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Stereochemical Assignments in Triphenyl-Phosphine, -arsine or -stibine Complexes. A Convenient Proton N.M.R. Technique

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Some years ago Keat noted [1] that the chemical shift separation, $\Delta\tau$, between *ortho* and *meta/para* protons in free triphenylphosphine is greatly increased – from $\Delta\tau$ = *ca.* 0 ppm to $\Delta\tau$ = 0.33 ppm – on changing the NMR solvent from $CDCl_3$ to C_6D_6. More recently we have observed that on conversion of triphenylphosphine to the oxide, $Ph_3P{=}O$, or sulphide, $Ph_3P{=}S$, the separation in deuterobenzene is further extended (to $\Delta\tau$ = 0.71 ppm and $\Delta\tau$ = 0.80 ppm respectively).

We have also found that a similar phenomenon occurs in the proton NMR spectra of platinum metal complexes of triphenyl-phosphine, -arsine, and -stibine and provides a convenient method for differentiating between *cis* and *trans* EPh_3 (E = P, As or Sb) ligand pairs. As a consequence of this it is also possible to distinguish between *fac* and *mer* ligand arrangements.

The proton nmr spectra (60 or 90 MHz) of triphenyl-phosphine, -arsine, or -stibine complexes taken in CD_2Cl_2 or $CDCl_3$ solution display an *ortho–meta/para* chemical shift difference ranging from a slight broadening of the phenyl envelope, to a clearly resolved separation of the *ortho* and *meta/para* proton resonances. In these solvents the chemical shift separations tend to be small (<0.5 ppm) and show little or no apparent correlation with coordination geometry.

However, when the same complexes are examined in C_6D_6 solution the phenyl signals for a given ligand are clearly resolved into two complex resonances – relative intensity 2:3 – attributable to *ortho* and *meta/para* protons respectively. The *ortho* resonances occur at lower field [2]. Furthermore, the magnitude of the separation between the centres of these two resonances is dependent on the coordination geometry of the complex concerned. For a *trans* pair of EPh_3 ligands the separation is >0.5 ppm (typically 0.6–1.0 ppm), whereas for a *cis* pair the separation is <0.5 ppm (typically 0.2–0.4 ppm). Similarly, *fac* arrangements, in which all three EPh_3 ligands are mutually *cis*, show a small separation (<0.5 ppm). In contrast, *mer* EPh_3 arrangements in which two of the ligands are mutually *trans*, and the other ligand is *cis* to this pair show resonance patterns containing a large (>0.5 ppm) *trans* pair separation (relative intensity:2), and also a small (<0.5 ppm) *cis* ligand separation (relative intensity:1); the *meta/para* resonances of the EPh_3 ligands are co-incidental.

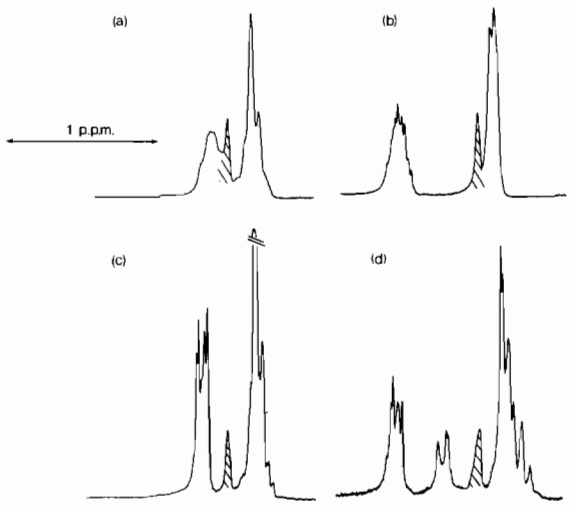

Fig. 1. Aromatic proton resonances for: (a), $[Ru(O_2CCF_3)_2(CO)(PPh_3)_2]$ (*cis*-PPh_3 ligands); (b) $[RuH(O_2CCF_3)(CO)(PPh_3)_2]$ (*trans*-PPh_3 ligands); (c) [*fac*-$IrH_3(AsPh_3)_3$], and (d) [*mer*-$IrCl_3(AsPh_3)_3$] taken at MHz in deuterobenzene. The shaded resonance is due to residual benzene in the deuterated solvent.

The size of the separation, as measured for *ca.* sixty platinum metal complexes, appears to be remarkably irresponsive to changes in the identity of the central metal atom, its oxidation state, and the nature of the auxillary ligands. Moreover, the relationship between stereochemical arrangements of the EPh_3 ligands and the chemical shift separation, appears to hold for square planar, trigonal bipyramidal, square pyramidal, and octahedral coordination arrangements.

Spectra illustrating application of the technique to: $[Ru(O_2CCF_3)_2(CO)(PPh_3)_2]$ (*cis*-PPh_3), $[RuH(O_2CCF_3)(CO)(PPh_3)_2]$ (*trans*-PPh_3), *fac*$[IrH_3(AsPh_3)_3]$, and *mer*-$[IrCl_3(AsPh_3)_3]$ are given in Fig. 1.

When the ancillary ligands include one or more hydride entities. the proton NMR distinction between *cis* and *trans* pairs of EPh_3 ligands becomes less pronounced (*ortho–meta/para* separations of *ca.* 0.4 and 0.6 ppm respectively). This behaviour may reflect the large *trans*-influence of the hydride ligand [3] (*vide infra*). However, the disparate size of

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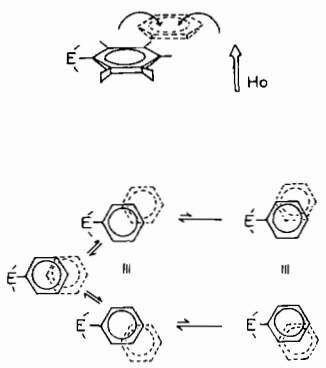

Fig. 2. Idealised solvent–solute interaction in benzene/EPh_3 solutions.

hydride and EPh_3 ligands is known to result in coordination geometry irregularities [4] which cause *cis* and *trans* ligand pairs to be less clearly delineated and could thus be expected to produce anomalies in the *ortho–meta/para* resonance separations.

The phenomenon noted above can be rationalised in terms of a solvation effect arising from the geometry and magnetic anisotropy of benzene. In non-aromatic solvents, *i.e.* $CDCl_3$ or CD_2Cl_2, resonances due to *o*, *m* and *p* phenyl protons show a typical aryl proton distribution with small chemical shift differences due to mesomeric and inductive effects in the phenyl ring. The overall result is the absence of any clearly established trend in *o*, *m*, or *p* proton resonance positions for the range of EPh_3 complexes examined, and no discernible correlation between *ortho–meta/para* resonance separation and molecular structure or geometry.

In contrast benzene, by virtue of its planar, aromatic nature, is capable of interacting with EPh_3 derivatives by partially interleaving the phenyl rings and thus preferentially shielding the *meta* and particularly the *para* protons while deshielding the *ortho* protons (Fig. 2). The degree of interaction between the benzene solvent and the phenyl rings of the solute will depend upon the ability of the solute to attract and retain the interleaving benzene molecules by dipole–induced dipole attractions [5]. Thus more polar species such as Ph_3EO and Ph_3ES interact more strongly with benzene solvent than do less polar species such as Ph_3E, and thus produce a larger *ortho–meta/para* resonance separation. In transition metal complexes the high *trans*-influence of the Ph_3E ligands leads to lengthening and an increase in dipole moment for the M–EPh_3 bonds in *trans*-complexes relative to those in the corresponding *cis*-isomers [6]. Consequently benzene solvates the Ph_3E ligands in *trans*-complexes more strongly than those of their *cis*-isomers and thus produces a much larger *ortho–meta/para* splitting in the former than in the latter.

The technique is of particular value for determination of stereochemistry in high symmetry complexes containing triphenylphosphine ligands [*i.e. cis*- or *trans*-$MX_2(PPh_3)_2$] which display no phosphorus–phosphorus couplings, and in triphenyl arsine complexes where ^{31}P NMR is not applicable.

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