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Preliminary communication

Relative donor properties of *sp*^{3} and *sp*^{2} hybridised phosphorus atoms of the azadiphosphetine ring system $\overline{\mathrm{RP(NR')P{=}C}}\mathrm{R'}$ ($\mathrm{R = Et_3C, R' = Bu^t}$) towards transition metals

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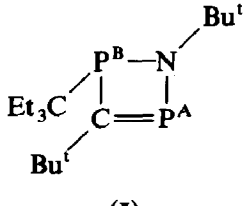
Abstract

Different types of ligating behaviour of the $\overline{\mathrm{RP(NR')P{=}C}}\mathrm{R'}$ ring system are reported; the *sp*^{2} hybridised phosphorus is the donor atom in Pt(0), W(0) and Rh(I) complexes, whereas ligation of the *sp*^{3} hybridised phosphorus atom is preferred by Pd(II), and both phosphorus atoms are ligated in dinuclear Pt(II) systems.

Tertiary phosphines containing *sp*^{3} hybridised phosphorus have been widely used in studies of the coordination and organometallic chemistry of transition metals. More recently a variety of compounds containing *sp* and *sp*^{2} hybridised phosphorus, typified by phospha-alkynes ($\mathrm{RC{\equiv}P}$) and phospha-alkenes ($\mathrm{R_2C{=}PR}$) have been synthesised, and both η^1- and η^2-ligating modes have been reported [1].

The recent synthesis of the cyclic species $\overline{\mathrm{RP(NR')P{=}C}}\mathrm{R'}$ ($\mathrm{R = Et_3C, R' = Bu^t}$) by Niecke and Barion [2] offers an interesting opportunity of studying the relative donor properties of *sp*^{2} and *sp*^{3} hybridised phosphorus atoms within the same molecule.



(I)

Since ligating modes of types (i)–(iii) towards a transition metal centre can be envisaged, we sought evidence that the preferred interaction might depend on the

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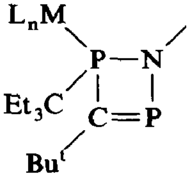
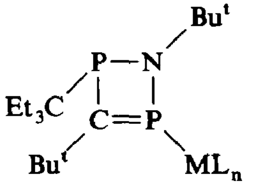
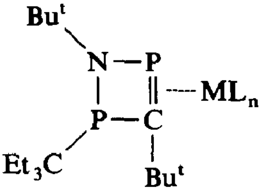
electronic nature of the $[ML_n]$ fragment.



(i)

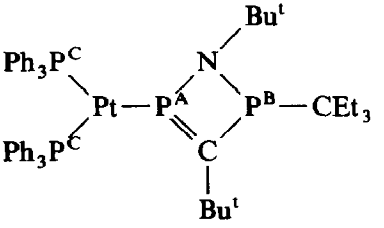


(ii)



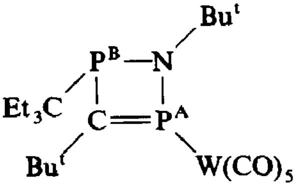
(iii)

Treatment of **I** with $[Pt(PPh_3)_2(C_2H_4)]$ in toluene at room temperature readily affords the cream-coloured complex $[Pt(PPh_3)_2(\overline{PR(NR')P{=}CR'})]$ (**II**), in which the azadiphosphetine ring is η^1-ligated to platinum through the sp^2 hybridised phosphorus atom, as evidenced by its characteristic $^{31}P\{^1H\}$ and ^{195}Pt NMR spectra *. The observation of a single resonance for the two P^C nuclei (and the resulting triplet pattern pattern for P^A) shows that either the plane of the azadiphosphetine ring lies perpendicular to that containing Pt and the two PPh_3 ligands or there is rapid rotation around the $Pt{-}P^A$ bond. The large $^1J_{PtP^A}$ coupling constant (4683 Hz) rules out the possibility of any η^2-ligation of the P=C bond to the metal in solution.

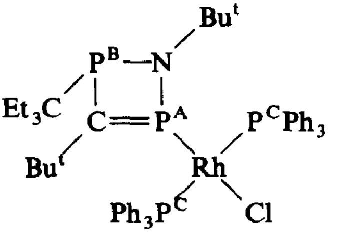


(II)

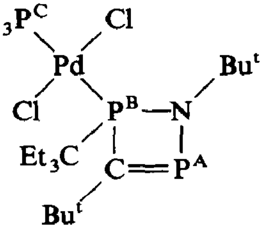
Similarly, treatment of **I** with $[W(CO)_5THF]$ gives $[W(CO)_5(\overline{PR(NR')P = CR'})]$ (**III**) (ν(C≡O): 2100m, 2060w, 1990m, 1950s cm^{-1}), which displays a similar η^1-ligating mode of the ring as in **II** *. One equivalent of **I** readily reacts with $[RhCl(PPh_3)_3]$ in CH_2Cl_2 to give the yellow complex *trans*-$[RhCl(PPh_3)_2(\overline{PR(NR')P = CR'})]$ (**IV**), in which the ring is η^1-ligated to rhodium via the sp^2 hybridised phosphorus, as evidenced by the characteristic $^{31}P\{^1H\}$ NMR spectrum *.



(III)



(IV)



(V)

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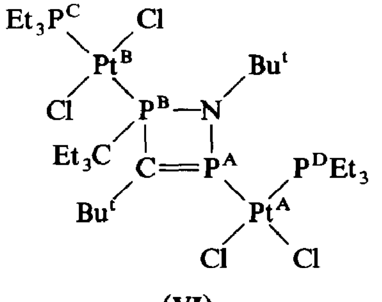
* ^{31}P NMR data (in ppm relative to H_3PO_4): for **II**: δ_{P^A} 319.0, δ_{P^B} 131.6, δ_{P^C} 48.6; $^1J_{Pt^A}$ 4683, $^1J_{PtP^C}$ 4380, $^2J_{P^AP^B}$ 44 $^2J_{P^BP^C}$ 152 Hz; for **III**: δ_{P^A} 257.6, δ_{P^B} 141.0; $^1J_{WP^A}$ 254, $^2J_{P^AP^B}$ 57 Hz; for **IV**: δ_{P^A} 260.3, δ_{P^B} 109.8, δ_{P^C} 30.5; $^1J_{RhP^A}$ 210, $^1J_{RhP^C}$ 137, $^2J_{P^AP^B}$ 64, $^2J_{P^AP^C}$ 122 Hz; for **V**: δ_{P^A} 339.8, δ_{P^B} 144.5, δ_{P^C} 29.8; $^2J_{P^BP^C}$ 537 Hz; for **VI**: δ_{P^A} 204.0, δ_{P^B} 122.6, δ_{P^C} 14.5, δ_{P^D} 9.6; $^1J_{Pt^AP^D}$ 3208, $^1J_{Pt^AP^B}$ 127, $^1J_{Pt^AP^D}$ 3208, $^1J_{Pt^BP^B}$ 2346, $^1J_{Pt^BP^C}$ 2581, $^2J_{P^AP^B}$ 28, $^2J_{P^AP^D}$ 18, $^2J_{P^BP^C}$ 468, $^4J_{P^DP^A}$ 18 Hz. ^{195}Pt NMR data (in ppm relative to K_2PtCl_4): for **II**: δ_{Pt} -3047.7; $^1J_{PtP^C}$ 4383, $^1J_{PtP^A}$ 4684 Hz; for **VI** δ_{Pt^A} -2483.6, δ_{Pt^B} -2233.5; $^1J_{Pt^AP^A}$ 4196, $^1J_{Pt^BP^B}$ 2375, $^1J_{Pt^AP^D}$ 3201, $^1J_{Pt^BP^C}$ 2578, $^3J_{Pt^AP^B}$ 128, $^3J_{Pt^AP^A}$ 108 Hz.

In contrast to the above observations, the reaction of two equivalents of **I** with $[Pd_2Cl_4(PEt_3)_2]$ in CH_2Cl_2 gives **V**, in which the ring is attached to the palladium(II) through the sp^3 hybridised phosphorus *. The large $^2J_{P^BP^C}$ coupling constant (537 Hz) is consistent with P^B and P^C being in mutually *trans* positions.

A similar reaction of **I** with $[Pt_2Cl_4(PEt_3)_2]$ in CH_2Cl_2 gives the complex $[Pt_2Cl_4(PEt_3)_2(\overline{PR(NR')P{=}CR'})]$ (**VI**), in which both phosphorus atoms of the ring are ligated to platinum(II). It seems likely that the reaction proceeds via an intermediate similar to (**V**).

Interestingly, the NMR data on **VI** clearly show that one PEt_3 ligand is *trans* to the sp^3 hybridised phosphorus of the ring whereas the other is *cis* to the sp^2 hybridised phosphorus.



(VI)

The differing ligating behaviour of the two types of phosphorus in the azadiphosphetine ring system can be understood in terms of the preference of the "softer" metal centre for interaction with the phosphorus lone-pair orbital having the greatest degree of *s*-character **.

Interestingly, no evidence has been yet obtained for η^2-ligation of the P=C bond as in iii, but it is well known from studies on certain phospha-alkene complexes of Pt(0) that there is only a small energy difference between η^1- and η^2-ligating modes, and for example a change of phase is sufficient to cause a transformation from η^1- to η^2-ligation in the case of $[Pt(PPh_3)_2(Ph_2C{=}P(mesityl))]$ [5,6]. It may be possible to observe type-iii bonding in complexes similar to **I** but with different substituents on Pt(0).

Acknowledgements. We thank the SERC for their continuing support for the work, the Brazilian Government and (CNPq) for financial support (for RM and BFTP), and Johnson Matthey PLC for the loan of platinum metal salts.

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** This would be in line with known differences between "hard" NR_3 and "soft" PR_3 ligands for which the smaller bond angles at phosphorus imply a larger *s*-character, in the P lone-pair orbital. Likewise, PF_3 can be regarded as the "softest" of the PX_3 ligands because the electronegative fluorine substituents induce the greatest degree of *s*-character into the P lone-pair orbital [3]. Accordingly PF_3 and its derivatives form a particularly wide range of complexes with transition metals in low oxidation states, i.e. with "soft" metal centres [4].

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