Trans-influences Operating across a Binuclear Metal Centre.

A ^{31}P NMR Study of the Mixed Adducts $\{(CH_3O)_3P\}$-$Rh(O_2CCH_3)_4RhL$

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Since their discovery in 1960, rhodium(II) carboxylates $[Rh_2(O_2CR)_4]$ and their axial adducts $[Rh_2(O_2CR)_4L_2]$ have been the subject of much controversy concerning the nature of the axial Rh–Rh and Rh–L bonds [1]. More recently attention has directed to the study of *trans*-influences operating along the L–Rh–Rh–L axis. The unusually long axial Rh–L linkages – *ca.* 0.1 to 0.2 Å longer than those found in comparable mononuclear rhodium(I) or rhodium(III) complexes – have been attributed to the high *trans*-influence of the Rh–Rh bond. Conversely the sensitivity of the Rh–Rh bond length to the nature of the axial ligands L is thought to be due to variations in the *trans* influence of the latter, although the changes in this case are less marked possibly because of the inherent shortness of the Rh–Rh bond and the constraining effect of the carboxylate cage [2]. However, no attempt has been made to assess *trans*-influence interactions operating across the binuclear Rh_2^{II} centre between dissimilar ligands in mixed adducts of the form $LRh(O_2CR)_4RhL'$. Indeed to the best of our knowledge no investigation of *trans* influences extending across a binuclear metal centre has ever been reported. We have now used an NMR technique, similar in principle to those employed in the study of *trans*-influences within mononuclear complexes [3], to assess *trans* influences operating in mixed adducts of rhodium(II) acetate $\{(CH_3O)_3P\}Rh(O_2CCH_3)_4RhL$, using $P(OCH_3)_3$ as the indicator ligand.

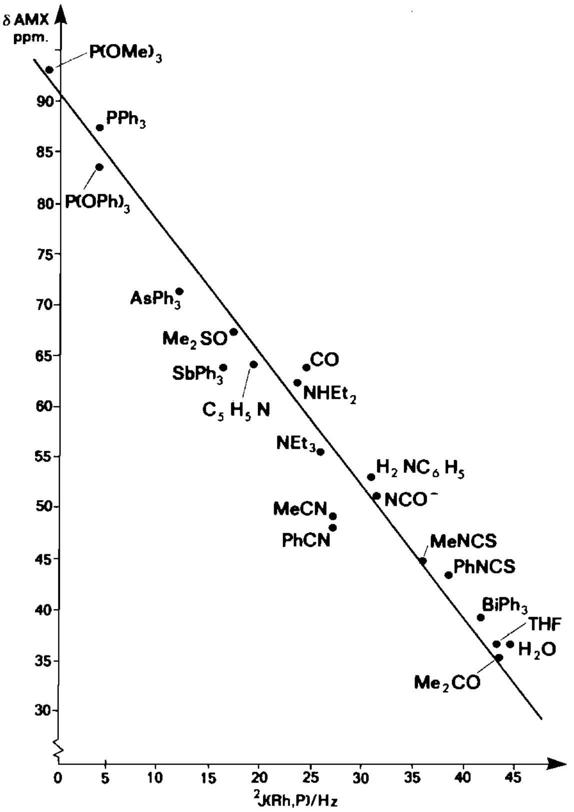

Fig. 1. Graph of the P chemical shift δ AMX of $\{(CH_3O)_3P\}$-$Rh(O_2CCH_3)_4RhL$ (ppm) against $^2J(^{103}Rh, ^{31}P)$ (Hz).

In a recent communication [4] we reported that the low temperature (213 K) $^{31}P\{^1H\}$ NMR spectra of '$Rh_2(O_2CCH_3)_4\{P(OCH_3)_3\}_2$' in CD_2Cl_2 solution showed the presence of the mono-adduct $Rh_2(O_2CCH_3)_4\{P(OCH_3)_3\}$ (X part of AMX pattern, δ_p 36.7 ppm) and the bis-adduct $[Rh_2(O_2CCH_3)_4\{P(OCH_3)_3\}_2]$ (XX′ part of an AA′XX′ pattern, δ_p = 93.5 ppm) (A, A′ and M = Rh, X, X′ = P). The large chemical shift difference (*ca.* 60 ppm) between the ^{31}P NMR signals of the two species pointed to the operation of a strong *trans*-influence across the binuclear Rh_2^{II} centre. To investigate this phenomenon more fully we have prepared in solution a series of mixed adducts $\{(CH_3O)_3P\}Rh(O_2CCH_3)_4RhL$ and have recorded their low-temperature $^{31}P\{^1H\}$ NMR spectra. The results of these experiments clearly establish the presence of a strong *trans*-influence operating between $P(OCH_3)_3$ and L ligands along the Rh_2^{II} axis.

The mixed adducts $\{(CH_3O)_3P\}Rh(O_2CCH_3)_4RhL$ were prepared in solution by mixing the complex $Rh_2(O_2CCH_3)_4$, the bis(trimethyl phosphite) adduct $Rh_2(O_2CCH_3)_4\{P(OCH_3)_3\}_2$ and the free ligand **L** in the NMR solvent (CD_2Cl_2). The solutions were then cooled to 213 K and the $^{31}P\{^1H\}$ NMR spectra were recorded. In each case the spectrum consisted of the XX′ portion of an AA′XX′ pattern attributable to the bis adduct $Rh_2(O_2CCH_3)_4\{P(OCH_3)_3\}_2$ and the X part of an AMX pattern arising from the mixed adduct $\{(CH_3O)_3P\}Rh(O_2CCH_3)_4RhL$. Using this technique spectra have been recorded for *ca.* 30 mixed adducts involving P*, As, Sb, Bi, N and O donor ligands. A plot of the ^{31}P NMR chemical shift of the mixed adducts (δ_{AMX}) *versus* the

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coupling constant ${}^2J({}^{103}Rh^{31}P)$ gives a good straight line graph (see Fig. 1); the ordering of the points on this line corresponds to a *trans*-influence series for the ligands L. The sequence of the ligands in order of decreasing *trans*-influence – $P(OCH_3)_3 > P(OPh)_3 \approx PPh_3 > AsPh_3 > SbPh_3 \approx py > NH(C_2H_5)_2 > N(C_2H_5)_3 > C_6H_5NH_2 > NCO^- > CH_3CN \approx PhCN > CH_3NCS > PhNCS > BiPh_3 > H_2O \approx (CH_3)_2CO \approx$ THF – is very similar to that found for several other series of complexes where σ-bonding effects are thought to be dominant [5, 6].

Data for adducts containing S-donor ligands also generate points which lie on the straight line plot. However, since the values of δ_{AMX} and ${}^2J$ (${}^{103}Rh^{31}P$) recorded for these complexes span wide ranges (*ca.* 30 ppm and 20 Hz respectively), the S-donor ligands involved do not appear as a coherent group in our *trans*-influence series. It is possible that the large differences in *trans*-influence displayed by the different S-donor ligands reflect variations in steric-hindrance (${}^tBu_2S$ *vs.* C_4H_8S) and sulphur oxidation state or hybridisation [$(CH_3)_2SO$ *vs.* CS_2]. Measurements on a more extensive series of S-donor adducts designed to throw further light on this problem are in progress.

There is also an approximately linear correlation between the magnitudes of the δ_{AMX} values obtained for the various $(CH_3O)_3P/L$ adducts and the Rh–Rh bond distances found for the corresponding bis adducts $Rh_2(O_2CCH_3)_4L_2$ where these are known. However, the significance of this correlation will only be fully tested when more structural data become available.

The coupling ${}^1J({}^{103}Rh^{31}P)$ involves the rhodium atom most remote from the ligand L and is thus least affected by changes in the nature of that ligand. There is some evidence of a linear correlation between ${}^1J(RhP)$ and ${}^2J(RhP)$, however in view of the small range of values (*ca.* 16 Hz) found for the former parameter little significance can be placed on this result. The appearance of only one anionic ligand (NCO^-) in our *trans*-influence series reflects problems encountered in trying to find an nmr solvent capable of maintaining the salts $M[XRh(O_2CCH_3)_4Rh\{P(OCH_3)\}]$ in solution at low temperatures. Attempts to resolve this problem are in progress.

References

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*Spectra obtained when L = P donor ligand are more complex but yield the same information on analysis.