Dynamic Equilibria Involving 1,3-Diaryltriazenido Derivatives of Rhodium(I), Palladium(II), and Platinum(II)

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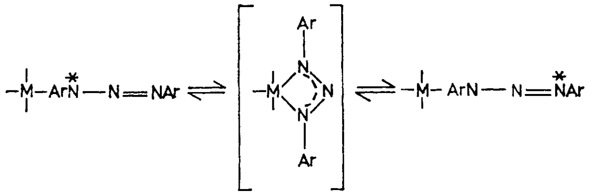
Summary Variable temperature n.m.r. studies on some 1,3-diaryltriazenido derivatives of square planar rhodium(I), palladium(II), and platinum(II) reveal the occurrence of dynamic equilibria involving monodentate 1,3-diaryltriazenido ligands.

IN a previous communication[1] we reported the synthesis and characterisation of monodentate 1,3-diaryltriazenido derivatives of the platinum metals. Variable temperature n.m.r. studies, performed on these complexes in $CDCl_3$ solution, now reveal the occurrence of dynamic equilibria involving co-ordinated monodentate 1,3-diaryltriazenido groups [equation (1)]. The ability of many organic ligands, including the closely related σ-allyl group, to participate in dynamic equilibria is fully established and numerous examples have been reported;[2] however the present work is the first instance of this behaviour occurring with catenated nitrogen ligands.



(1)

The n.m.r. signal (*ca.* τ 7·8) arising from the *p*-methyl protons of the monodentate 1,3-di-p-tolyltriazenido derivative, $[Pt(MeC_6H_4N \mathrel{\underset{\cdots}{-}} N \mathrel{\underset{\cdots}{-}} NC_6H_4Me)_2(PPh_3)_2]$, displays temperature dependent behaviour (Figure) typical of these systems. Other monodentate 1,3-diaryltriazenido derivatives which exhibit similar spectra are, $Pt(dat)_2(PPh_3)_2$, $PtCl(dat)(PPh_3)_2$, $Pt(dat)_2(diphos)$, $Pd(dat)_2(PPh_3)_2$ and $Rh(dat)(CO)(PPh_3)_2$† [dat = di-*p*-tolyl-, di-*p*-anisyl-, or *p*-tolyl-*p*-anisyltriazenido anion; diphos = $Ph_2P(CH_2)_3PPh_2$]. Data from preliminary kinetic studies indicate that the exchange processes are first order and that their activation energies, which decrease in the order $Pt^{II} > Pd^{II} > Rh^{I}$, are less than 12 kcal mol^{-1}. N.m.r. spectra taken for $CDCl_3$ solutions, each containing two different triazenido complexes, indicate that intermolecular triazenido ligand transfer occurs slowly, taking several hours to reach equilibrium at 25 °C. These results suggest that the exchange processes proceed *via* five-co-ordinate intermediates of the type illustrated above; they do not support alternative mechanisms involving binuclear species. Detailed kinetic studies are in progress.

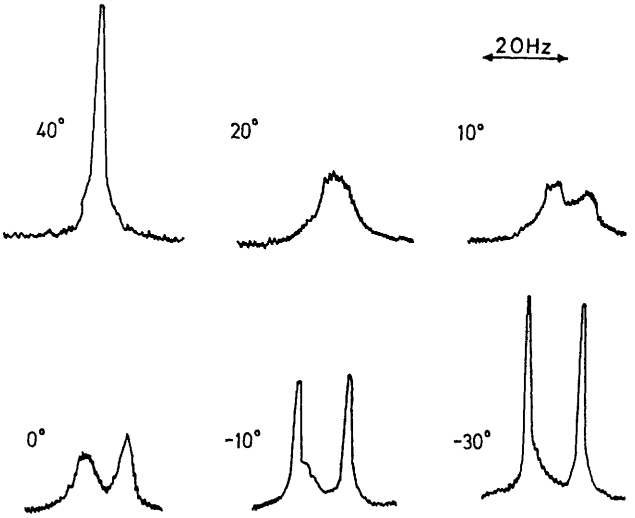


FIGURE *N.m.r. temperature dependence of the* p-*methyl protons of* $Pt(MeC_6H_4N \mathrel{\underset{\cdots}{-}} N \mathrel{\underset{\cdots}{-}} NC_6H_4Me)_2(PPh_3)_2$, 1 cm = 20 Hz.

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† The decoalescence temperatures for the very labile rhodium derivatives lie below the limit (−90 °C) of our equipment; however, clear evidence of line broadening in spectra of CS_2 solutions at low temperatures was apparent.

[1] S. D. Robinson and M. F. Uttley, *Chem. Comm.*, 1971, 1315.

[2] K. Vrieze and P. W. N. M. van Leeuwen, *Progr. Inorg. Chem.*, **1971**, **14**, 1.