Anomalous ^{1}H Nuclear Magnetic Resonance Spectra of New Osmium Complexes

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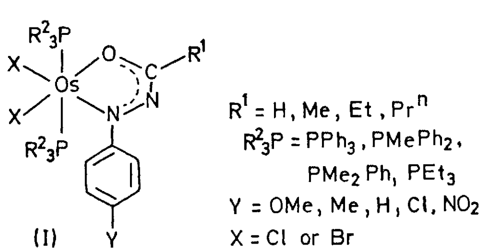
Summary The ^{1}H n.m.r. spectra of some apparently diamagnetic osmium acylaryldiazene complexes show shifts of a magnitude and pattern characteristic of paramagnetic complexes; but the shifts are restricted to only certain protons of the diazene ligand.

We report that the ^{1}H n.m.r. spectra of some apparently diamagnetic osmium complexes of structure (I) show chemical shifts of a magnitude only normally encountered for complexes with first or second order paramagnetism.[1,2] Moreover, these shifts are restricted to certain protons of only one of the ligands, the protons of the other ligands showing no abnormal shifts. This is in contrast to the sharp line spectra of paramagnetic complexes, where protons of all the ligands usually show pronounced shifts.

Shifts ($\Delta\tau$), relative to the corresponding hydrazine, PhNHNHCOR, of up to 10·3 τ are observed for certain protons of the alkyl group R^1. When $R^1 = Y = H$, (in I) the formyl proton is scarcely shifted ($\Delta\tau = 0{\cdot}95\,\tau$) and for $R^1 = Et$ or Pr^n and Y = H only the methylene protons adjacent to the chelate ligand show marked shifts ($\Delta\tau = 4{\cdot}25$ and $5{\cdot}17\,\tau$ respectively). The magnitude for the shifts is highly dependent on the nature of Y (*e.g.* when $R^1 = Me$ and $PR^2_3 = PPh_3$, for $Y = p\mathrm{NO_2}$, $\Delta\tau = 10{\cdot}3\,\tau$ and for Y = *p*-MeO, $\Delta\tau = 4{\cdot}21\tau$) and to a lesser extent on the tertiary phosphine and halogen ligands. Plots of τ values *versus* Hammet σ-constants for Y give straight lines for the R^1 group protons and for the *ortho*- and *meta*-protons of the C_6H_4Y group, suggesting a high degree of delocalisation.



(I)

In view of these large shifts it is surprising that the ^1H n.m.r. spectra of the tertiary phosphine ligands occur around 8·2 τ in the normal region for diamagnetic osmium complexes.[3] They show 1:2:1 triplets for the complexes (I; $R^1 = Me$, $PR^2_3 = PPh_2Me$, X = Cl, Y = H and (I; $R^1 = CH_2Ph$, $PR^2_3 = PPh_2Me$, X = Cl, Y = H) confirming the *trans*-configuration shown in the Figure. The ^{31}P n.m.r. spectra of the latter complex and of (I; $R^1 = CH_2Ph$, $PR_3{}^2 = PPhMe_2$, X = Cl, Y = H) show singlets at δ + 153·6 and 157·6 respectively (from P_4O_6) as expected for two essentially equivalent phosphorus atoms.

The anomalous ^1H n.m.r. spectra do not seem to be an intrinsic property of this diazene type of ligand, as the spectra of PhCO–N=N–Ph and $[MoCl_2(NPh)(PhCON_2Ph')(PMe_2Ph)]$ show no abnormalities, whereas the spectrum of $[OsCl_2(PhCON_2Ph')(PPh_3)_2]$ shows absorptions by the *ortho*-protons of Ph′ as a doublet centred at 6·35 τ and the *para*-protons as a triplet centred at 9·22 τ.

The alternation in the sign of shift observed for the C_6H_4Y group protons and the straight line obtained for plots of chemical shifts *versus* temperature are consistent with a paramagnetic origin for the shifts. However, the complexes are diamagnetic at 300 and 80 K, and the only observable e.s.r. signals in the temperature range 20—300 K are *ca.* 10^4 weaker than those of other paramagnetic complexes. A possible explanation for this apparent contradiction is that the shifts, and their localisation, result from the mixing-in of a paramagnetic state, localised on the chelate ligand, with a diamagnetic ground state, the resulting unpaired electron density being too low to detect by conventional bulk susceptibility methods. But since the evidence of a paramagnetic basis for the shifts is indirect, the possibility of a purely diamagnetic origin cannot be entirely ignored.

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[3] J. Chatt, D. P. Melville, and R. L. Richards, *J. Chem. Soc.* (*A*), 1971, 1169.