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^{1}H Nuclear magnetic resonance spectra of some cationic platinum(II) carbene complexes

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We have recently examined the reactivity of cationic platinum(II) complexes towards acetylenes and nitriles to give alkoxycarbene[1] and imino ether complexes[2] and have now extended these investigations to isocyanides[3] and their carbene derivatives.

Richards *et al.* have recently reported[4] the preparation of several carbene complexes of the type *trans*-$\{PtX[C(NHR)R'](PEt_3)_2\}^+ClO_4^-$ (X = Cl, Br; R = Ph; Me; R' = PhNH, EtNH, EtO), although they were unable to isolate the pure ethoxy (amino) carbene derivatives, and their use of the symmetrically substituted phosphine, PEt_3, did not permit extensive NMR measurements. Dimethylphenylphosphine is particularly useful for NMR studies and we have prepared several new carbene complexes to investigate their stereochemistry. *cis*-Bis(dimethylphenylphosphine)dichloroplatinum(II) reacted with two moles of ethyl isocyanide in the presence of sodium hexafluorophosphate (eqn. 1) to give the dipositive cation (I) which, when allowed to react with nucleophilic reagents gives a variety of carbene complexes (II) (eqn. 2).

$$Cl_2PtQ_2 + 2EtNC + 2Na^+PF_6^- \xrightarrow{MeOH} \underset{(I)}{[Pt(CNEt)_2Q_2](PF_6)_2} \qquad (1)$$

$$I + L\text{-}H \rightarrow \underset{(II)}{trans\text{-}\{(EtNC)PtQ_2[C(NHEt)L]\}(PF_6)_2} \qquad (2)$$

$(Q = PMe_2Ph; L = EtO–, p\text{-}MeC_6H_4NH–, PhNH–, PhCH_2S–)$

The reactions proceed slowly, in yields of about 40%; however, due to the very low solubilities of the isocyanide complexes (I) and the high solubilities of the carbene complexes (II) in polar solvents, purification of the carbene complexes can easily be achieved.

The phosphine methyl resonances appear in the NMR spectra as 1/3/1 triplets due to strong phosphorus–phosphorus coupling[5] of mutually *trans* phosphines, flanked by

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TABLE 1

INFRARED[a] AND ^{1}H NMR DATA[b] FOR CARBENE COMPLEXES

Complex	Phosphine–methyls			Ethyl resonances		ν(N–H)	ν(N≡C)	$\Delta\nu$(N≡C)[c]
	$\delta(CH_3)$	J(P–H)	J(Pt–H)	$\delta(CH_3)$	$\delta(CH_2)$			
$[(Et{-}NC)_2Pt(PMe_2Ph)_2](PF_6)_2$	insoluble					–	2294	143
$[(Et{-}NC)Pt(PMe_2Ph)_2(C\begin{array}{l}\diagup O{-}Et\\ \diagdown NH{-}Et\end{array})](PF_6)_2$	2.10 2.11 2.14 2.15	6.0 6.0 6.4 6.4	32.5 32.5 31.6 31.6	1.01 1.09 1.11	3.05 3.63	3382	2271	120
$[(Et{-}NC)Pt(PMe_2Ph)_2(C\begin{array}{l}\diagup NH{-}C_6H_5\\ \diagdown NH{-}Et\end{array})](PF_6)_2$	1.99 2.00 2.16 2.17	8.2 8.0 8.0 8.0	32.4 31.6 32.8 32.8	1.14 1.22	3.51 3.64	3341 3389	2265	114
$[(Et{-}NC)Pt(PMe_2Ph)_2(C\begin{array}{l}\diagup NH{-}C_6H_4{-}CH_3\\ \diagdown NH{-}Et\end{array})](PF_6)_2$[d]	1.91 1.94 2.07 2.11	6.9 6.9 7.6 7.6	32.4 32.4 31.6 31.6	1.12 1.14	3.42 3.57	3346 3393	2264	113
$[(Et{-}NC)Pt(PMe_2Ph)_2(C\begin{array}{l}\diagup SCH_2{-}C_6H_5\\ \diagdown NH{-}Et\end{array})](PF_6)_2$	2.03[e]	8.0	31.2	1.19 1.23	3.52 3.58	3342	2257	106

[a] Accurate to ± 2 cm^{-1}. [b] Spectra recorded using dichloromethane as solvent and internal standard. Chemical shifts in ppm and coupling constants in Hz. [c] ν(N≡C) (complex)–ν(N≡C) (free ligand). [d] $\delta(CH_3)$ = 2.31. [e] Other resonances were complex and could not be interpreted.

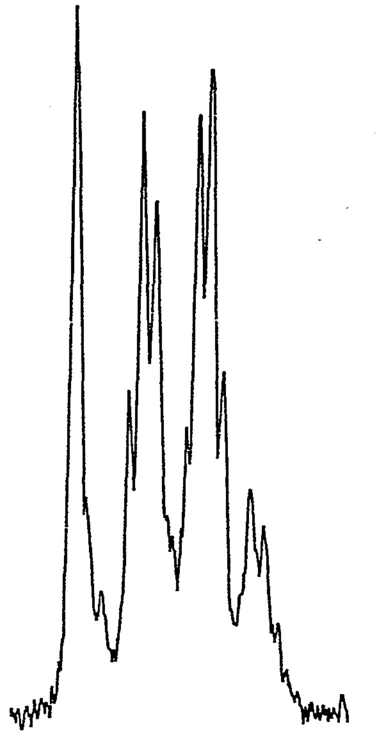
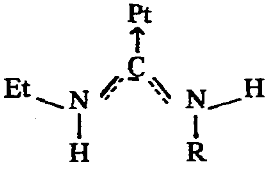
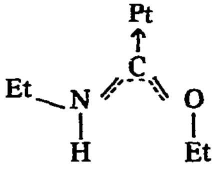
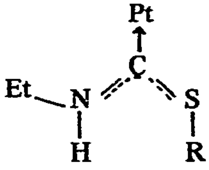


Fig.1. Phosphine–methyl resonances of *trans*-$\{(EtNC)Pt(PMe_2Ph)_2[C(NHEt)(NH\text{-}C_6H_4\text{-}Me)]\}(PF_6)_2$ recorded on a CH_2Cl_2 solution at 31° using a sweep width of 500 Hz.

satellites of one-quarter intensity as a result of coupling with ^{195}Pt. The NMR spectra (Fig.1) clearly indicate the presence of four inequivalent phosphine methyl groups due to the absence of a σ-plane of symmetry along the C–Pt–C axis and resulting from restricted rotation about the platinum–carbene bond. The NMR spectra also indicate the presence of only one isomer in solution and the most likely structures are shown below, resulting from a 1,2-*cis*-addition of the nucleophile across the CN triple bond.







The X-ray structure by Richards[6] indeed shows that such *cis*-addition can occur, and that the carbene plane is perpendicular to the platinum square plane. It is difficult to predict, *a priori*, whether this is the most stable configuration. In the completely planar structure, extensive π-bonding involving the carbene carbon $2p_z$ and platinum $5d_{xz}$ orbitals is possible, although there must also be considerable steric interaction between the carbene and phosphines. That the structure with the carbene perpendicular to the plane of the complex has been observed, in which the carbene carbon $2p_z$ orbital is competing with the phosphines for in-plane π-bonding with the Pt $5d_{xy}$ orbitals, suggests that π-bonding possibilities are less important than steric requirements.

The bis(isocyanide) platinum cation (I) shows a much larger $\Delta\nu(N\equiv C)$ than the carbene cations and since $\Delta\nu(N\equiv C)$ reflects the total positive charge on platinum[3], the carbene is a stronger σ-donor and/or weaker π-acceptor than the parent isocyanide. A comparison of the coupling constants $J(Pt{-}C{-}H)$ in the complexes *trans*-$[PtMe(PMe_2Ph)_2L]^+PF_6^-$; where L = methoxycarbene[1] and ethyl isocyanide[3], gives values of 51 and 63 Hz respectively indicating that the carbene is indeed a much better σ-donor than the isocyanide.

IR and NMR data are given in Table I.

REFERENCES

1 (a) M.H. Chisholm and H.C. Clark, *Chem. Commun.*, (1970) 763; (b) M.H. Chisholm and H.C. Clark, *Inorg. Chem.*, in press.
2 (a) H.C. Clark and L.E. Manzer, *Chem. Commun.*, (1971) 387; (b) H.C. Clark and L.E. Manzer, *Inorg. Chem.*, submitted for publication.
3 H.C. Clark and L.E. Manzer, *Inorg. Chem.*, submitted for publication.
4 E.M. Badley, B.J.L. Kilby and R.L. Richards, *J. Organometal. Chem.*, 27 (1971) C37.
5 R.K. Harris, *Can. J. Chem.*, 42 (1964) 2275.
6 (a) E.M. Badley, J. Chatt, R.L. Richards and G.A. Sim, *Chem. Commun.*, (1969) 1322; (b) E.M. Badley, J. Chatt, R.L. Richards, *J. Chem. Soc., A*, (1971) 21.