The reaction of electrophilic terminal phosphinidene complexes with enolizable ketones: C–H *vs* O–H *vs* C–C insertion of phosphorus

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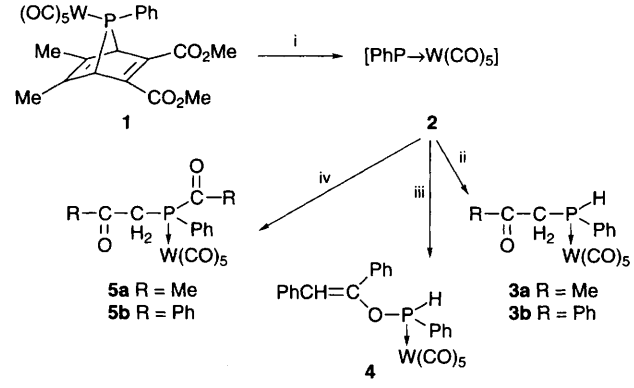
Transient [PhP→W(CO)$_5$], as generated from the appropriate 7-phosphanorbornadiene precursor, reacts at 120 °C with various enolizable ketones or β-diketones to give the products resulting from the insertion of phosphorus into either the α-CH, the enol OH, or the acyl-CH$_2$ bonds.

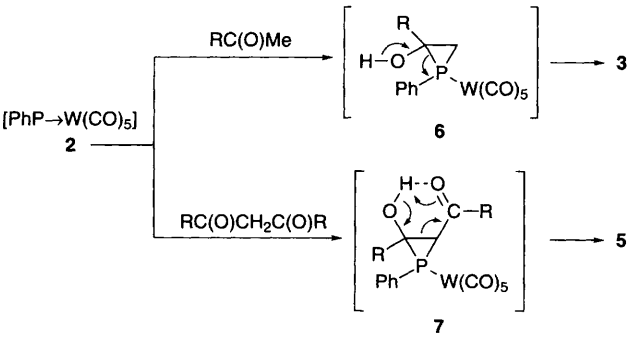
Recently, it has been shown that a bulky terminal phosphinidene complex, generated from an azaphosphirene precursor, reacts with benzaldehyde to give a stable [1 + 2] cycloadduct.[1] This interesting observation led us to reinvestigate the reaction of terminal phosphinidene complexes, classically generated by thermal decomposition of 7-phosphanorbornadiene complexes,[2,3] with a series of carbonyl compounds. We describe here our observations with enolizable ketones. All our experiments were carried out with transient [PhP→W(CO)$_5$] **2** generated at 120 °C from the appropriate phosphanorbornadiene precursor. The reaction of transient **2** with acetone gives almost exclusively the C–H insertion product **3a**.† the ^{31}P NMR spectrum of **3a** displays a high field resonance (δ −35.9 in $CDCl_3$) and a large $^1J_{P-H}$ coupling (353 Hz). The reaction of **2** with acetophenone leads to the corresponding product **3b**,† albeit in lower yield and accompanied by a side product at δ 94.6 (in toluene). The reaction of **2** with α-phenylacetophenone takes an entirely different course. The product **4**† results, at least formally, from the insertion of phosphorus into the O–H bond of the enol tautomer of the ketone.[4] The ^{31}P NMR spectrum of **4** displays a resonance at low fields (δ 93.8 in $CDCl_3$) and a large $^1J_{P-H}$ coupling (353 Hz). Still another pathway is followed by the reaction of **2** with β-diketones. The phosphorus inserts into the acyl-CH$_2$ bond. Compound **5a**† displays a ^{31}P NMR resonance at δ 16.6 and no $^1J_{P-H}$ coupling.

The simplest way to rationalize these observations is to suppose that the terminal phosphinidene complex **2** reacts with the enol tautomers of the ketones, either at the C=C double bond or at the O–H bond. The formation of products **3** and **5** can be explained as shown in Scheme 2. The opening of the ring of **6** is closely related to the hydrolytic cleavage of 2-alkoxyphosphirane complexes.[5]

This series of experiments, together with the work of Streubel *et al.*,[1] underlines the drastic differences between the chemistry of electrophilic and nucleophilic terminal phosphinidene complexes. The nucleophilic complexes are indeed known to react with carbonyl compounds to give phosphaalkenes *via* a Wittig-type transformation.[6,7]



Scheme 1 *Reagents and conditions*: i, toluene, 120 °C, 4 h; ii, RC(O)Me in excess (3:1); iii, PhCH$_2$C(O)Ph in excess; iv, RC(O)CH$_2$C(O)R in excess



Scheme 2

Footnote

† *Selected spectroscopic data* for **3a**: purified by chromatography on silica gel (hexane–CH_2Cl_2), 50% yield; ^{31}P NMR ($CDCl_3$): δ −35.9 ($^1J_{^{31}P-^{183}W}$ 233 Hz, $^1J_{P-H}$ 353 Hz); ^{1}H NMR ($CDCl_3$): δ 2.05 (s, 3 H, Me), 3.29 (m, 1 H, $^2J_{H-H}$ 15.1 Hz, $^2J_{H-P}$ *ca.* 5 Hz, CH$_a$), 3.43 (m, 1 H, $^2J_{H-P}$ *ca.* 8 Hz, CH$_b$), 6.20 (dd, 1 H, $^3J_{H-H_a}$ 4.8 Hz, $^3J_{H-H_b}$ 8.3 Hz, H–P); ^{13}C NMR ($CDCl_3$): δ 31.69 (s, Me), 44.76 (d, $^1J_{C-P}$ 20.4 Hz, CH$_2$–P), 195.95 (d, $^2J_{C-P}$ 6.7 Hz, W–CO *cis*), 202.41 (d, $^2J_{C-P}$ 6.5 Hz, CO); *m/z* (^{184}W) 462 (M$^+$ − CO, 33%), 406 (M$^+$ − 3CO, 31), 348 (M$^+$ − 5CO, 100); IR (CCl_4) (CO) 2074 (s), 2034.6 (m), 1983.5 (s), 1967.6–1922.0 (vs, broad), 1682.3 (m).

For **3b**: 16% yield; ^{31}P NMR ($CDCl_3$): δ −34.3 ($^1J_{^{31}P-^{183}W}$) 233 Hz, $^1J_{P-H}$ 353 Hz); ^{1}H NMR ($CDCl_3$): δ 3.84 (m, 1 H, $^2J_{H-H}$ 15.3 Hz, $^2J_{H-P}$ *ca.* 5 Hz, CH$_a$), 3.95 (m, 1 H, $^2J_{H-P}$ *ca.* 8 Hz, CH$_b$), 6.31 (dd, 1 H, $^3J_{H-H_a}$ 5.2 Hz, $^3J_{H-H_b}$ 7.4 Hz, $^1J_{H-P}$ 353 Hz, H–P); ^{13}C NMR ($CDCl_3$): δ 40.81 (d, $^1J_{C-P}$ 22.3 Hz, CH$_2$–P), 195.10 (d, $^2J_{C-P}$ 6.0 Hz, CO), 196.54 (d, $^2J_{C-P}$ 7.4 Hz, W–CO *cis*), 199.32 (d, $^2J_{C-P}$ 22.9 Hz, W–CO *trans*); *m/z* (^{184}W) 524 (M$^+$ − CO, 33%), 468 (M$^+$ − 3CO, 92), 412 (M$^+$ − 5CO, 100); IR (CCl_4) (CO) 2074.8 (s), 1984.3 (s), 1947.7 (vs), 1718.0 (s).

For **4**: 32% yield; ^{31}P NMR ($CDCl_3$): δ 93.8 ($^1J_{^{31}P-^{183}W}$ 280 Hz, $^1J_{P-H}$ 353 Hz); ^{1}H NMR ($CDCl_3$): δ 6.10 (d, $^4J_{H-P}$ 2.2 Hz, =CH), 8.05 (d, $^1J_{H-P}$ 353.7 Hz, H–P); ^{13}C NMR ($CDCl_3$): δ 117.87 (d, $^3J_{C-P}$ 7.1 Hz, =CH), 152.14 (d, $^2J_{C-P}$ 15.8 Hz, =C–O), 196.08 (d, $^2J_{C-P}$ 7.8 Hz, W–CO *cis*), 199.56 (d, $^2J_{C-P}$ 27.5 Hz, W–CO *trans*); *m/z* (^{184}W) 628 (M$^+$, 28%), 600 (M$^+$ − CO, 18), 544 (M$^+$ − 3CO, 100), 488 (M$^+$ − 5CO, 100); IR (CH_2Cl_2) (CO) 2077.2 (s), 1945.6 (vs).

For **5a**: 19% yield; ^{31}P NMR ($CDCl_3$): δ 16.6 ($^1J_{^{31}P-^{183}W}$ 229 Hz); ^{1}H NMR ($CDCl_3$): δ 2.15 (d, $^4J_{H-P}$ 1.4 Hz, 3 H, Me), 2.33 (d, $^3J_{H-P}$ 4.7 Hz, 3 H Me), 3.62 (*AB*x, 1 H, $^2J_{H-H}$ 16.9 Hz, $^2J_{H-P}$ 5.0 Hz, CH$_a$), 3.81 (*AB*X, 1 H, $^2J_{H-P}$ 9.5 Hz, CH$_b$); ^{13}C NMR ($CDCl_3$): δ 29.81 [d, $^2J_{C-P}$ 44.4 Hz, *Me*C(O)P], 32.31 [d, $^3J_{C-P}$ 2.4 Hz, *Me*C(O)C], 45.37 (d, $^1J_{C-P}$ 28.2 Hz, CH$_2$), 196.44 (d, $^2J_{C-P}$ 6.1 Hz, W–CO *cis*), 198.43 (d, $^2J_{C-P}$ 23.3 Hz, W–CO *trans*), 202.70 (s, CO), 213.87 (d, $^1J_{C-P}$ 12.2 Hz, CO); *m/z* (^{184}W) 504 (M$^+$ − CO, 72%), 448 (M$^+$ − 3CO, 86), 392 (M$^+$ − 5CO, 100); IR (CH_2Cl_2) (CO) 2075.8 (m), 1986.0 (w), 1942.3 (vs), 1714.4 (w), 1684.5 (w). Compound **5a** is partly hydrolysed on the column to give **3a** (*ca.* 5% yield).

For **5b**: 53% yield; ^{31}P NMR ($CDCl_3$): δ 17.3 ($^1J_{^{31}P-^{183}W}$ 235 Hz); ^{1}H NMR ($CDCl_3$): 4.19 (*A*BX, 1 H, $^2J_{H-H}$ 16.5 Hz, $^2J_{H-P}$ 4.8 Hz, CH_a), 4.48 (A*B*X, 1 H, $^2J_{H-P}$ 12.0 Hz, CH_b); ^{13}C NMR ($CDCl_3$): δ 43.12 (d, $^1J_{C-P}$ 32.1 Hz, CH_2), 194.85 (s, CO), 196.61 (d, $^2J_{C-P}$ 7.1 Hz, W–CO *cis*), 198.67 (d, $^2J_{C-P}$ 24.8 Hz, W–CO *trans*), 205.19 (d, $^1J_{C-P}$ 14.1 Hz, CO); *m/z* (^{184}W) 628 ($M^+ - CO$, 25%), 572 ($M^+ - 3CO$, 44), 516 ($M^+ - 5CO$, 57), 77 (100); IR (CH_2Cl_2) (CO) 2075 (m), 1943.1 (vs).

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