Five-co-ordinate Complexes of Platinum(II)

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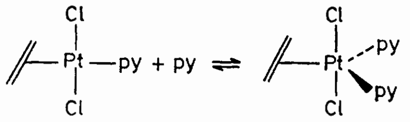
Summary N.m.r. spectroscopy provides evidence for five-co-ordinate pyridineplatinum(II) complexes which are probably the intermediates in associative substitution processes.

NUCLEOPHILIC attack by pyridine on [*a*-(π-C_2H_4)-*c*-(py)-$PtCl_2$] (I) (py = pyridine) can lead to two types of reaction: ligand exchange,[1] or $\pi \rightarrow \sigma$ rearrangement of the co-ordinated olefin.[2] By studying the ^1H n.m.r. spectrum of this system we have observed that an addition reaction can occur producing a five-co-ordinate species, which probably is the intermediate in the ligand exchange process.

The C_2H_4 protons of (I) in $CDCl_3$ absorb at δ 4·9, $J(^{195}Pt-^{1}H)$ 61 Hz. On addition of pyridine at −40 °C, for example, we find this resonance moves to higher field {in addition to giving the two triplets at δ 2·45, J(Pt–H) 86 Hz, and δ 4·54, J(Pt–H) 36 Hz due to [*a*-(pyCH_2CH_2)-*c*-(py)$PtCl_2$], produced by $\pi \rightarrow \sigma$ rearrangement[2] of the ethene}. Unlike these last absorptions the δ-value of the newly reported resonance is very sensitive to the amount of pyridine present, showing that a new species must be formed in rapid equilibrium with (I).

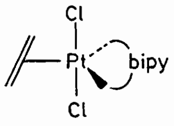
On increase in concentration of pyridine, the resonance (value δ_{av}) moves from δ 4·9 to 3·9. Between the limits, the value of δ_{av} falls with decrease in temperature. The quantity $(4·9 - \delta_{av})$ is proportional to the concentration of pyridine at low concentrations, but when the concentration of pyridine is large δ_{av} converges to 3·9. The equilibrium (1) is implied. Support for the existence of (II), the five-co-ordinate species formed in this equilibrium, is provided by the δ-value of 3·9 and J(Pt–H) 70 Hz seen at high pyridine concentration which are close to δ 3·67 and J(Pt–H) 70 Hz observed[3] in the analogous bipyridyl (bipy) complex (III).

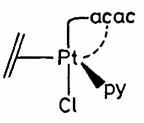

(1)

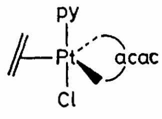
(I) (II)

[*a*-(π-C_2H_4)-*b*-ClPt(acac)] (acac = acetylacetonato) behaves in a similar manner. In $CDCl_3$ at −45 °C this compound has the following resonances: C_2H_4, an extremely narrow doublet, δ 4·63 [J(Pt–H) 66, J(H–H) 3 Hz]; CH_3 δ 2·26 [J(Pt–H) 4 Hz] and 2·08 [J(Pt–H) 4 Hz]; CH δ 5·775 [J(Pt–H) 8·5 Hz]. On addition of pyridine between −40 and −50 °C, these absorptions move converging to: C_2H_4, a clear doublet, δ 3·67 [J(Pt–H) 73, J(H–H) 13·2 Hz]; CH_3 δ 2·08 [J(Pt–H) 4 Hz] and 1·86 [J(Pt–H) 4·1 Hz]; CH 5·48 [J(Pt–H) 8·5 Hz]. Additional evidence for an increase in co-ordination number is thus provided by the rise in J(H–H).

The inequivalence of the CH_3 resonances in the five-co-ordinate species indicates that it is (IV) rather than (V). A five-co-ordinate system together with the isomerism of (II) and (IV) is particularly relevant to substitution in platinum(II) complexes which is considered to be associative, to go through a trigonal bipyramidal intermediate and to involve exchange *trans* to various labilizing ligands such as ethene.


(III)


(IV)


(V)

N.m.r. measurements were made at 60 and at 220 MHz. We thank Dr. I. A. Stenhouse, Dr. A. J. G. Crawshaw, and Mr. M. W. Cooper for assistance.

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