^{19}F Nuclear Magnetic Resonance Spectra of Fluoro-complexes of Platinum and Palladium

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Summary ^{19}F N.m.r. spectra of $[MF(PR_3)_3][BF_4]$, M = Pd or Pt, unequivocally confirm the assigned structures and comparison of coupling parameters with those in isostructural hydrido-complexes suggests a very small *s* character for the platinum–fluorine bond.

THERE is much current interest[1–3] in the study of fluoro-complexes of platinum metals which also have tertiary phosphines as ligands. However, in no case has any direct spectroscopic or structural evidence for the presence of a metal–fluorine bond been obtained and in particular no ^{19}F n.m.r. spectra have been observed. We report ^{19}F spectra for platinum and palladium complexes of the type, $[MF(PR_3)_3][BF_4]$. These spectra unequivocally confirm the presence of square planar cations with co-ordinated fluorine and also permit comparison of coupling constants with those observed for isostructural hydrido-complexes, $[MH(PR_3)_3]^+$. Such comparisons are likely to yield valuable information for the study of bonding and *trans*-effect phenomena in platinum metal complexes and also for the theory of nuclear spin–spin coupling.

TABLE. *Nuclear magnetic resonance parameters for platinum metal complexes*

Complex	Coupling constants (in Hz)[a] $^{31}P_{trans}$–X	$^{31}P_{cis}$–X	^{195}Pt–X	Chemical shift (p.p.m. from $CFCl_3$ external reference)
$[PdF(PEt_3)_3][BF_4]$	160	30	—	+253[b]
$[PtF(PEt_3)_3[BF_4]$	140	32	250	+252[c]
$[PtF(PEt_3)_2(PPh_3)][BF_4]$	155	30	200	+258[d]
$[PtF(PPh_3)_3][BF_4]$	144	38	see text	+230[b]
$[PtH(PEt_3)_3][BF_4]$[e]	157	15	788	—
$[PtH(PPh_3)_3][(CF_3COO)_2H]$[f]	160	17	774	—

[a] X = ^{19}F or ^{1}H directly bonded to the metal. [b] Nitromethane solution. [c] Acetone solution. [d] Dichloromethane solution. [e] Ref. 6. [f] Ref. 4.

The $[MF(PR_3)_3][BF_4]$ complexes† are synthesized by reaction of silver fluoride with the corresponding chloro-complexes and their ^{19}F n.m.r. spectra are easily analysed by first order techniques to yield the parameters given in the Table. The cation spectra consist of the expected doublet from coupling with the single *trans*-phosphorus atom with

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† Molar conductance measurements in nitromethane give values typical of 1 : 1 electrolytes and satisfactory microanalyses have been obtained for all complexes except $[PdF(PEt_3)_3][BF_4]$ which has only been studied in solution. ν(Pt–F) = 460 cm^{-1} in $[PtF(PEt_3)_3][BF_4]$.

further splitting into triplets from coupling with two *cis*-phosphorus atoms. For $[PtF(PEt_3)_3]^+$ and $[PtF(PEt_3)_2(PPh_3)]^+$ sideband spectra due to coupling with ^{195}Pt (33% abundant) are clearly observed with 1/4 the intensity of the centre bands but for $[PtF(PPh_3)_3]^+$ the sidebands are weak and asymmetric. The origin of this effect is under investigation but we note that a ^1H resonance showing different sideband and centreband spectra has been observed previously[4] for $[PtH(PPh_3)_3]^+$. In any case, the presence of the two fluorine–phosphorus couplings is clear evidence that the fluorine in $[PtF(PPh_3)_3]^+$ is co-ordinated to platinum and that the structure is similar to the other cations reported here. It is also of interest that the reaction of $[Pt(PPh_3)_4]$ with hydrogen fluoride gives a product whose ^{19}F n.m.r. spectrum shows the presence of the $[PtF(PPh_3)_3]^+$ cation. This product was originally formulated[5] as $[PtF_2(PPh_3)_2]$ but it has recently been suggested[2] that the correct formula is $[PtF(PPh_3)_3][HF_2]$.

The magnitudes of the coupling constants for these fluoro-complexes may be compared with reported[4,6] values for $[PtH(PPh_3)_3]^+$ and $[PtH(PEt_3)_3]^+$ (see Table). The phosphorus–fluorine couplings are of similar magnitudes but an unexpected feature is the relatively small platinum–fluorine coupling. Small couplings between fluorine and transition metals have been observed previously for MoF_6 (44 Hz), WF_6 (48 Hz), and NbF_6^- (334 Hz) and Reeves and co-authors have interpreted these in terms of the Pople and Santry theory of spin–spin coupling by suggesting that small values of $|\psi_{ns}(0)|^2$ for the metals are the dominant factors.[7] However, J_{Pt-F} in PtF_6^{2-} is 2080 Hz[8] and J_{Pt-H} in $[PtH(PEt_3)_3]^+$ is 788 Hz.[6] The $|\psi_{Pt(6S)}(0)|^2$ terms will have similar values in these complexes and in the $[PtF(PR_3)_3]^+$ cations and consequently the low platinum–fluorine couplings in the cations must be due to another factor; presumably a very small *s* character for the Pt–F bond. If this is the case it should be reflected in increased *s* character in the platinum–phosphorus bonds with correspondingly large platinum–phosphorus coupling constants. Further studies are in progress to test this hypothesis.

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