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Reactivity of electrophilic terminal phosphinidene complexes toward phosphorus ylides

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Abstract

Stabilised phosphorus ylides react with transient terminal phosphinidene complexes [RP–W(CO)$_5$] (R = Ph, Me) to give products resulting from a formal insertion of P into a C–H bond via an initial nucleophilic attack of the ylidic carbon. © 2002 Elsevier Science B.V. All rights reserved.

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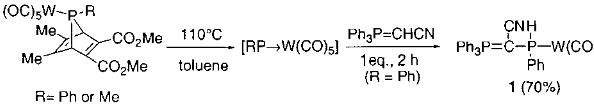
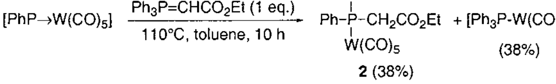
The versatile carbene-like chemistry of transient terminal phosphinidene–pentacarbonylmetal complexes [RP–M(CO)$_5$] (M = Cr, Mo, W) is currently under active investigation [1]. These species display an electrophilic behaviour, and their reactions with a series of oxygen, nitrogen and phosphorus nucleophiles have been studied in some depth. In most cases, the formation of transient or stable ylidic adducts has been demonstrated [2]. To the best of our knowledge, however, nothing is known about their reactivity toward carbon nucleophiles. It is clear that highly nucleophilic species, such as organolithium compounds, cannot give clean reactions with [RP–M(CO)$_5$] since side-attacks at the carbonyl groups are expected at both the phosphinidene complexes and their 7-phosphanorbornadiene precursors [3]. Against such a background, we decided to investigate the reactivity of [RP–W(CO)$_5$] (R = Ph, Me) toward a representative selection of phosphorus ylides chosen as typical mild carbon nucleophiles. The phosphinidene complexes were generated from the appropriate 7-phosphanorbornadiene precursors [3]. It soon appeared that only stabilised ylides gave reproducible and clear-cut results.

The reaction with Ph$_3$P=CHCN leads to a new ylide **1** [4], whose ylidic carbon resonates at 9.55 (CDCl$_3$) with ^1J couplings of 106.6 (Ph$_3$P) and 47.7 Hz. These data can be compared with those of the starting ylide: δ −1.86 and $^1J_{CP}$ = 134.8 Hz [5]. The formation of **1** can be simply explained by a nucleophilic attack of the ylidic carbon at the phosphinidene phosphorus, followed by a proton transfer (Eq. (1)).



(1)

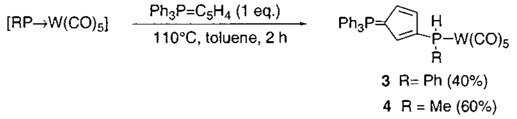
The result of the reaction with Ph$_3$P=CHCO$_2$Et is more unexpected. Complex **2** was unambiguously characterised by NMR and mass spectrometry [6]. An equimolar amount of [Ph$_3$P–W(CO)$_5$] was also isolated and characterised by ^{31}P-NMR and mass spectrometry (Eq. (2)). The mechanism of the reaction leading to **2** is presently unclear.



$$[\mathrm{PhP{\rightarrow}W(CO)_5}] \xrightarrow[\text{110°C, toluene, 10 h}]{\mathrm{Ph_3P{=}CHCO_2Et}\text{ (1 eq.)}} \mathrm{Ph{-}\underset{W(CO)_5}{\overset{OEt}{P}}{-}CH_2CO_2Et} + [\mathrm{Ph_3P{-}W(CO)_5}] \quad (2)$$

2 (38%) (38%)

With cyclopentadienylidenephosphoranes, the reaction is similar to the first case. The insertion of phosphinidene takes place at the β-carbon of the ring, probably for steric reasons, leading to complexes **3** and **4** [7] (Eq. (3)).



(3)

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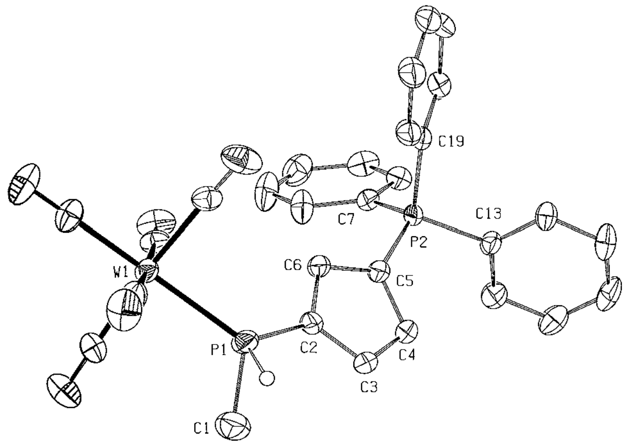

Fig. 1. Crystal structure of **4**. Significant bond distances (Å) and angles (°): P(1)–C(1), 1.796(4); P(1)–C(2), 1.793(3); P(1)–W(1), 2.530(1); C(2)–C(3), 1.416(4); C(3)–C(4), 1.376(4); C(4)–C(5), 1.417(4); C(5)–C(6), 1.431(4); C(6)–C(2), 1.395(4); P(2)–C(5), 1.731(3); P(2)–C(7), 1.803(3); P(2)–C(13), 1.794(3); P(2)–C(19), 1.811(3). C(2)–P(1)–W(1), 120.2(1); C(2)–P(1)–C(1), 104.1(2); C(1)–P(1)–W(1), 117.2(2); C(4)–C(5)–C(6), 107.6(3); C(4)–C(5)–P(2), 124.8(2); C(6)–C(5)–P(2), 127.5(2); C(5)–P(2)–C(7), 114.6(1); C(5)–P(2)–C(13), 109.3(1); C(5)–P(2)–C(19), 111.6(1).

Complex **4** has been characterised by X-ray crystal structure analysis [8]. The structural data (Fig. 1) indicate that the ylidic carbon is planar (Σangles = 359.9°) and that the P(2)–C(5) bond at 1.731(3) Å is in the normal range for a cyclopentadienylide [9]. Finally, the reaction of electrophilic terminal phosphinidene complexes with stabilised phosphorus ylides appears to be a relatively versatile method for synthesising P–C bonds.

1. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 175168 for compound **4**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

References

[1] For recent reviews, see: (a) K.B. Dillon, F. Mathey, J.F. Nixon, Phosphorus: The Carbon Copy, Wiley, Chichester, 1998, p. 19;
(b) K. Lammertsma, M.J.M. Vlaar, Eur. J. Org. Chem. (2002), in press;
(c) F. Mathey, N.H. Tran Huy, A. Marinetti, Helv. Chim. Acta 84 (2001) 2938.

[2] Typical examples: (a) **P**: P. Le Floch, A. Marinetti, L. Ricard, F. Mathey, J. Am. Chem. Soc. 112 (1990) 2407;
(b) **N**: R. Streubel, U. Schiemann, P.G. Jones, N.H. Tran Huy, F. Mathey, Angew. Chem. Int. Ed. Engl. 39 (2000) 3686;
(c) **O**: Y. Inubushi, N.H. Tran Huy, L. Ricard, F. Mathey, J. Organomet. Chem. 533 (1997) 83;
(d) R. Streubel, A. Ostrowski, H. Wilkens, F. Ruthe, J. Jeske, P.J. Jones, Angew. Chem. Int. Ed. Engl. 36 (1997) 378.

[3] A. Marinetti, F. Mathey, J. Fischer, A. Mitschler, J. Chem. Soc. Chem. Commun. (1982) 667.

[4] **1**: purified by chromatography on silica gel with CH_2Cl_2–Et_2O, 10:1. ^{31}P-NMR ($CDCl_3$): δ −31.08 (HPW), $^{2}J_{PP}$ 11.6 Hz, $^{1}J_{PH}$ 354.4 Hz, $^{1}J_{PW}$ 231.8 Hz; 23.4 (Ph_3P); ^{1}H-NMR ($CDCl_3$): δ 5.80 (dd, $^{1}J_{HP} = 354.7$ Hz, $^{3}J_{HP} = 6.9$ Hz, PH); ^{13}C-NMR ($CDCl_3$): δ 9.55 (dd, $^{1}J_{CP} = 106.6$ and 47.4 Hz, CP_2), 126.99 (dd, $^{2}J_{CP} = 17.5$ and 8.4 Hz, CN), 197.37 (d, $^{2}J_{CP} = 6.5$ Hz, *cis*-CO), 201.11 (d, $^{2}J_{CP} = 21.3$ Hz, *trans*-CO); EIMS (^{184}W); m/z: 707 ([$M^+ - CO + 2H$], 2.6%), 651 ([$M^+ - 3CO + 2H$], 16.9%), 594 ([$M^+ - 5CO + H$], 13%), 300 (Ph_3PCCN, 100%), 262 (Ph_3P, 84%).

[5] For a discussion on the ^{13}C-NMR data of phosphorus ylides, see: A.W. Johnson, Ylides and Imines of Phosphorus, Wiley, New York, 1993, p. 55.

[6] [Ph_3P–$W(CO)_5$] was first recovered by chromatography with hexane–CH_2Cl_2, 4:1, then **2** with hexane–CH_2Cl_2, 1:2. ^{31}P-NMR ($CDCl_3$): δ 114.1, $^{1}J_{PW} = 286.8$ Hz; ^{1}H-NMR ($CDCl_3$): δ 1.05 (m, CH_3), 1.32 (m, CH_3), 3.35 (m, P–CH_2), 3.86 (m, OCH_2), 3.98 (m, OCH_2), 7.43 (m, Ph); ^{13}C-NMR ($CDCl_3$): δ 14.50 (s, Me), 16.75 (d, $^{3}J_{CP} = 8.7$ Hz, Me(P–OEt)), 45.53 (d, $^{1}J_{CP} = 12.2$ Hz, P–CH_2), 62.10 (s, CO_2CH_2), 64.63 (d, $^{2}J_{CP} = 4.3$ Hz, P–O–CH_2), 167.64 (s, CO_2), 196.71 (d, $^{2}J_{CP} = 7.9$ Hz, *cis*-CO), 199.52 (d, $^{2}J_{CP} = 26.7$ Hz, *trans*-CO); MS; m/z: 537 ([$M^+ - CO + H$], 50%), 425 ([$M^+ - 5CO + H$], 75%), 382 (100%).

[7] **3**: purified by chromatography with hexane–CH_2Cl_2, 1:3. ^{31}P-NMR ($CDCl_3$): δ −40.7 (P–W), $^{1}J_{PW} = 220$ Hz, 14.0 (Ph_3P); ^{1}H-NMR ($CDCl_3$): δ 6.28, 6.33 and 6.66 (3m, Cp), 6.75 (d, $^{1}J_{HP} = 340.5$ Hz, PH); ^{13}C-NMR ($CDCl_3$): δ 84.88 (dd, $^{1}J_{CP} = 110.6$ Hz, $^{3}J_{CP} = 15.9$ Hz, P=C); MS; m/z: 760 ([$M^+ + 2$], 1.6%), 704 ([$M^+ + 2 - 2CO$], 63%), 262 (Ph_3P, 100%). **4** purified by chromatography with hexane–CH_2Cl_2, 1:3. ^{31}P-NMR ($CDCl_3$): δ −71.9 (P–W), $^{1}J_{PW} = 220.4$ Hz, 13.6 (Ph_3P); ^{1}H-NMR ($CDCl_3$): δ 5.98 (dd, $^{1}J_{HP} = 332$ Hz, PH), 6.28 and 6.47 (m, Cp); ^{13}C-NMR ($CDCl_3$): δ 84.53 (dd, $^{1}J_{CP} = 110.9$ Hz, $^{3}J_{CP} = 15.3$ Hz, P=C); MS; m/z: 698 ([$M^+ + 2$], 6.3%), 642 ([$M^+ + 2 - 2CO$], 100%), 262 (Ph_3P, 75%). Ph_3P=Cp: for comparison, ^{13}C-NMR ($CDCl_3$): δ 79.63 (d, $^{1}J_{CP} = 113.2$ Hz, C=P).

[8] Crystal data for **4** $C_{29}H_{22}O_5P_2W$, $M = 696.26$ g mol^{-1}, triclinic, $a = 10.619(5)$ Å, $b = 11.423(5)$ Å, $c = 12.628(5)$ Å, $\alpha = 65.710(5)°$, $\beta = 79.290(5)°$, $\gamma = 80.010(5)°$, $V = 1363.8(10)$ Å^3, $T = 150.0(1)$ K, space group P-1, $Z = 2$, μ(Mo–K$_\alpha$) = 4.389 cm^{-1}, 10 933 reflections measured, 7864 unique ($R_{int} = 0.0290$), which were used in all calculations. The final $wR(F^2)$ was 0.0730, $R_1 = 0.0322$ (all data).

[9] See Ref. [5], p. 48.