Transition-metal Catalysed Metathesis of Phosphorus–Phosphorus Double Bonds

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$W(PMe_3)_6$ is an efficient chloride ion abstracting reagent for the synthesis of RP=PR species from $RPCl_2$ precursors; moreover, the $W(PMe_3)_6$–$RPCl_2$ solutions catalyse the exchange of the diphosphene PR end-groups *via* a mechanism closely related to the olefin metathesis process.

We report a new synthesis of diphosphene compounds of the type RP=PR (R = R^1 or R^2) and $R^1P{=}PR^2$ [R^1 = $C_6H_2Bu^t_3$-2,4,6, R^2 = $C_6H_2(CF_3)_3$-2,4,6], and a novel transition-metal catalysed heteroatom metathesis reaction that exchanges their phosphinidene (PR) end-groups, a process that bears close resemblance to the technologically important olefin metathesis reaction,[1] and one that may hold general applicability for the synthesis of phosphorus–phosphorus and potentially other main group element–element multiple bonds.

The two most widely employed routes to RP=PR species involve either (i) treatment of $RPCl_2$ with the primary phosphine RPH_2 in the presence of base, typically 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), or (ii) the reaction of $RPCl_2$ with a chloride abstracting reagent such as elemental magnesium or bisimidazolidine base.[2,3] In view of the highly reducing nature and labile coordination sphere of the zerovalent tungsten complex, $W(PMe_3)_6$,[4] we envisaged that this species would also act as an efficient chloride ion abstractor, according to eqn. (1). We find that not only does $W(PMe_3)_6$ abstract chloride ions from $RPCl_2$ efficiently to generate diphosphenes but also that the resultant tungsten–phosphorus species is capable of catalysing the exchange of the diphosphene PR end-groups.

$$2\,RPCl_2 + W(PMe_3)_6 \xrightarrow{-3\,PMe_3} RP{=}PR + WCl_4(PMe_3)_3 \qquad (1)$$

Treatment of $W(PMe_3)_6$ with 2 equiv. of $RPCl_2$ (R = R^1 or R^2) in benzene at room temperature proceeds smoothly over several hours to give the diphosphenes, RP = PR, (R = R^1 or R^2) in virtually quantitative yield along with the tungsten(IV) by-product, $WCl_4(PMe_3)_3$, which is clearly evident in the ^{1}H NMR spectrum as a paramagnetic contact-shifted resonance at δ −8.5.[5] When $W(PMe_3)_6$ is treated with a 1 : 1 mixture of R^1PCl_2 and R^2PCl_2 in benzene, the semi-liquid unsymmetrical diphosphene, $R^1P{=}PR^2$,‡ is generated in >95% yield according to ^{31}P NMR spectroscopy [see Fig. 1(*a*)]. Somewhat surprisingly, however, upon removal of the reaction solvent, the solid *symmetrical* diphosphenes are precipitated [Fig. 1(*b*)], indicating the presence of a species in solution that is capable of catalysing the exchange of the diphosphene PR end-groups. That the exchange does not occur in the absence of the tungsten species was shown by stirring a mixture of the two symmetrical diphosphenes in benzene solution at room temperature; none of the unsymmetrical diphosphene is formed under these conditions. However, when a trace amount of a solution derived from the $W(PMe_3)_6$–$RPCl_2$ mixture is added to this solution, exchange of the PR end-groups occurs to establish the same (equilibrium) mixture of the symmetrical and unsymmetrical diphosphene species (Scheme 1).

In order to isolate the unsymmetrical diphosphene, it is first necessary to destroy the catalyst. A convenient method involves treating the solution mixture with benzaldehyde, a procedure analogous to that used to kill well-defined alkylidene olefin metathesis catalysts and one which generates the phosphaalkene species $R^2P{=}CHPh$[6] and $R^1P{=}CHPh$.[7] These we were able to detect by their characteristic ^{31}P NMR resonances at δ 218.1 and 257.4; together they lend strong support for metal–phosphinidene species of the type [$M{=}PR^2$] and [$M{=}PR^1$] being present in the catalyst solution. Schrock and coworkers, for example, have shown that the isolable tantalum phosphinidene compound LTa=PR [L = $(Me_3SiNCH_2)_3N$] reacts with benzaldehyde to generate RP=CHPh and the oxo complex LTa=O.[9] Although we have been unable to detect a phosphinidene species directly [^{31}P NMR shifts of metal–phosphinidenes can

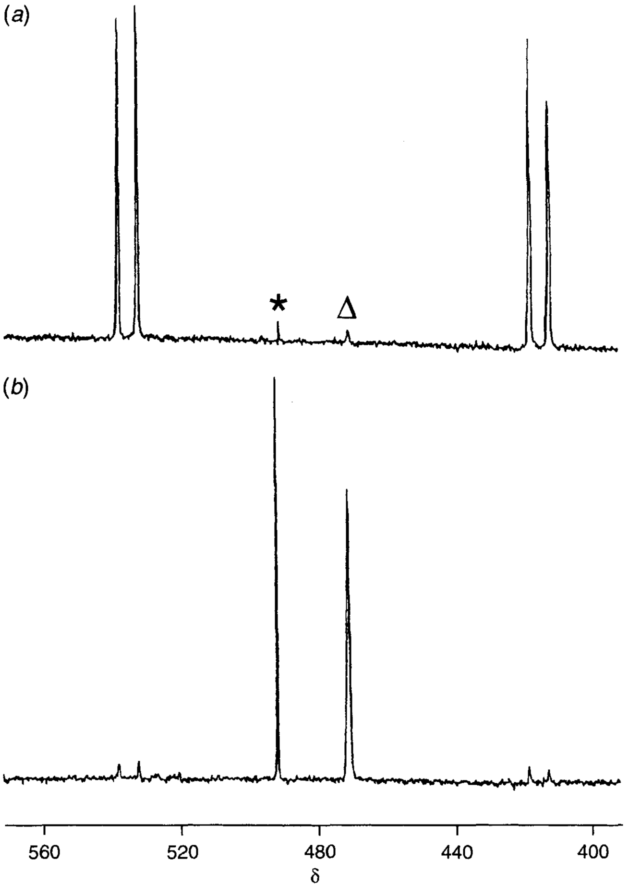
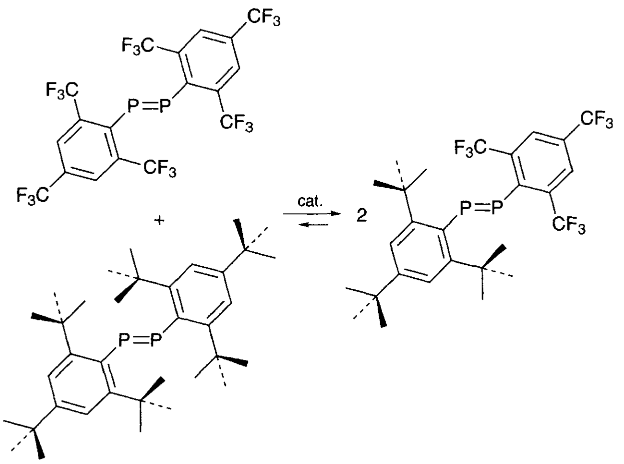
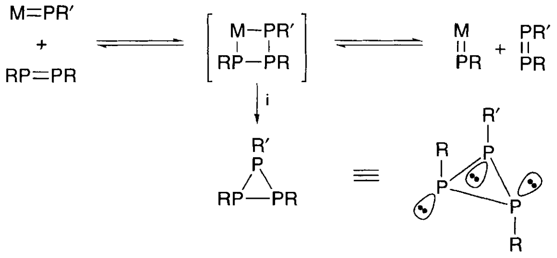


Fig. 1 (*a*) ^{31}P NMR spectrum of $R^1P{=}PR^2$, generated upon treatment of a 1 : 1 mixture of R^1PCl_2 and R^2PCl_2 with $W(PMe_3)_6$ in benzene (* and Δ indicate resonances due to the symmetrical diphosphenes, $R^1P{=}PR^1$ and $R^2P{=}PR^2$, respectively). (*b*) ^{31}P NMR spectrum of the precipitated solids.



Scheme 1



Scheme 2 i, R,R′ = $C_6H_2Me_3$-2,4,6 or $C_6H_2Pr^i_3$-2,4,6

occur over a wide frequency range, *e.g.* δ 666–800 for (η-$C_5H_5)_2Mo(=PR)$[8] to δ 175–230 for LTa(=PR)[9], we are encouraged to propose a mechanism for PR end-group exchange that involves the intermediacy of M=PR species (Scheme 2), a mechanism that is attractive in its close resemblance to the metal–alkylidene catalysed exchange of CHR end-groups in olefin metathesis.

A further analogy to the reaction chemistry of metal carbenes towards alkenes is seen when smaller R substituents are employed. For example, treatment of $W(PMe_3)_6$ with R^3PCl_2 (R^3 = $C_6H_2Pr^i_3$-2,4,6) initially affords the symmetrical diphosphene $R^3P{=}PR^3$ (δ 517) which is gradually consumed over a period of 8 hours to give the tricyclophosphane, $P_3R^3_3$. This displays characteristic doublet and triplet resonances at δ −99 and −133 (J_{PP} = 180 Hz) in its ^{31}P NMR spectrum. When the size of the substituent is reduced to mesityl (mes), the diphosphene is no longer observed [(mes)P=P(mes) is unstable[10]] and the sole product is then $P_3(mes)_3$ (δ −109 and −143, J_{PP} = 184 Hz). This cyclotrimerisation of PR groups parallels the cyclopropanation reaction observed in reactions of certain metal carbenes with alkenes, and further reinforces the analogy between the hydrocarbon and phosphorus systems.

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Footnotes

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‡ Satisfactory elemental analyses have been obtained; by this method $R^1P{=}PR^2$ is usually isolated as a pure, viscous oil that sublines at 85 °C (5×10^{-2} Torr). However, crystals precipitate slowly (days) from the viscous melt upon prolonged standing at room temp.

Selected spectroscopic data for **1**: ^1H NMR (C_6D_6, 400 MHz, 298 K) δ 7.91 (s, 2H, aryl H), 7.53 (s, 2H, aryl H), 1.61 [s, 18H, $C(CH_3)_3$], 1.51 [s, 9H, $C(CH_3)_3$]; ^{31}P NMR (C_6D_6, 101 MHz, 298 K) δ 536 (d, 1P, R^1P, $^1J_{PP}$ 574 Hz), 417 (d, 1P, R^2P, $^1J_{PP}$ 574, $^4J_{PF}$ 21 Hz); ^{19}F NMR (C_6D_6, 235 MHz, 298 K) δ −56.66 (t, 6F, *o*-CF_3, $^4J_{PF}$ 21 Hz), −63.53 (s, 3F, *p*-CF_3).

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