Contact Shifts and Decoupling in Proton Magnetic Resonance Spectra of Rhenium(III) Complexes

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THE proton magnetic resonance spectra of rhenium complexes of the type $[ReCl_3(PMe_2Ph)_3]$ have several interesting features and one unique one. The large chemical shifts referred to corresponding shifts in similar diamagnetic complexes (see Table) are witness to hyperfine contact interactions between the nuclei and unpaired electrons in both the rhenium(III) and ruthenium(III) cases. Unlike ruthenium(III), however, for which line widths of about 20 c./sec. are found, rhenium(III) produces sharp lines less than 4 c./sec. wide (see Figure). This behaviour has been observed previously in paramagnetic molecules only for complexes of nickel(II).[1] The contact shifts are markedly solvent dependant and are expected to be sensitive to temperature.

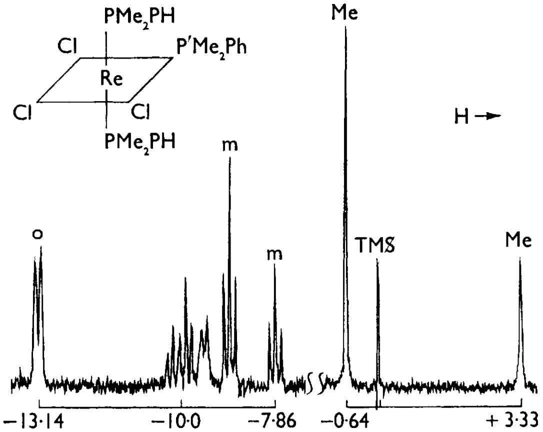
The unique observation is the absence of phosphorus-proton coupling in $[ReCl_3(PMe_2Ph)_3]$, whereas splittings of about 10 c./sec. occur in the methyl spectral region of the analogous diamagnetic complexes of iridium(III)[2] and rhodium(III). The explanation of this decoupling is a rapid relaxation of the phosphorus nuclei through an electron-nuclear mechanism which is present only in paramagnetic cases. This effect is expected to broaden the phosphorus-31 spectra of $[ReCl_3(PMe_2Ph)_3]$. The other couplings in this compound are between protons and are unaffected. The situation for ruthenium(III) is not so clear because of the larger line widths which are of the same order as the expected splittings.

	Ru†	Rh	Ir	Re†
Me_2P'	−4·9	−1·29	−1·25*	+3·33
Me_2P	−4·5	−1·79	−1·91*	−0·64
Line width ..	20	1·5	2·0	4·0

* Ref. 2. † Paramagnetic.

Chemical shifts (p.p.m. relative to tetramethylsilane) and line widths (in c./sec.) of methyl resonances in solutions of the complexes $MCl_3(PMe_2Ph)_3$ *in deuterochloroform.* P′ *refers to the phosphorus* trans *to* Cl; P *is* trans *to* P.

The complex $[ReCl_3(PEt_2Ph)_3]$ behaves similarly to its methyl analogue and exhibits hyperfine contact shifts. Its spectrum is complicated further by inequivalence of the methylene protons and by additional proton-proton coupling. Both these effects are present also in the diamagnetic complexes $[IrCl_3(PEt_2Ph)_3]$ and $[RhCl_3(PEt_2Ph)_3]$. An additional spectral effect in these cases and in *trans*-$[PtCl_2(PEt_3)_2]$ arises from 'virtual coupling'[3] when two phosphines are in *trans*-position.[2] The presence of this effect and the production of methyl signals arising from inequivalent phosphine ligands establishes the meridial structures having C_{2v} symmetry for the octahedral complexes (see Figure).



The proton magnetic resonance spectrum at 60 *Mc./sec. of* $[ReCl_3(PMe_2Ph)_3]$ *in deuterochloroform at* 35°. *Shifts in p.p.m. with respect to tetramethylsilane (T.M.S.) as internal reference.* o, m, m′ *refer to the* ortho *and* meta *protons on the phenyl rings of the* P *and* P′ *ligands, respectively.*
The group of lines centred around −10·0 *p.p.m. are:* ortho′ *doublet at* −9·44 *p.p.m. and* para, para′ *multiplets at* −9·87 *p.p.m. and* 10·14 *p.p.m.*

We are investigating the effects of conformation on the internal chemical shifts of the ethyl groups in all the complexes mentioned above.

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