 144—146 °C (Found: C, 31.7; H, 6.04; N, 2.67. $C_{13}H_{30}ClNP_2Pt$ requires C, 31.7; H, 6.14; N, 2.85%). Infrared spectrum in Nujol: ν(CN) at 2 120m cm^{-1}.

The complex *trans*-$[PtBr(CN)(PEt_3)_2]$ was prepared by addition of NaBr to $[PtCl(CN)(PEt_3)_2]$ in acetone–water (10 : 1). The crude product was recrystallised first from CH_2Cl_2 and then from acetone to give the pure complex, m.p. 132—136 °C (Found: C, 29.2; H, 5.60; N, 2.57. $C_{13}H_{30}BrNP_2Pt$ requires C, 29.1; H, 5.65; N, 2.63%); ν(CN) (in Nujol) at 2 120m cm^{-1}.

The complex *trans*-$[Pt(CN)I(PEt_3)_2]$ was prepared by a similar method to the bromide using NaI, m.p. 127—129 °C (Found: C, 26.7; H, 5.36; N, 2.24. $C_{13}H_{30}INP_2Pt$ requires C, 26.7; H, 5.18; N, 2.40%); ν(CN) (in Nujol) at 2 120m cm^{-1}.

[7/1939 *Received, 4th November,* 1977]

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[6] E. A. V. Ebsworth, J. M. Edward, and D. W. H. Rankin, *J.C.S. Dalton*, 1976, 1667.

[7] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1962, 5075.

[8] P. M. Treichel and R. W. Hess, *Chem. Comm.*, 1970, 1626.