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Preliminary communication

INSERTION OF ISOCYANIDE INTO A PLATINUM—HYDRIDE BOND; THE SYNTHESIS OF NEW SECONDARY CARBENE COMPLEXES

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Summary

The complex *trans*-[PtH(CNR)(PEt$_3$)$_2$]Cl (R = *p*-tolyl) undergoes insertion of isocyanide into the platinum—hydride bond in non-polar solvents, probably via the five coordinate intermediate, HPtCl(CNR)(PEt$_3$)$_2$, to give *trans*-PtCl(CHNR)(PEt$_3$)$_2$; protonation or methylation of this insertion product at nitrogen affords cationic secondary carbene complexes.

Transfer of hydrogen from a transition metal to coordinated alkynes, alkenes, carbon dioxide [1], nitric oxide [2], dinitrogen [3], carbon disulphide [4], sulphur dioxide [5] and the ketimide [6] ligand has been reported. The first hydrogen transfer from a transition metal to coordinated isocyanide was reported [7] with the isolation of the complexes, Ru(CHNR)(R'CO$_2$)(CO)(PPh$_3$)$_2$ (R = *p*-tolyl; R' = methyl, ethyl or phenyl), in the reaction of Ru(O$_2$)(CO)(CNR)(PPh$_3$)$_2$ [8] with alcohols. Subsequently, these and other ruthenium complexes containing the formimidoyl ligand were prepared [9] in quantitative yields from RuH(R'CO$_2$)(CNR)(PPh$_3$)$_2$. Such hydrogen transfer reactions may also be considered as insertion of the unsaturated ligand into the transition metal—hydride bond. An important property of this novel ligand is that it may undergo electrophilic attack at nitrogen to afford secondary carbene complexes. An alternative route to secondary carbene complexes has been devised [10] by Lappert.

On the slow dropwise addition of isocyanide to a rapidly stirred ethereal solution of *trans*-HPtCl(PEt$_3$)$_2$, the complex *trans*-[PtH(CNR)(PEt$_3$)$_2$]Cl is obtained as a colourless precipitate in quantitative yields. Conductivity measurements in methanol (71 Ω^{-1} cm^2 mol^{-1}) and nitrobenzene (25 Ω^{-1} cm^2 mol^{-1}) confirm the ionic nature of this product. It readily undergoes insertion of isocyanide into the platinum—hydride bond, in solution, to give *trans*-PtCl(CHNR)(PEt$_3$)$_2$ (I). As in the ruthenium complexes prepared previously, the formimidoyl ligand is characterized in the IR spectrum by a sharp band near 2800 cm^{-1} (ν(CH)) and a strong band at 1560 cm^{-1} (ν(C=N)) and in the ^{1}H NMR spectrum by a

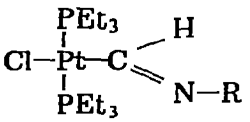
TABLE 1

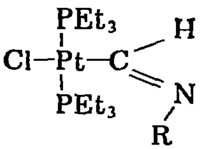
IR AND ^{1}H NMR DATA

Complex	Infrared frequencies [a] (cm^{-1})	^{1}H NMR signals [b]
[PtH(CNR)(PEt$_3$)$_2$]Cl	ν(C≡N) 2190vs	τ(PtH) 16.39 J(PtH) 888 Hz J(PH) 14.8 Hz τ(Me(p-tolyl)) 7.53
PtCl(CHNR)(PEt$_3$)$_2$	ν(CH) 2810m ν(C=N) 1560s (br) 1582s (sh)	τ(PtCH) −0.66, −0.60 ^{2}J(PtCH) 93, 117 Hz ^{3}J(PPtCH) 5.8, 5.8 Hz τ(Me(p-tolyl)) 7.62
[PtCl(CHNHR)(PEt$_3$)$_2$]ClO$_4$	ν(C=N) 1572s	τ(PtCH) −1.15 ^{2}J(PtCH) 40 Hz ^{3}J(PPtCH) 4 Hz τ(Me(p-tolyl)) 7.64
[PtCl(CHNHR)(PEt$_3$)$_2$]Cl	ν(C=N) 1535s	τ(PtCH) −1.59 ^{2}J(PtCH) 36 Hz ^{3}J(PPtCH) 5 Hz J(CH—NMe) very small τ(NMe) 5.81 τ(Me(p-tolyl)) 7.58
[Pt(CHNMeR)(CNR)(PEt$_3$)$_2$](ClO$_4$)$_2$	ν(C≡N) 2205vs ν(C=N) 1560m (br)	τ(PtCH) −1.36 ^{2}J(PtCH) 25 Hz ^{3}J(PPtCH) 4.5 Hz τ(NMe) 5.62 τ(Me(p-tolyl)) 7.58, 7.50
[Pt(CHNMeR)(PPh$_3$)(PEt$_3$)$_2$](ClO$_4$)$_2$	ν(C=N) 1538s	τ(PtCH) −1.4, −1.6 ^{2}J(PtCH) 42 Hz τ(NMe) 5.88, 5.98 τ(Me(p-tolyl)) 7.63, 7.66

[a] IR spectra measured as Nujol mulls on a Perkin—Elmer 621 Spectrometer. [b] NMR spectra measured in $CDCl_3$ on a Varian HA 100 Spectrometer. [c] R = p-tolyl. [d] All compounds were colourless with *trans*-triethylphosphine group and had satisfactory elemental analysis.

signal in the low field (single H of formimidoyl). The hydrogen atom in the electronically similar formyl ligand of [Fe(HCO)(CO)$_5$]$^-$, prepared [11] by Collman and Winter is even more acidic. (ν(CH) 2690, 2540 cm^{-1}, τ(H of formyl) —4.95). Unlike the ruthenium complexes, (I) exists as an isomeric mixture due to *syn* and *anti* configurations of the *p*-tolyl group about the carbon—nitrogen double bond. Hence, the downfield signal appears as two overlapping triplets of triplets and ν(C=N) as a doublet. For spectroscopic data see Table 1.





The rate of insertion increases with an increase in temperature or with a decrease in polarity of the solvent. (MeOH: no reaction at 35°C over 3 days; CH_2Cl_2: quantitative insertion at 35°C overnight; CH_2Cl_2/n-C_5H_{12}: quantitative insertion at 35°C in 2 hours; C_6H_6: instantaneous insertion on dissolution with heating, to 60°C). This suggests a mechanism with a neutral intermediate arising from the strong tendency of the chloride ion to coordinate in a non-polar solvent. In support of this, the complex [PtH(CNR)(PEt$_3$)$_2$]ClO$_4$ (R = *p*-tolyl) does not undergo insertion under any of the above conditions. The analogous complexes

$[PtH(CNR)(PEt_3)_2]ClO_4$ (R = *p*-anisyl, t-butyl) have also been reported [12] as stable indefinitely, in solution. During the insertion reaction, the hydride triplet of the starting material collapses to a singlet and the signals from the phosphine ethyl groups lose their resolution. Of the two neutral intermediates $HPtCl(CNR)(PEt_3)_2$ and $HPtCl(CNR)(PEt_3)$ (i.e. phosphine dissociation) that could account for this effect, the five coordinate complex is favoured, since substitution of a phosphine by chloride at room temperature is unlikely. The phosphine scrambling could be attributed either to an equilibrium between the starting material and five coordinate intermediate or to rapid interconversion between trigonal bipyramidal and square pyramidal structures in the intermediate itself. Treichel has suggested [13] a mechanism with a five coordinate intermediate for the insertion of isocyanide into the platinum—carbon bond of $RPtXL_2$ complexes (RX = MeI, PhCl, PhBr, PhI; L = phosphine). As the insertion product formed, the hydride signal diminished and disappeared and the signals from the ethyl groups were again clearly resolved, demonstrating *trans* stereochemistry for the phosphine ligands in the product.

At room temperature, the ratio of isomers in the product was about 4/1 but at 60°C the ratio approached 1/1. The reason could be a steric one. The ease of formation of the more sterically hindered product, with the *p*-tolyl group directed towards a phosphine could be increased at higher temperatures. However, no further isomerisation of the mixture was observed in benzene heated under reflux for 3 hours.

The platinum complex, *trans*-$PtCl(CHNR)(PEt_3)_2$, reacts reversibly with perchloric acid and hydrochloric acid, at room temperature, and with dimethyl sulphate, in the presence of sodium perchlorate, to give the new secondary carbene complexes, *trans*-$[PtCl(CHNHR)(PEt_3)_2]X$ ($X = ClO_4$, Cl) and *trans*-$[PtCl(CHNMeR)(PEt_3)_2]ClO_4$. Removal of the chloride ligand from the latter using silver perchlorate, followed by reaction with isocyanide or triphenylphosphine, affords the doubly-charged cationic complexes $[Pt(CHNMeR)(L)(PEt_3)_2](ClO_4)_2$, ($L = CNR$ or PPh_3).

$$\begin{tikzcd}
{[PtH(CNR)(PEt_3)_2]Cl} \arrow[d] & \\
PtCl(CHNR)(PEt_3)_2 \arrow[r, shift left, "HX"] \arrow[d, "\begin{matrix}Me_2SO_4,\\ NaClO_4\end{matrix}"] & {[PtCl(CHNHR)(PEt_3)_2]X} \arrow[l, shift left, "NEt_3"] \\
{[PtCl(CHNMeR)(PEt_3)_2]ClO_4} \arrow[r, "AgClO_4", "L"'] & {[Pt(CHNMeR)(L)(PEt_3)_2](ClO_4)_2}
\end{tikzcd}$$

($L = CNR, PPh_3$)

Bands attributed to NH stretching and bending frequencies were evident in the IR spectra of the protonated carbene complexes. These disappeared on deuteration, while bands assigned to $\nu(ND)$ appeared in the expected positions. There is evidence for hydrogen bonding in the complex $[PtCl(CHNHR)(PEt_3)_2]Cl$ since $\nu(NH)$ appears as a broad band at 2580 cm^{-1}.

Acknowledgments

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