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

**D. Gudat,[a] M. F. Meidine,[b] J. F. Nixon,[b]* and E. Niecke[a]***

[a] *Institut für Anorganische Chemie, Universität Bonn Gerhard-Domagk-Str. 1, D-5300 Bonn 1, Federal Republic of Germany*

[b] *School of Chemistry and Molecular Sciences, University of Sussex, Falmer, Brighton BN1 9QJ, U.K.*

Phospha-alkenes X–P=CTMS$_2$ (X = F, Cl, I; TMS = SiMe$_3$) display different reaction behaviour towards metal complexes (Bu$_3$P)$_2$Ni(cod) (cod = cyclo-octa-1,5-diene) or (Ph$_3$P)$_2$Pt(C$_2$H$_4$), respectively, undergoing either co-ordination to give $\eta^2$-phospha-alkene complexes or alternatively oxidative addition of the P–X bond, forming phospha-alkenyl-metal(II) complexes, [(R$_3$P)$_2$M(X)($\sigma$-P=CTMS$_2$)].

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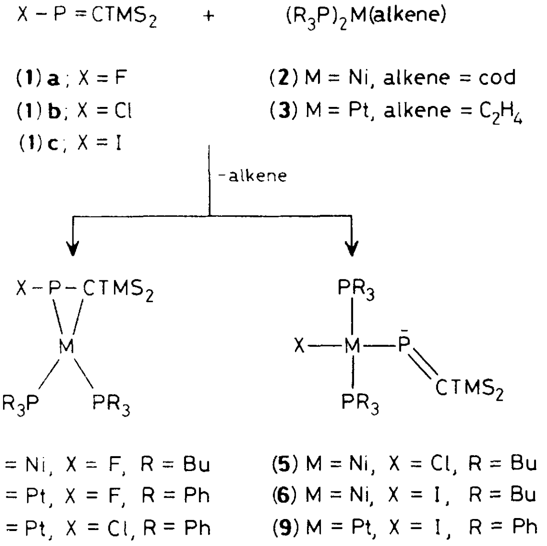
Phospha-alkenes react with a wide variety of transition metal compounds *via* ligand exchange to give complexes in which the phospha-alkenes may act as 2e- or 4e-donors and bonding of the ligand to the metal centre can occur through the phosphorus lone pair ($\eta^1$-co-ordination), the $\pi$-electrons of the double bond ($\eta^2$-co-ordination), or a combination of both.[1] A different type of interaction, however, was observed during the reaction of Me$_5$C$_5$–P=C(SiMe$_3$)$_2$ with complexes of type [L$_3$M(CO)$_3$] (M = Mo, W; L = MeCN)[2] or [(R$_3$P)Ni-(alkene)$_2$],[3] which proceeded *via* oxidative addition of the

**Table 1.** $^{31}P\{^1H\}$ and $^{19}F$ n.m.r. data of complexes $[(\eta^2\text{-X–P}_m\text{=CTMS}_2)M(P_{a,b}R_3)_2]$ and $[(P_aR_3)_2M(X)\ (\sigma\text{-P}_x\text{=CTMS}_2)]$ (**4**—**9**).

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

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



**Scheme 1**

metal at the P–C($C_5Me_5$) single bond. The $\eta^5$-$Me_5C_5$-metal complexes thus formed contain a phosphorus–metal σ-bond and a phospha-alkenyl fragment acting as either a 1e-[3] or 3e-donor.[2] By analogy, generation of transition metal complexes containing iminophosphanyl[3] or diphosphenyl ligands[4] 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 phospha-alkenes are readily cleaved by organic[5] and organometallic nucleophiles[6,7] with substitution at phosphorus and retention of the double bond, we investigated the reactivity of derivatives X–P=C($SiMe_3$)$_2$ [X = F (**1a**),[8] Cl (**1b**),[9] I (**1c**)][8] with $d^{10}$-metal-alkene complexes, $(Bu_3P)_2Ni(cod)$, (**2**), and $(Ph_3P)_2Pt(C_2H_4)$, (**3**).

Treatment of [$^2H_6$]-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 $[NiX_2(PBu_3)_2]$ together with other, as yet unidentified products.

Structural formulation of compounds (**4**—**9**) was made on the basis of their $^{31}P\{^1H\}$ 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 phospha-alkene resonance showed the considerable co-ordination shift[1,10] and small magnitude of $^1J_{Pt,P}$[11] expected for bis(t-phosphine) ($\eta^2$-phospha-alkene)metal(0) complexes. The value of $^1J_{P,F}$ in (**4**, **7**) shows a marked decrease with respect to free ligand ($^1J_{P,F}$ 1087 Hz[8]) or the $\eta^1$-complex $[(Ph_3P)_2RhCl(\eta^1\text{-F–P=CR}_2)]$ ($^1J_{P,F}$ 1127 Hz[12]), suggesting a decrease in s-character for the P–F bond as a consequence of the $\eta^2$-co-ordination. $^{31}P\{^1H\}$ N.m.r. spectra of (**5**), (**6**) and (**9**) exhibit two multiplets of an $AX_2$ 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 $^2J_{P_AP_X}$ suggests their formulation as *trans*-bis(t-phosphine) (σ-phospha-alkenyl)-halogenometal(II) complexes. The phospha-alkenyl ligand in (**9**) exhibits an unusually low value (98 Hz) for $^1J_{Pt,P}$, which is however in accord with the small magnitude of $^1J_{M,P}$ in other systems containing phosphorus–metal single bonds.[3,13] In the $^{13}C\{^1H\}$ 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 ($^1J_{P,C}$ 105 Hz); (**6**) δ 183.9 ($^1J_{P,C}$ 104 Hz); (**9**) δ 180.6 ($^1J_{P,C}$ 106 Hz)].[2,3,8] These findings are consistent with the presence of bent phospha-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]

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† *Selected* $^{13}C\{^1H\}$*-n.m.r. data* (20.0 MHz, ext. TMS): (**5**) (20 °C, [$^2H_6$]-benzene) δ 3.1 (m, $SiC_3$); (−50 °C, [$^2H_6$]-toluene) δ 3.4 (m, $SiC_3$) and 2.7 (d, $SiC_3$).

Our findings indicate that the reactivity of phospha-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**) [$E$(P–F) 490 kJ mol$^{-1}$ [14]] favours $\eta^2$-co-ordination with retention of the P–X bond, whereas in the case of a weaker bond in (**1c**) [$E$(P–I) 184 kJ mol$^{-1}$ [14]) the oxidative addition is preferred. Compound (**1b**) represents an intermediate situation [$E$(P–Cl) 319 kJ mol$^{-1}$ [14]], and the product of the reaction depends on the nature of the transition metal fragment, since both complexation [with $Ni(CO)_4$ [13] 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 phospha-alkenes, and the behaviour of the phospha-alkenes involving other labile *P*-element single bonds towards low valent metal complexes is currently under study.

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