Novel Through-space Hydrogen–Fluorine Spin–Spin Coupling in Some Five-co-ordinate Platinum(II) Fluoro-olefin Complexes Stabilized by the Hydrotris-(1-pyrazolyl)borate Ligand

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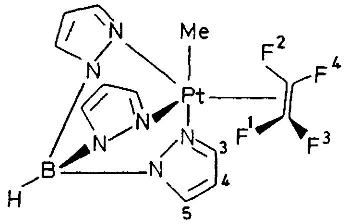
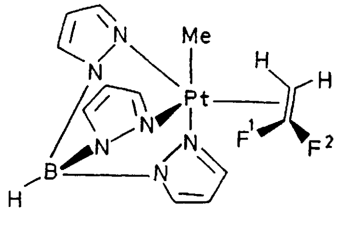
Summary Novel spin–spin hydrogen–fluorine couplings have been observed between the axial platinum methyl hydrogens or the axial 3-H pyrazolyl ring hydrogen and the fluorine nuclei of some five co-ordinate fluoro-olefin complexes; these couplings may arise from through-space interactions.

Most electron-coupled spin–spin interactions between two nuclei are dominated by the Fermi contact mechanism;[1] however, in certain instances where two nuclei are very close together a 'through-space' coupling may also be observed.[2] Examples of through-space couplings in organometallic chemistry[3,4] are rare and are only observed when one or more of the nuclei has a non-bonding pair of electrons which can interact with the second nucleus (*e.g.* ^{19}F, ^{199}Hg, ^{31}P). We describe an unusual coupling between hydrogen and fluorine which we attribute to a through-space interaction.

The hydrotris-(1-pyrazolyl)borate ligand, $HB(NC_3H_3)_3^-$, has recently been shown[5] to stabilize five-co-ordinate complexes of platinum(II). The ^1H n.m.r. spectra of the tetrafluoroethylene (I) and 1,1-difluoroethylene (II) complexes are particularly interesting. The complexes are trigonal bipyramidal and the C=C double bond is constrained within the trigonal plane of the platinum and two equatorial nitrogen atoms. The four substituents on the olefin form a plane roughly perpendicular to the equatorial PtN_2 plane. Double resonance n.m.r. experiments[5] have enabled us to assign all the 3-H, 4-H, and 5-H resonances, on the basis of the relative magnitudes of the Pt–H coupling constants. The platinum–methyl resonance of (I) appears as a 1 : 2 : 1 triplet owing to coupling with only two of four olefin-fluorine nuclei [J(H–F) 2·0 Hz] and the resonance is flanked by ^{195}Pt satellites ($I = \frac{1}{2}$, 33·8%) of one fourth intensity [^2J(Pt–H) 71·5 Hz]. Similarly, the axial 3-H proton resonance, with the 4-H axial proton decoupled, also appears as a 1 : 2 : 1 triplet owing to coupling with two of the four fluorine atoms [J(H–F) 2·0 Hz]. The platinum–methyl resonance and 4-H decoupled-axial 3-H resonance for the 1,1-difluoroethylene complex (II) appear as 1 : 1 doublets owing to coupling with only one of the two fluorine atoms, with coupling constants of 2·0 and 2·5 Hz respectively.

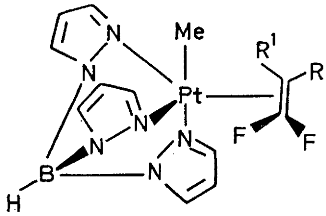


(I)



(II)

The n.m.r. spectrum of the trifluoroethylene complex (III) indicated that two geometrical isomers were obtained.

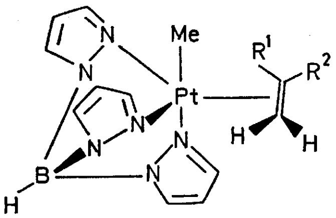


(III) a; R^1=H, R^2=F
b; R^1=F, R^2=H

The platinum methyl resonance of one isomer appeared as a 1:1 doublet [J(H–F) 2·0 Hz] owing to coupling with only one fluorine atom, and the platinum methyl resonance of the second isomer appeared as a 1:1:1:1 doublet of doublets owing to coupling between the platinum methyl hydrogens and two non-equivalent fluorine atoms, with values of J(H–F) 2·0, 2·5 Hz. We therefore assign these resonances to complexes (IIIa) and (IIIb) respectively. Unfortunately the 3-H axial resonances for these complexes were hidden beneath other 3-H and 5-H resonances.

Finally we have prepared a complex (IV) with trifluoromethacrylonitrile [$CH_2{=}C(CF_3)(CN)$] and, as expected, the n.m.r. spectrum showed the presence of two geometrical isomers. The platinum methyl resonance of one isomer appeared as a singlet flanked by ^{195}Pt satellites [J(Pt–H) 64·5 Hz], whereas the corresponding resonance of the second isomer appeared as a quartet owing to coupling with the three fluorines of the CF_3 group [J(H–F) 3·0 Hz]; this resonance was also accompanied by quartet ^{195}Pt satellites [^2J(Pt–H) 66·5 Hz]. We assign these resonances to complexes (IVa) and (IVb) respectively. The coupling constant between the methyl hydrogens and the CF_3 fluorine atoms in (IVb) is larger than the observed H–F coupling constants in complexes (I), (II), and (III), and further supports a through-space rather than a through-bond coupling mechanism.

This conclusion is also strongly supported by data obtained from ^{19}F n.m.r. spectra. For the tetrafluoroethylene complex (I), a complicated AA′BB′X spectrum was observed ignoring the proton coupling. Two sets of resonances of equal intensity are observed centred at 132 (AA′), and 121 p.p.m. (BB′) upfield from $CFCl_3$. All of the lines in the 132 p.p.m. resonances appear as quartets which in the heteronuclear double resonance experiment $^{19}\mathrm{F}\{^{1}\mathrm{H}\}$ collapse into singlets. This confirms that these two fluorines are coupled to three protons, so that these resonances can be assigned to F^1 and F^2. The value of J(H–F) is 2·0 Hz and of J(Pt–F) is 325 Hz. Similarly, all the lines in the resonances centred at 121 p.p.m. appeared as doublets and in the proton-decoupled ^{19}F spectrum collapsed into singlets. Thus, these two fluorines (F^3 and F^4) are coupled to one proton, 3-H axial. The value of J(H–F) is 2 Hz and of J(Pt–F) is 185 Hz. Note that F^1 and F^2 have a much larger value for J(Pt–F) than F^3 and F^4.



(IV) a; R^1=CN, R^2=CF_3
b; R^1=CF_3, R^2=CN

Similarly, for the 1,1′-difluoroethylene complex (II), a complicated ^{19}F spectrum is observed with two sets of resonances at 106 and 95 p.p.m. Quartet splitting could be distinguished in the 106 p.p.m. resonances and fine doublet splitting in the 95 p.p.m. resonance. The proton decoupled spectrum showed only two sets of doublets with ^{195}Pt satellites, the doublet pattern arising from F^1–F^2 spin–spin coupling. Thus, the 106 p.p.m. resonances are assigned to F^1 with J(Pt–F^1) 280 Hz, and the 95 p.p.m. resonances to F^2 with J(Pt–F^2) 160 Hz. Again, note the larger coupling of F^1 to Pt.

These results argue convincingly that these hydrogen-fluorine couplings occur by a through-space mechanism. An *X*-ray crystal structure of (II) is in progress.

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