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Modes of Coordination of Dihalogenodiazadiphosphetidine Ring Systems, $(PXNR)_2$, in Transition Metal Complexes

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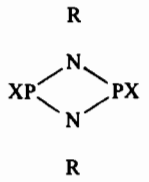
Introduction

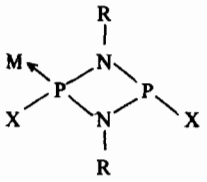
Dihalogenodiazadiphosphetidine ring systems (I) are now well known [2–7] and interest in their coordinating ability derives from the availability of four potential donor sites:



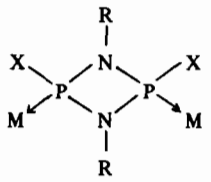
(I) (X = F, Cl; R = alkyl, aryl)

The ring (I) (X = Cl, R = Bu^t) is slightly puckered with mutually *cis*-chlorine atoms lying on the same side of the ring as the nitrogen atoms [8, 9] and ^{19}F and ^{31}P nmr studies of (I) (X = F, R = Bu^t) suggest a similar stereochemistry [10–12].

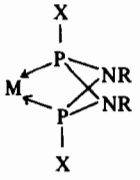
Transition metal dihalogenodiazadiphosphetidine complexes can have the structures (II) → (VI) shown below, assuming that nitrogen alone is not the donor site.



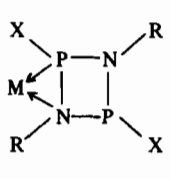
(II)



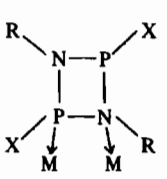
(III)



(IV)



(V)



(VI)

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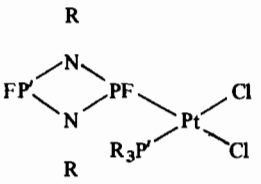
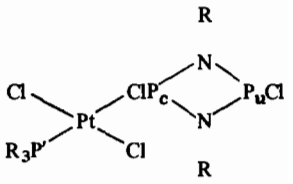
To date few coordination complexes have been described, but $Fe_2(CO)_7(PClNBu^t)_2$ [13] and $Me_2(CO)_{10}[P(NMe_2)N(SiMe_3)]_2$ (M = Cr, Mo) [14] have been assigned the bridging structure (III) on the basis of i.r. spectroscopic data. A recent report by Willey *et al.* [1] of metal complexes containing bridging {type (II)} and chelating {type (IV)} rings, prompts us to report a *selection* of results from our more extensive studies in this area in which nmr spectroscopy provides unambiguous information regarding the bonding modes of dihalogenodiazadiphosphetidines.

Results and Discussion

Monomeric complexes of the type $PtCl_2(PR_3)(PXNR)_2$ (R = Bu^t, X = F, Cl; PR_3 = PPr^n_3, PBu^n_3, PPh_3, PMe_2Ph, PEt_2Ph) in which the ring exhibits type (II) coordination are readily formed by treatment of $Pt_2Cl_4(PR_3)_2$ with two equivalents of (I) (R = Bu^t; X = F, Cl). Both *cis*- and *trans*-isomers, typified by (VII) and (VIII), are formed, depending to some extent on the solvent system used but more on the nature of the dihalogenodiazadiphosphetidine.



(VII)



(VIII)

The stereochemistry of each complex was unambiguously determined by ^{31}P and (where appropriate) ^{19}F nmr spectroscopy and subsequently confirmed by a single-crystal X-ray structural determination of *cis*-$PtCl_2(PEt_3)(PFNBu^t)_2$ [15].

The $^{31}P\{^1H\}$ nmr spectrum of (VIII) (R = Bu^t, PR_3 = PBu^n_3) shown in Fig. 1 which is typical, exhibits two phosphorus resonances for the inequivalent ^{31}P nuclei of the coordinated ring to significantly higher field of the free ligand $\{(PClNBu^t)_2$ has δ_P = −210.9 ppm [6]$\}$†. Only the resonance of the phosphorus P_c directly coordinated to platinum (δ_{P_c} = −147.3 ppm) exhibits ^{195}Pt satellites ($^1J_{PtP_c}$ = 3254 Hz) and the signal is split further by coupling to the *trans*-PEt_3 ligand ($^2J_{P_cP'}$ = 681 Hz) and to the uncoordinated phosphorus atom of the ring (δ_{P_u} = −183.2 ppm; $^2J_{P_cP_u}$ = 32 Hz).

†^{31}P chemical shifts were measured relative to external $P(OMe)_3$ and corrected relative to H_3PO_4 by $\delta_P = \delta_P$ (observed) −141 ppm. Downfield shifts are negative.

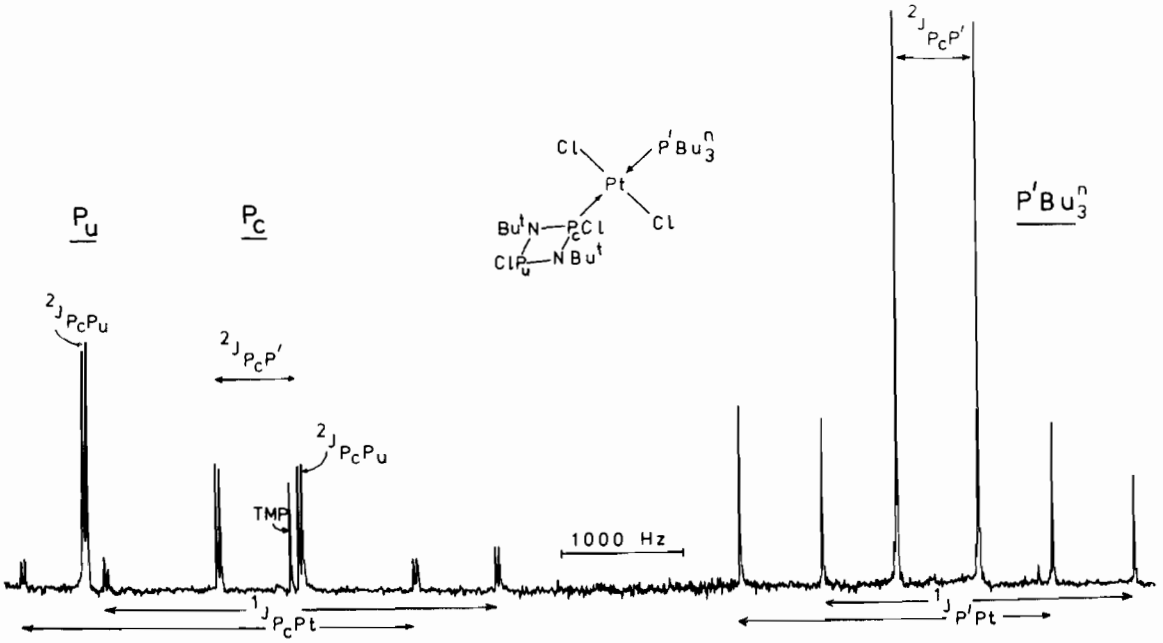


Fig. 1. $^{31}P\{^1H\}$ n.m.r. spectrum of *trans*-$PtCl_2(PBu^n_3)(PClNBu^t)_2$.

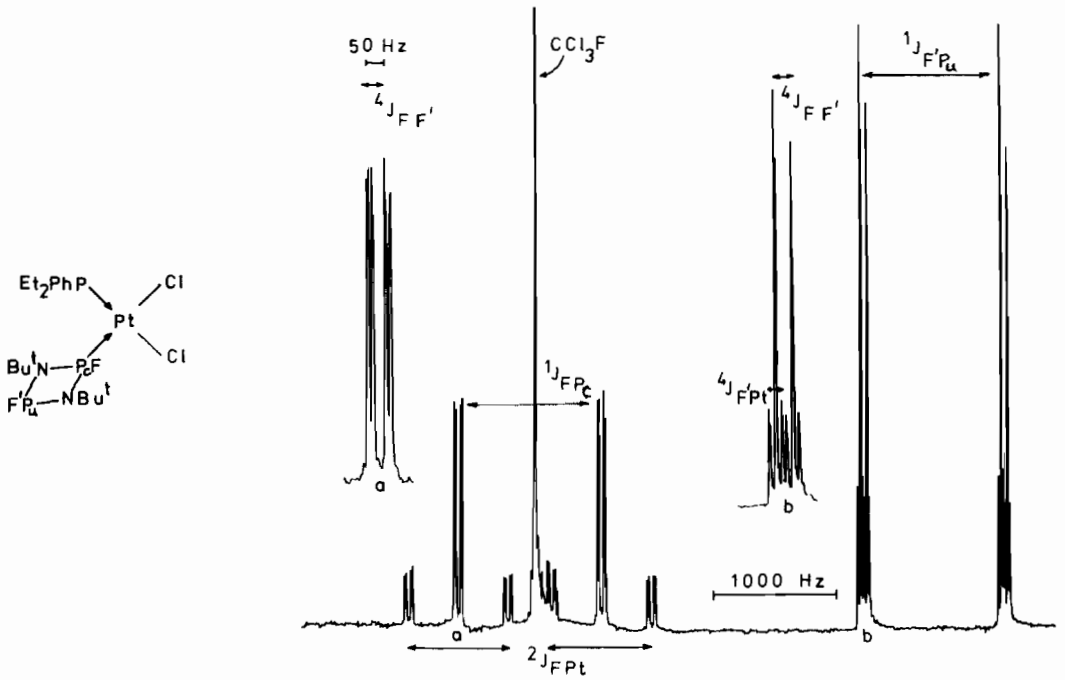


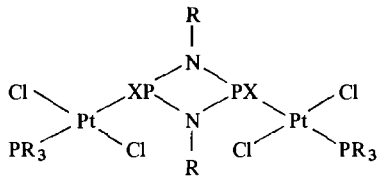
Fig. 2. ^{19}F n.m.r. spectrum of *cis*-$PtCl_2(PEt_2Ph)(PFNBu^t)_2$.

The ^{19}F nmr spectrum of (VII) (R = Bu^t, PR_3 = PEt_2Ph) (Fig. 2) likewise exhibits two distinctly different resonances for the fluorines attached to the coordinated (ϕ_F = −0.5 ppm) and uncoordinated ($\phi_{F'}$ = +35.2 ppm) phosphorus nuclei. In addition to the large directly-bonded $^1J_{PF}$ coupling, further fine structure arises from coupling to ^{195}Pt ($^2J_{FPt}$ = 835 Hz; $^4J_{F'Pt}$ = 39 Hz) and cross-ring coupling ($^4J_{FF'}$ = 53 Hz). The large magnitude of the latter strongly suggests that the two fluorines are on the *same* side of the ring.

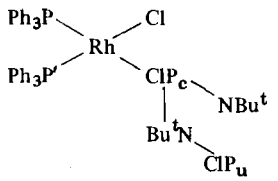
Mononuclear palladium complexes similar to (VIII) were made by analogous routes and biligate monometallic dihalogenodiazadiphosphetidine com-

plexes of the type *cis*- and *trans*-$PtCl_2L_2$, (IX) and (X), [L = (I); X = F, Cl; R = Bu^t] have been prepared by displacement of cyclo-octa-1,5-diene from $PtCl_2$-(h^4-C_8H_{12}). ^{31}P and ^{19}F nmr studies [16] establish that in these complexes the ring exhibits type (II) coordination and the molecular structure of *cis*-$PtCl_2$-$[(PFNBu^t)_2]_2$ has been determined by a single-crystal X-ray diffraction study [15]. In one case an intermediate complex $PtCl_2(h^2$-$C_8H_{12})(PClNBu^t)_2$ was characterised.

Several dinuclear complexes (XI), $Pt_2Cl_4(PR_3)_2$-$(PXNR)_2$ (PR_3 = PMe_2Ph, PEt_2Ph, PEt_3, PBu^n_3) have also been isolated from the reaction between Pt_2Cl_4-$(PR_3)_2$ and (I) (X = F, Cl; R = Bu^t). In these complexes the ring acts as a bridging ligand {type (III) coordination} and nmr analysis of the complicated spin system establishes that the phosphorus atoms of the ring are *trans*- to the PR_3 ligands [16].



(XI)



(XV)

A series of rhodium complexes of the dihalogenodiazadiphosphetidine ring system have also been synthesised, *e.g.* displacement of ethylene by (I) (X = F; R = Pr^i, Bu^t) from $Rh(L)(C_2H_4)_2$ (L = h^5-C_5H_5, h^5-C_9H_7) gave the orange complexes (XII): Rh(L)-$[(PFNR)_2]_2$ in which type (II) coordination is established by ^{19}F and ^{31}P nmr studies [16]. Displacement of ethylene from $[RhCl(C_2H_4)_2]_2$ by (I) (R = Bu^t, X = F, Cl; R = Pr^i, X = Cl) gives the insoluble compounds $[RhCl(PXNR)_2]_n$, (XIII), while deep red crystals of $[RhCl\{(PClNBu^t)_2\}_2]_x$, (XIV), can be isolated from the analogous cyclooctadiene or butadiene precursors under slightly different reaction conditions. An intermediate complex, $RhCl(h^4$-$C_8H_{12})(PClNBu^t)_2$, was characterised by ^{31}P nmr spectroscopy. (XIII) (X = F, R = Bu^t) reacts with CO to afford $RhCl(CO)(PFNBu^t)_2$ and quantitative ring displacement occurs with diphos to yield RhCl-$(diphos)_2$ [11].

The ^{31}P nmr spectrum of $RhCl(PPh_3)_2$ $(PXNBu^t)_2$, (X = F, Cl) (XV), made from $RhCl(PPh_3)_3$, unambiguously establishes that only one phosphorus of the ring is bound to the metal and the PPh_3 ligands are non-equivalent. The most likely structure for (XV) is shown, but the nmr data indicate that there may be considerable distortion from square-planar geometry and a 5-coordinate complex having type (V) coordination cannot be ruled out ($^1J_{RhP_c}$ = 288.1 Hz, $^2J_{P_cP'}$ = 31 Hz, $^1J_{RhP}$ = 134 Hz, $^1J_{RhP'}$ = 142 Hz; δ_{P_c} = −161.0 ppm, δ_{P_u} = −174.1 ppm).

Since we find no evidence for the chelating mode {type (IV) coordination} in any of the complexes so far studied, it is surprising that Willey *et al.* [1] assign this structural type to $Fe(CO)_3(PClNBu^t)_2$ and $TiCl_4$-$(PClNBu^t)_2$ despite alternatives not excluded by analytical or spectroscopic data. Furthermore, their assignment of type (III) coordination for $[RhCl(CO)$-$(PClNBu^t)_2]_2$ is not in accord with our nmr results on dihalogenodiazadiphosphetidine–rhodium systems, where we have only observed bonding *via* a single phosphorus. Willey *et al.* do not report any value for $^1J_{RhP}$ in $[RhCl(CO)(PClNBu^t)_2]_2$ and their ^{31}P chemical shift data for the ring complexes, which do not fall in the range we have observed for a variety of complexes, are more suggestive of ring oxidation products containing pentavalent phosphorus.

When Group (VI) metal carbonyl derivatives $M(CO)_4(C_7H_8)$ or $M(CO)_5(CH_3CN)$ (M = Cr, Mo, W) are treated with (I) (X = F, R = Bu^t), complex mixtures are obtained with $M(CO)_5(PFNBu^t)_2$ as major product. ^{19}F and ^{31}P nmr studies establish type (II) coordination for the latter. The insolubility of higher substituted derivatives limits structural assignment by nmr spectroscopy. Full details of synthetic, spectroscopic and X-ray crystallographic studies on all dihalogenodiazadiphosphetidine complexes will be published later.

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