The Reactions of Isocyanide Complexes of Platinum(II): a Convenient Route to Carbene Complexes

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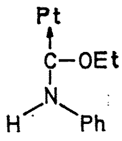
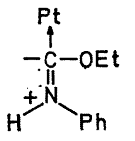
Summary A series of isocyanide complexes has been prepared of which $[PtCl_2(PhNC)(PEt_3)]$ is typical: this complex reacts with ethanol to give a crystalline compound, shown by an *X*-ray structure determination to be a complex of ethoxy(phenylamino)carbene.

PROMPTED by the observation that isocyanides may be reduced enzymatically to hydrocarbons,[1] probably *via* co-ordination of an isocyanide to a metal, we have investigated the reactions of isocyanide molecules when co-ordinated to platinum(II).

The series of complexes $[PtX_2(RNC)(PR^1_3)]$ ($X = Cl$, Br, I; $R = Me$, Et, Ph; $PR^1_3 = PMe_2Ph, PEt_2Ph, PEt_3$) has been prepared by reaction (1) in high yield. The $N{\equiv}C$ stretching frequency of the co-ordinated isocyanides increases relative to the free ligand as is generally found for metals in oxidation state one or higher.[2]



(I)



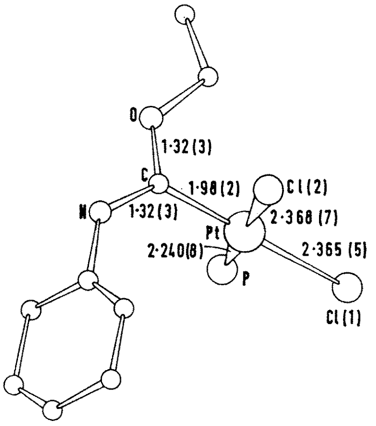
(II)

$$[Pt_2Cl_4(PR^1_3)_2] + RNC \rightarrow 2[PtCl_2(RNC)(PR^1_3)]$$

$$\Big\downarrow \text{LiX}$$

$$[PtX_2(RNC)(PR^1_3)] + LiCl \quad (1)$$

We find that co-ordinated isocyanide is reactive towards a wide variety of reagents; for example, reduction of the PhNC complexes with $NaBH_4$ gives methane (plus a little ethylene and ethane) which must originate from the isocyanide carbon. More remarkably, the compound $[PtCl_2(PhNC)(PEt_3)]$ reacts with ethanol to give a white, sparingly soluble crystalline complex (A) (m.p. 212°) which shows no $\nu(N{\equiv}C)$ in the i.r. spectrum (mull) but has two medium intensity bands at 3130 and 3090 cm.$^{-1}$ together with bands in the 1600—1300 cm.$^{-1}$ region. It is diamagnetic and a non-conductor in nitrobenzene solution. The low solubility of (A) prevents n.m.r. measurements.



FIGURE

The structure of (A) has been determined by *X*-ray single-crystal methods and is shown in the Figure (ethyl groups of the phosphine are omitted for clarity) (current $R = 6{\cdot}5\%$ for 1778 independent reflections).

This structure suggests that (A) may be regarded as a carbene complex (1) or the isomeric ylide (II), both forms merely representing extreme electronic structures.

The O–C–(Pt)–N unit is essentially planar and lies approximately at right angles to the plane of the platinum and the other ligands. Both the C–N and the C–O bond lengths are shorter than expected for normal single bonds and closely similar to those found in carbene complexes of chromium [where the carbene carbon carries only one electronegative atom (see ref. 3 and references therein)], indicating the existence of a π-system involving mainly the oxygen, carbon, and nitrogen atoms with, as shown below, little participation of the platinum atom.

The Pt–C bond length is significantly longer than Pt–CO bond lengths and close to the Pt–C bond length in the parent isocyanide complex (see Table). Similarly, chromium–carbene bond lengths are significantly longer than chromium–carbonyl bond lengths.[3]

TABLE

Compound	Pt–C	Reference
cis-[$PtCl_2\{C(OEt)NHPh\}(PEt_3)$]	1·98(2)	this work
cis-[$PtCl_2(PhNC)(PEt_3)$]	1·94(3)	5
cis-[$PtCl_2(CO)(PEt_3)$]	1·75(9)	5
trans-[$PtCl(CO)(PEt_3)_2$][BF_4]	1·78	6
trans-[$PtCl_2(CO)(ONC_6H_4OMe)$]	1·74(4)	7

Because of the above similarities to the chromium system, (A) may be regarded as the carbene (I), but we assign the band at 3130 cm.$^{-1}$ (shifted to a broad band at 2240 cm.$^{-1}$ on deuteriation) to N–H stretching which is lower by 200—300 cm.$^{-1}$ than ν(N–H) of the $Cr(CO)_5C(R^1R^2NH)Me$ compounds,[4] perhaps because the nitrogen atom of (A) carries some positive charge as in (II). Therefore, the structure of (A) may be regarded as that of a carbene complex, but with a contribution of the ylide form.

A series of such complexes, [$PtX_2(PEt_3)\{C(R)NHPh\}$] (X = Cl, Br; R = OMe, OEt, OPr^n, NHPh, $NHBu^s$) has been prepared by use of the appropriate alcohol or primary amine and [$PtCl_2(MeNC)(PEt_3)$] gives [$PtCl_2\{C(NHMe)$-$NHPh\}(PEt_3)$] with aniline. We find that secondary amines produce amine hydrochloride from the phenyl isocyanide complex: this reaction is under investigation. The reactions of (A) itself are being studied and we are extending this carbene synthesis to other metals.

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