Lewis Acid Adducts of a Platinum(II) Hydridocyanide Complex

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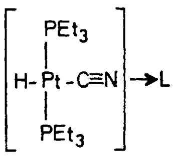
Summary A number of Lewis acid (L) adducts of the type *trans*-[$HPt(PEt_3)_2CN$] $\rightarrow$ L have been prepared; the coupling constant ^1J(Pt–H) is used as a measure of the relative acceptor strengths of the Lewis acids and co-ordination of the cyanide to a Lewis acid weakens the Pt–C bond.

LEWIS acids are industrially important cocatalysts, and a study of the nature of their interaction with transition-metal complexes is important in understanding the mechanisms of these catalytic processes. Relative acceptor strengths of Lewis acids have been measured by i.r.[1] and more recently by e.s.r. spectroscopy.[2] We now report a convenient method for measuring relative Lewis acidities using n.m.r. spectroscopy.

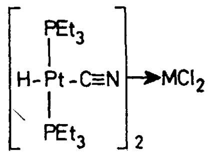
The cyanide in *trans*-[$HPt(PEt_3)_2CN$][3] readily co-ordinates to a variety of Lewis acids (Table) and two types of complexes (**1**) and (**2**) have been isolated.

Complexes of type (**1**) were isolated from the reaction of *trans*-[$PtHCN(PEt_3)_2$][3] with the Lewis acid in toluene. The second type of complex (**2**) was prepared by refluxing a solution of the hydrated metal chloride and [$PtHCN(PEt_3)_2$] in MeCN.



$$\left[\mathrm{H{-}\overset{PEt_3}{\underset{PEt_3}{Pt}}{-}C{\equiv}N}\right]\rightarrow\mathrm{L}$$

(1)



$$\left[\mathrm{H{-}\overset{PEt_3}{\underset{PEt_3}{Pt}}{-}C{\equiv}N}\right]_2\rightarrow\mathrm{MCl_2}$$

(2)

The adducts of cobalt(II) and nickel(II) chloride are paramagnetic with magnetic moments and electronic spectra characteristic of a tetrahedral environment. The adduct with [$(\eta^5\text{-}C_5H_5)_2TiCl$] is paramagnetic and no n.m.r. signal was observed. The e.s.r. spectrum at room temperature in toluene shows a single resonance at g 1·980 ±0·001, flanked by ^{195}Pt satellites ($I = \frac{1}{2}$; 33·8% natural abundance), $\langle a_{\mathrm{Pt}}\rangle$ 7 G and ^{47,49}Ti satellites, $\langle a_{\mathrm{Ti}}\rangle$ *ca.* 12 G. The magnitude of the hyperfine coupling to platinum suggests that there is considerable delocalization of the electron from titanium through the C≡N bond to platinum. We were unable to locate the hydride resonance in the n.m.r. spectrum of the $NiCl_2$ adduct. The hydride resonance in the $CoCl_2$ complex was 15·53 p.p.m downfield from internal Me_4Si. Assuming that the HPtCNCo unit is linear, the contact shift[4] would be hyperfine rather than pseudo-contact in origin, arising from electron delocalization from cobalt on to platinum. The diamagnetic complexes show resonances characteristic of mutually *trans*-Et_3P ligands and a platinum hydride resonance split into a triplet due to coupling with two equivalent ^{31}P nuclei. Platinum satellites are also observed and the magnitude of ^1J(Pt–H) varies with the Lewis acid (Table). A recent calorimetric study[5] on the formation of a series of complexes *trans*-$[MePt(PMe_2Ph)_2L][PF_6]$ has shown that the magnitude of ^2J(Pt–H) decreases as the Pt–L bond strength increases. Therefore, it is reasonable to assume that since the values of ^1J(Pt–H) for the complexes in the Table are all greater than in *trans*-$[PtHCN(PEt_3)_2]$ (778 Hz),[6] Lewis acid co-ordination weakens the Pt–CN bond, the strongest Lewis acid giving the greatest ^1J(Pt–H). We can therefore arrange the Lewis acids in order of decreasing Lewis acidity: $AlCl_3 > B(p\text{-tolyl})_3 > B(\text{naphthyl})_3 \approx B(o\text{-tolyl})_3 > BEt_3 \gtrsim CoCl_2 \gtrsim B(CH_2Ph)_3 > ZnCl_2 > B(OPh)_3 > Al(Me)_3$. The small differences in bond strengths for the $B(o\text{-tolyl})_3$ and $B(\text{naphthyl})_3$ adducts compared with $B(p\text{-tolyl})_3$ are probably due to steric rather than electronic effects.[5] The substitution of halide by methyl on aluminum and aryl by alkyl on boron decreases Lewis acidity as expected. The decrease in Pt–CN bond strength on co-ordination to a Lewis acid may result from a polarization of the bond as follows:

Table

Comparison of ^1J(Pt–H) for various Lewis acid (L) adducts of *trans*-$[PtH(PEt_3)_2CN]$

L	Type	^1J(Pt–H)[a]/Hz
$AlCl_3$	(1)	860
$B(p\text{-tolyl})_3$	(1)	854
$B(\text{napththyl})_3$	(1)	851
$B(o\text{-tolyl})_3$	(1)	851
BEt_3	(1)	844
$CoCl_2$	(2)	843
$B(CH_2Ph)_3$	(1)	842
$ZnCl_2$	(2)	832
$B(OPh)_3$	(1)	820
$Al(Me)_3$	(1)	816
$NiCl_2$	(2)	—
$(\eta^5\text{-}C_5H_5)_2TiCl$ ..	(1)	—

[a] Coupling constants are accurate to ±1 Hz. The spectra were recorded in C_6D_6 solutions at 220 MHz.

$$\text{Pt–}\overset{\delta+}{\text{C}}\equiv\overset{\delta-}{\text{N}}\text{–L}$$

This n.m.r. method provides a unique and simple method for measuring relative Lewis acidities.

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