

Reaction of *P*-Halogeno-phospha-alkenes with Alkene Complexes of Nickel and Platinum: η^2 -Co-ordination and Unusual Oxidative Addition Behaviour

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Phospha-alkenes $X-P=CTMS_2$ ($X = F, Cl, I$; $TMS = SiMe_3$) display different reaction behaviour towards metal complexes $(Bu_3P)_2Ni(cod)$ ($cod = cyclo-octa-1,5-diene$) or $(Ph_3P)_2Pt(C_2H_4)$, respectively, undergoing either co-ordination to give η^2 -phospha-alkene complexes or alternatively oxidative addition of the $P-X$ bond, forming phospha-alkenyl-metal(II) complexes, $[(R_3P)_2M(X)(\sigma-P=CTMS_2)]$.

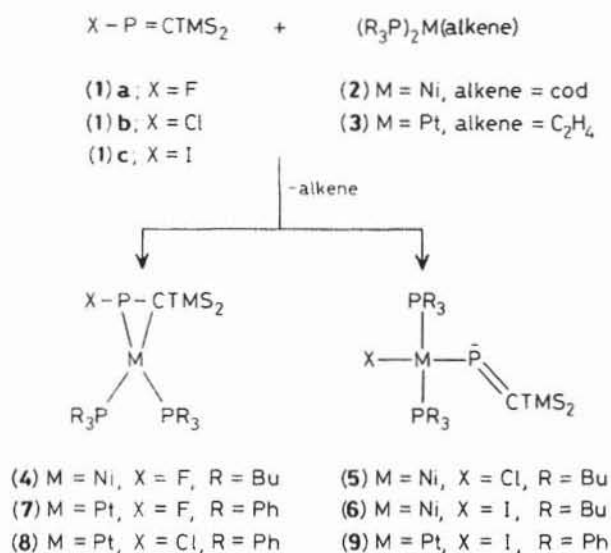
Phospha-alkenes react with a wide variety of transition metal compounds *via* ligand exchange to give complexes in which the phospha-alkenes may act as 2e- or 4e-donors and bonding of the ligand to the metal centre can occur through the phosphorus lone pair (η^1 -co-ordination), the π -electrons of

the double bond (η^2 -co-ordination), or a combination of both.¹ A different type of interaction, however, was observed during the reaction of $Me_5C_5-P=C(SiMe_3)_2$ with complexes of type $[L_3M(CO)_3]$ ($M = Mo, W$; $L = MeCN$)² or $[(R_3P)Ni(alkene)_2]$,³ which proceeded *via* oxidative addition of the

Table 1. $^{31}\text{P}\{^1\text{H}\}$ and ^{19}F n.m.r. data of complexes $[(\eta^2\text{-X-P}=\text{CTMS}_2)\text{M}(\text{P}_{a,b}\text{R}_3)_2]$ and $[(\text{P}_{a,b}\text{R}_3)_2\text{M}(\text{X})(\sigma\text{-P}_x=\text{CTMS}_2)]$ (4–9).

| | $\delta^{31}\text{P}^a$ | $^1J_{\text{Pt,P}}^b$ | $^2J_{\text{P,P}}^b$ | $\delta^{19}\text{F}^a$ | $^nJ_{\text{P,F}}^b$ |
|-----|--|-----------------------|--|-------------------------|--|
| (4) | 227.9 P_m 8.5 P_a 5.6 P_b | | 21.8 $J_{m,a}$ 24.0 $J_{m,b}$ 21.3 $J_{a,b}$ | -176.8 | 872 $J_{\text{F,Pm}}$ 2.2 $J_{\text{F,Pa}}$ 11.6 $J_{\text{F,Pb}}$ |
| (5) | 663.4 P_x -0.6 P_a | | 12.6 | | |
| (6) | 645.4 P_x 0.2 P_a | | 6.5 | | |
| (7) | 184.3 P_m 23.2 P_a 25.3 P_b | 446 3879 3145 | 8.0 $J_{m,a}$ 39 $J_{m,b}$ 20 $J_{a,b}$ | -166.3 ^c | 907 $J_{\text{F,Pm}}$ 14 $J_{\text{F,Pb}}$ |
| (8) | 128.6 P_m 19.5 P_a 23.0 P_b | 432 3772 3311 | 6 $J_{m,a}$ 40 $J_{m,b}$ 15 $J_{a,b}$ | | |
| (9) | 585.0 P_x 16.2 P_a | 98 3404 | 3.6 | | |

^a In p.p.m. ^b In Hz. ^c $^2J_{\text{Pt,F}}$ 104 Hz.



metal at the P-C(C_5Me_5) single bond. The $\eta^5\text{-Me}_5\text{C}_5\text{-metal}$ complexes thus formed contain a phosphorus-metal σ -bond and a phospho-alkenyl fragment acting as either a $1e^-$ or $3e^-$ donor.² By analogy, generation of transition metal complexes containing iminophosphanyl³ or diphosphenyl ligands⁴ has been reported, starting from Me_5C_5 -substituted iminophosphane and diphosphene precursors.

We explored whether this type of oxidative addition was limited to Me_5C_5 -substituted phosphorus p - π -systems, or whether it might be extended to other systems containing reactive P-X single bonds. Since P-halogen bonds in phosphoalkenes are readily cleaved by organic⁵ and organometallic nucleophiles^{6,7} with substitution at phosphorus and retention of the double bond, we investigated the reactivity of derivatives $\text{X-P}=\text{C}(\text{SiMe}_3)_2$ [X = F (1a),⁸ Cl (1b),⁹ I (1c)]⁸ with d^{10} -metal-alkene complexes, $(\text{Bu}_3\text{P})_2\text{Ni}(\text{cod})$, (2), and $(\text{Ph}_3\text{P})_2\text{Pt}(\text{C}_2\text{H}_4)$, (3).

Treatment of $[\text{H}_6]$ -benzene solutions of (2) or (3) at ambient temperature with 1 equiv. of (1a–c) immediately produced yellow to deep red coloured solutions. ^1H and ^{31}P n.m.r. spectroscopic analyses confirmed the selective formation of complexes (4–9) (Figure 1), and ethylene or cyclo-

octa-1,5-diene as the only spectroscopically detectable by-products. The Pt complexes (7–9) were isolated as cream to orange coloured microcrystalline solids, following treatment of conc. solutions with hexane. After several hours, solutions of (4) displayed additional n.m.r. signals arising from decomposition, and no pure product could be isolated. Compounds (5) and (6) were found to be stable in solution for several hours in the presence of cyclo-octa-1,5-diene, enabling n.m.r. spectroscopic characterization. Attempts to remove the solvent and excess alkene *in vacuo*, however, led to decomposition and formation of $[\text{NiX}_2(\text{PBu}_3)_2]$ together with other, as yet unidentified products.

Structural formulation of compounds (4–9) was made on the basis of their $^{31}\text{P}\{^1\text{H}\}$ n.m.r. data (Table 1). For (4), (7) and (8), ABM or ABMX type spectra were observed (A, B, M = ^{31}P ; X = ^{19}F), which for the phospho-alkene resonance showed the considerable co-ordination shift^{1,10} and small magnitude of $^1J_{\text{Pt,P}}$ ¹¹ expected for bis(*t*-phosphine) (η^2 -phospho-alkene)metal(0) complexes. The value of $^1J_{\text{P,F}}$ in (4, 7) shows a marked decrease with respect to free ligand ($^1J_{\text{P,F}}$ 1087 Hz⁸) or the η^1 -complex $[(\text{Ph}_3\text{P})_2\text{RhCl}(\eta^1\text{-F-P}=\text{CR}_2)]$ ($^1J_{\text{P,F}}$ 1127 Hz¹²), suggesting a decrease in *s*-character for the P-F bond as a consequence of the η^2 -co-ordination. $^{31}\text{P}\{^1\text{H}\}$ N.m.r. spectra of (5), (6) and (9) exhibit two multiplets of an AX₂ system with the chemical shift of the X-part (δ 584–663 p.p.m.) in the downfield region which is characteristic of transition metal substituted phosphorus p - π -systems.^{2–4,6,7} The observed equivalence of the phosphine ligands together with the comparatively small value of $^2J_{\text{P}_A\text{P}_X}$ suggests their formulation as *trans*-bis(*t*-phosphine) (σ -phospho-alkenyl)-halogenometal(II) complexes. The phospho-alkenyl ligand in (9) exhibits an unusually low value (98 Hz) for $^1J_{\text{Pt,P}}$, which is however in accord with the small magnitude of $^1J_{\text{M,P}}$ in other systems containing phosphorus-metal single bonds.^{3,13} In the $^{13}\text{C}\{^1\text{H}\}$ n.m.r. spectra of (5), (6) and (9) the presence of a P=C double bond is indicated by a characteristic downfield multiplet [(5) δ 188.7 ($^1J_{\text{P,C}}$ 105 Hz); (6) δ 183.9 ($^1J_{\text{P,C}}$ 104 Hz); (9) δ 180.6 ($^1J_{\text{P,C}}$ 106 Hz)].^{2,3,8} These findings are consistent with the presence of bent phospho-alkenyl ligands acting as $1e^-$ donors,^{2,3} the observed equivalence of the Me_3Si resonances at ambient temperature[†] being a dynamic phenomenon caused by a rapid isomerization of the double bond.²

[†] Selected $^{13}\text{C}\{^1\text{H}\}$ -n.m.r. data (20.0 MHz, ext. TMS): (5) (20°C, $[\text{H}_6]$ -benzene) δ 3.1 (m, SiC_3); (-50°C, $[\text{H}_6]$ -toluene) δ 3.4 (m, SiC_3) and 2.7 (d, SiC_3).

Our findings indicate that the reactivity of phospho-alkenes (**1a–c**) towards transition metals is determined by a delicate balance of different factors.

The presence of a P–X bond of high bond energy (E) in (**1a**) [$E(\text{P–F})$ 490 kJ mol⁻¹¹⁴] favours η^2 -co-ordination with retention of the P–X bond, whereas in the case of a weaker bond in (**1c**) [$E(\text{P–I})$ 184 kJ mol⁻¹¹⁴] the oxidative addition is preferred. Compound (**1b**) represents an intermediate situation [$E(\text{P–Cl})$ 319 kJ mol⁻¹¹⁴], and the product of the reaction depends on the nature of the transition metal fragment, since both complexation [with Ni(CO)₄¹³ and (**3**)] and insertion reactions [with (**2**)] are observed. Clearly, the strength of an individual P–X bond is of major importance for the reactivity of P -functionalized phospho-alkenes, and the behaviour of the phospho-alkenes involving other labile P -element single bonds towards low valent metal complexes is currently under study.

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