Communications to the Editor

Steric and Electronic Effects in Enthalpies of Platinum–Ligand Bond Formation in *trans*-$(CH_3Pt[P(CH_3)_2C_6H_5]_2L)^+(PF_6)^-$ Complexes

Sir:

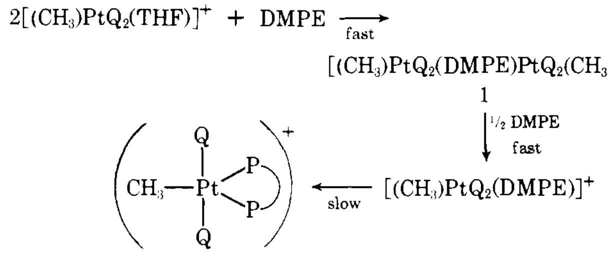
The relative importance of steric and electronic effects in determining metal–phosphorus bond strengths is not well understood. From studies of phosphorus competition for Ni(0) and NiL_4 dissociation, we concluded that the stability of the complexes is primarily dependent on ligand size rather than electronic character.[1] We now wish to report some results on the enthalpies (ΔH) of the reaction of a variety of group 5 donor ligands (L) with *trans*-$[CH_3PtQ_2(THF)](PF_6)$ [Q = $P(CH_3)_2(C_6H_5)$], which clearly illustrate the importance of steric effects on metal phosphorus bond strengths.

The apparatus used has been described by Partenheimer.[2] In a typical run, the ligand was added stepwise in varying amounts from 0.5 to 10 equiv to a solution of 0.2 mmol of *trans*-$[CH_3PtQ_2(THF)](PF_6)$[3] in 200 ml of THF. In most cases no reaction occurred after the addition of 1 molar equiv of ligand to the platinum complex. The enthalpies measured with excess L and corrected for heat of solution are listed in Table I. Figure 1 shows a plot of ΔH vs. the cone angle[4] for a variety of phosphorus ligands. Several important conclusions can be drawn. (1) The enthalpy is clearly dependent on the size of L and decreases in the series $P(CH_3)_3$, $P(CH_3)_2(C_6H_5)$, $P(CH_3)(C_6H_5)_2$, and $P(C_6H_5)_3$ (points 6, 8, 12, and 15) as methyl groups are replaced by phenyl. An even greater decrease is seen in the series $P(CH_3)_3$, $P(C_2H_5)_3$, $P(i\text{-}C_3H_7)_3$ and $P(t\text{-}C_4H_9)_3$ (points 6, 10, 26, and 30). (2) Electronic effects cannot be neglected when substituents of high electronegativity are present. Compare the enthalpies of pairs of ligands with identical cone angles, $P(CH_2CH_3)_3$ and $P(CH_2CH_2CN)_3$ (24.3 and 17.6 kcal/mol) and $P(OC_6H_5)_3$ and $P(O\text{-}p\text{-}C_6H_4CN)_3$ (21.4 and 18.8 kcal/mol). (3) The displacement energy for group 5A ligands decreases in the order $P(C_6H_5)_3 > As(C_6H_5)_3 > Sb(C_6H_5)_3$. (4) Phosphites are slightly weaker ligands than phosphines of similar size for Pt(II). (5) From the present limited NMR data (Table I), there is an inverse correlation between ^2J(Pt-H) for the platinum methyl and $-\Delta H$. Variations in ^2J(Pt-H) and therefore ^1J(Pt-C)[5] with L in *trans*-$CH_3PtQ_2L^+$ have been used to establish an NMR trans-influence series.[6] These coupling constants appear to give a relative measure of the thermodynamic stability of the complexes. (6) Calorimetric titrations indicate that five-coordinate complexes do not form at 25° on adding excess ligand except possibly for the chelating diphosphine $(CH_3)_2PCH_2CH_2P(CH_3)_2$ (DMPE). The addition of 0.5 equiv of DMPE results in a rapid reaction with the evolution of 27.8 kcal/mol to form the bridged species **1**. A second 0.5 equiv of DMPE results in further evolution of heat in two steps. The final slow step is presumably due to chelation by DMPE, resulting in either a five-coordinate complex or displacement of one $P(CH_3)_2(C_6H_5)$ ligand. (7) In cases where the reaction is slow enough to follow, the rate appears to be first order in both platinum complex and added ligand.

Table I. A Comparison of Enthalpies, Cone Angles, and Coupling Constants for a Variety of Ligands

No.	L	$-\Delta H$,[a] (kcal/mol)	Cone angle[b] (deg)	^2J(PtH) (Hz)
1	$\overline{CCH_2CH_2CH_2O}$[c]	34.4		51
2	$(CH_3)_2PCH_2CH_2P(CH_3)_2$	27.8	107	
3	$P(OCH_2)_3CCH_2CH_2CH_3$	26.3	101	
4	$P(OCH_3)_3$	26.4	107	
5	$P(OCH_2CH_2Cl)_3$	26.4	110	
6	$P(CH_3)_3$	26.2	118	
7	$P(OC_2H_5)_3$	25.2	109	
8	$P(CH_3)_2(C_6H_5)$	25.0	127	57
9	$P(O\text{-}i\text{-}C_3H_7)_3$	24.9	130	
10	$P(C_2H_5)_3$	24.3	130	
11	$P(CH_2C_6H_5)_3$	23.2	165[d]	
12	$P(CH_3)(C_6H_5)_2$	22.1	136	
13	$P(OC_6H_5)_3$	21.4	128	58
14	$P(O\text{-}p\text{-}C_6H_4OCH_3)_3$	21.3	128	
15	$P(C_6H_5)_3$	19.5	145	60
16	$P(OCH_2CCl_3)_3$	19.4	115[e]	
17	$P(O\text{-}o\text{-}C_6H_4CH_3)_3$	19.3	141	
18	$P(O\text{-}o\text{-}C_6H_4(C_6H_5))_3$	17.8	152[d]	
19	$P(O\text{-}o\text{-}C_6H_4CN)_3$	18.8	128	
20	$P(O\text{-}t\text{-}C_4H_9)_3$	17.9	172[d]	
21	$P(CH_2CH_2CN)_3$	17.6	130	
22	$P(O\text{-}o\text{-}C_6H_4\text{-}i\text{-}C_3H_7)_3$	17.1	148[d]	
23	$P(C_6H_{11})_3$	15.9	179	
24	$As(CH_3)_3$	15.4	118[f]	
25	$As(C_6H_5)_3$	12.8	145[f]	67
26	$P(i\text{-}C_3H_7)_3$	12.7	160	
27	Pyridine	12.2		74
28	$P(O\text{-}o\text{-}C_6H_4\text{-}t\text{-}C_4H_9)_3$	9.1	170[d]	
29	$Sb(C_6H_5)_3$	6.1	145[f]	
30	$P(t\text{-}C_4H_9)_3$	4.8	182	
31	$N{\equiv}CC_6H_5$	4.7		80
32	$N{\equiv}CCH_3$	4.2		80
33	$P(o\text{-}C_6H_4CH_3)_3$	1.9	194	
34	$P(O\text{-}o\text{-}C_6H_3(CH_3)_2)_3$	0.5	190[d]	

[a] The enthalpies are estimated to be accurate to ±0.5 kcal/mol. [b] Taken from ref 1 and/or 2 unless noted otherwise. [c] $HC{\equiv}CCH_2CH_2OH$ was added to form the carbene. [d] Previously unpublished values. [e] Revised from ref 1 in the basis of new measurements. [f] The cone angles are assumed to be similar to those of the analogous phosphorus ligands.



Preliminary ^{31}P NMR studies confirm that reaction 1 is the dominant one in most cases. For very bulky phosphorus ligands, however (cone angles greater than ~140°), cis-substituted products become more important. Thus $P(O\text{-}o\text{-}C_6H_4CH_3)_3$ (141°) gives about 30% *cis*-$[CH_3PtQ_2L]^+$ and 70% of the trans isomer. $P(O\text{-}o\text{-}C_6H_4\text{-}tert\text{-}C_4H_9)_3$ (170°) gives predominantly reaction 2;[7] apparently this very large ligand will not tolerate two Q's in the same complex.

$$trans\text{-}[CH_3PtQ_2(THF)]^+ + L \longrightarrow trans\text{-}[CH_3PtQ_2L]^+ + THF \quad (1)$$

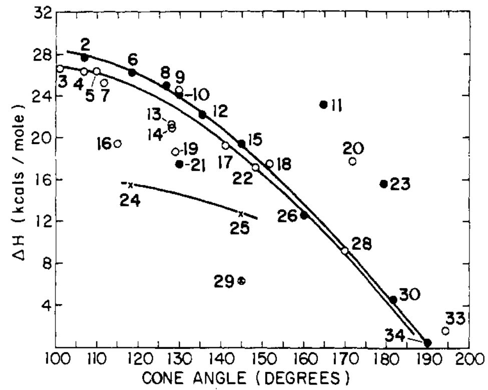
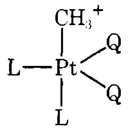


Figure 1. Heat evolved per mole of *trans*-$[CH_3PtQ_2(THF)](PF_6)$ in the reactions with excess L as a function of ligand cone angle: ●, phosphine; ○, phosphite; ×, arsine, and ⊗, stibine. Ligand numbers refer to Table I.

$$2\,trans\text{-}[CH_3PtQ_2(NCR)]^+ + L \longrightarrow trans\text{-}[CH_3PtQL(NCR)]^+ + [CH_3PtQ_3]^+ + NCR \quad (2)$$

Small phosphorus ligands (cone angles less than ~120°) give rapid exchange of free and coordinated ligands at 25°. Five-coordinate complexes whose structures depend on L are observed in the low temperature limit spectra below −80°. The ABM_2 and A_3M spectra observed for L= $P(OMe)_3$ and $P(OCH_2)_3CCH_2CH_2CH_3$, respectively, indicate the trigonal bipyramidal structures **2** and **3**.



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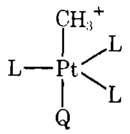

3

Values of $^1J(Pt\text{-}Q)$ in *trans*-$[CH_3PtQ_2L]^+$ reflect a strengthening of the Pt-Q bond as the phosphorus ligand L increases in size (L = $P(OCH_2)_3CPr$, 2490 Hz; $P(OPh)_3$, 2530; $P(O\text{-}o\text{-tolyl})_3$, 2554; $P(O\text{-}o\text{-}C_6H_4\text{-}i\text{Pr})_3$, 2562).

Further ^{31}P and ^1H NMR studies are in progress.

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References and Notes

(1) C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 2956 (1970); C. A. Tolman, W. C. Seidel, and L. W. Gosser, *J. Am. Chem. Soc.*, **96**, 53 (1974).
(2) W. Partenheimer, *Inorg. Chem.*, **11**, 743 (1972), and W. Partenheimer and E. F. Hoy, *Inorg. Chem.*, **12**, 2085 (1973), report the only calorimetric studies on group 5 donor reactions of which we are aware.
(3) Many of the complexes have been isolated and characterized in previous studies: (a) H. C. Clark and J. D. Ruddick, *Inorg. Chem.*, **9**, 1226 (1970); (b) M. H. Chisholm and H. C. Clark, *ibid.*, **10**, 1711 (1971); (c) H. C. Clark and L. E. Manzer, *ibid.*, **10**, 2699 (1971); (d) *ibid.*, **11**, 503 (1972); (e) M. H. Chisholm, H. C. Clark, and L. E. Manzer, *ibid.*, **11**, 1269 (1972).
(4) The cone angle gives a quantitative measure of steric effects in phosphorus ligands and has been described in detail in ref 1 and 2.
(5) M. H. Chisholm, H. C. Clark, L. E. Manzer, J. B. Stothers, and J. E. H. Ward, *J. Am. Chem. Soc.*, **95**, 8574 (1973).
(6) The trans influence may be measured by a number of methods including NMR. For a recent review see: T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, **10**, 335 (1973).
(7) The nitrile complex with NCR = $p\text{-}NCC_6H_4OCH_3$ was used in some of the ^{31}P studies in place of THF because it is a stable, easily handled crystalline solid.

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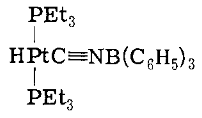
Linkage Isomerism of the Cyanide Ligand in a Platinum(II) Complex

Sir:

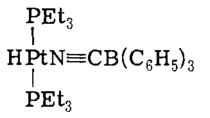
Linkage isomerism is common in complexes containing SCN^- as a ligand.[1] In many cases both the M-SCN and M-NCS isomers have been isolated and characterized.[2] The cyanide ion CN^- is potentially capable of ambidentate bonding but the vast majority of cyanide complexes contain cyanide bonded to metal through the pair of electrons on the carbon atom.[3] A few complexes have been characterized in which the cyanide is bridging between two metal atoms, e.g., Cu-CN-Cu.[3b,4] Recently a new class of compounds, *trans*-$HPt(PEt_3)_2CN\rightarrow$(Lewis acid), have been reported.[3a,5]

We now report the preparation of a novel pair of complexes, (I and II) containing ambidentate cyanide. These are the first examples of linkage isomerism of the cyanide ligand in a platinum(II) compound, where both isomers have been isolated and characterized.



$$\mathrm{H\overset{\displaystyle PEt_3}{\underset{\displaystyle PEt_3}{Pt}}C{\equiv}NB(C_6H_5)_3}$$

I



$$\mathrm{H\overset{\displaystyle PEt_3}{\underset{\displaystyle PEt_3}{Pt}}N{\equiv}CB(C_6H_5)_3}$$

II

Isomer I was isolated from the reaction of *trans*-$HPt(PEt_3)_2CN$ with triphenylborane in toluene as an air-stable white crystalline solid (mp 110–111°). The second isomer was prepared by the reaction of *trans*-$HPt(PEt_3)_2Cl$ with sodium cyanotriphenylborane in tetrahydrofuran and was obtained as a white crystalline solid (mp 106–107°). Both complexes are air stable although the reaction involving triphenylborane must be performed under an atmosphere of nitrogen.

The 220-MHz ^1H NMR spectra of the two complexes are similar in the range τ 0–10 and show resonances typical of mutually trans triethylphosphine ligands. The high field spectra show resonances at τ 27.69 and 28.15 for isomers I and II, respectively. Each appears as a triplet due to coupling with the two equivalent ^{31}P nuclei confirming the trans configuration. The magnitude of $^1J(Pt\text{-}H)$ is very different for the two isomers. Isomer I has a value of $^1J(Pt\text{-}H)$ = 852 Hz, slightly larger than that found in *trans*-$PtHCN(PEt_3)_2$ (778 Hz).[6] This results from a weakening of the metal cyanide bond on coordination to a Lewis acid.[7] The value of $^1J(Pt\text{-}H)$ for isomer II is 1061 Hz, very similar to that found for N-bonded thiocyanate in *trans*-$PtH(NCS)(PEt_3)_2$[6] (1086 Hz). The infrared spectra of both complexes show a strong peak at 2192 cm^{-1} due to $\nu(C{\equiv}N)$ and a weak peak at 2082 and 2236 cm^{-1} for isomers I and II respectively, due to $\nu(Pt{-}H)$. Although the vibrations are probably coupled the higher value of $\nu(Pt{-}H)$ for N-bonded compared with C-bonded cyanide is consistent with the weaker trans influence[8] of the N-bonded isomer.

The ^{11}B NMR spectra obtained at 28.88 MHz are diagnostic of the mode of coordination. For comparison with I and II we have also run the ^{11}B NMR of *trans*-$PtH(PEt_3)_2CN\rightarrow B(CH_2C_6H_5)_3$[5] (III). Resonances are observed at 17.5, 27.5, and 25.1 ppm downfield from trimethylborate with line widths of 800, 225, and 675 Hz for compounds I, II, and III, respectively. The much broader lines are associated with the compounds containing Pt-C and N-B bonds, the broadening presumably resulting from interaction of the ^{11}B nuclear spin (I = 3/2, 80.4% natural abundance) with the ^{14}N nuclear spin (I = 1, 99.6% natural abundance).