Preliminary communication

The NMR spectra of carbene complexes of platinum(II)

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The carbene complexes of platinum(II) which we recently described¹, cis-{PtX₂ [C(NHR)R¹] (PEt₃)} (X = Cl or Br; R = Ph or Me; R¹ = OMe, OEt, OPr-n, NHPh, NHMe or NBu-s) are poorly soluble and reliable NMR spectra were not obtained. We have now synthesised, by a similar route, more soluble carbene complexes (Eq. 1), and have examined their ¹H NMR spectra.

trans-[PtX(CNR)(PEt₃)₂]ClO₄ + QH →

trans-{ $PtX[C(NHR)Q](PEt_3)_2$ } ClO₄ (1)

(RNC = PhNC or MeNC; Q = PhNH, EtNH or EtO; X = Cl or Br)

The parent isocyanide complexes were prepared by the method of Church and Mays² and a *trans*-configuration can be assigned to these and the derived carbene complexes since the P-CH₃ resonance is a 1/4/6/4/1 quintet due to strong *trans*-phosphorus-phosphorus coupling³. The spectra are also consistent with free rotation about the platinum-carbon bond, as is found in the methoxycarbene analogues⁴.

Like the carbene complexes of chromium^{5,6}, these compounds show restricted rotation about the C-N or C-O bonds of the carbene ligand. Thus two distinct phenyl patterns are seen for *trans*-{PtCl[C(NHPh)₂](PEt₃)₂} ClO₄ in CDCl₃ solution (Table 1). Since spectra at 60 and 100 MHz and deuteriation studies show that this pattern is not a doublet due to proton coupling, it could result from either configuration (A) of the carbene ligand, or an approximately equal mixture of configurations (B) and (C).



Since models indicate configuration (A) to be sterically favoured, and this is the configuration for the ion $\{CH_3C[NH(CH_3)]_2\}^{+7}$, we consider configuration (A) predominates in solution. The other carbene complexes show similar restricted rotation and

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Complex	τ (±0.01)	³ J(H-C-C-H) (Hz ±0.04)	³ J(H-N-C-H) (Hz ±0.04)	Assignment
trans-{ $PtC1[C(NHPh)_2](PEt_3)_2$ } ⁺	(1.8–1.95) (2.6–2.9)	_		phenyl isomers
trans-{ $PtC![C(NHPh)NHEt](PEt_3)_2$ } ⁺	(1.9-2.1) (2.65-3.0)	-		phenyl isomers
	6.20 8.64	7.0 7.0	5.0	N–CH ₂ –CH ₃ N–CH ₂ –CH ₃
<i>trans</i> -{PtCl[C(NHPh)OEt](PEt ₃) ₂ } ⁺	2.3–2.9 4.95–5.4 8.55	- 7.0	- - -	phenyl OCH ₂ CH ₃ OCH ₂ CH ₃
<i>cis</i> -{PtCl ₂ [C(NHPh)OEt](PPr-n ₃)}	(1.95–2.2) (2.7–2.85)	-	-	phenyl isomers
	4.8-5.3 8.72	7.0	_	$O-CH_2-CH_3$ $O-CH_2-CH_3$

TABLE 1 ¹H NMR SPECTRA OF CARBENE COMPLEXES ^a

^a In CDCl₃ solution using tetramethylsilane as internal standard and a Varian HA 100 instrument.

assignments are given in Table 1. With alcohols reaction (1) does not go to completion and trans-{ $PtCl[C(OEt)NHPh](PEt_3)_2$ } ClO₄ was only obtained as a mixture with the parent phenylisocyanide complex, but the carbene ligand resonances could be assigned (Table 1).

Spectra of the *cis*-complexes containing PEt₃ may be obtained in $(CD_3)_2SO$ solution, but a reaction occurs with the solvent. However, *cis*-{PtCl₂ [C(OEt)NHPh](PPr-n₃)} is more soluble and exists as a mixture of isomers in CDCl₃ solution (Table 1).

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