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Combining Phosphinidene Units with Malonate Anion: Synthesis of Highly Functional Phosphine Complexes

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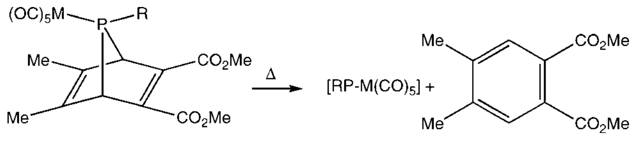
ABSTRACT: *Malonate anion traps the [RP-W(CO)$_5$] bridge of 7-phosphanorbornadiene complexes* **1–3** *to give functional secondary phosphine complexes [RP(H)-CH(CO$_2$Et)$_2$]W(CO)$_5$ (***7–9***). Metalation of these complexes by NaH in THF occurs at the malonic CH group, but the alkylation of the resulting carbanions preferentially takes place at phosphorus. When R stands for β-chloroethyl, the corresponding carbanion cyclizes to give the functional phosphirane complex* **11**. © 2004 Wiley Periodicals, Inc. Heteroatom Chem 15:258–262, 2004; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20014

INTRODUCTION

Transient electrophilic terminal phosphinidene complexes [RP-M(CO)$_5$] (M = Cr, Mo, W) as generated from the appropriate 7-phosphanorbornadiene complexes [Eq. (1)] display a carbene-like chemistry which has been the subject of intensive study for two decades [1,2].



(1)

However, quite surprisingly, only a very few attempts have been made to react these species with carbon nucleophiles. In fact, a highly reactive carbon nucleophile such as an organolithium reagent tends to attack the 7-phosphanorbornadiene precursor at its electron-poor double bond Marinetti, A.; Mathey, F. (Unpublished results), thus preventing the collapse of the bridge and the generation of the phosphinidene unit. A first well-documented trapping reaction of these phosphinidene units by stabilized phosphine ylids acting as weak carbon nucleophiles has been reported very recently [3,4]. In this work, we wish to describe the reaction of a typical mild carbon nucleophile, i.e. the malonate anion, with the phosphinidene 7-phosphanorbornadiene precursors.

RESULTS AND DISCUSSION

Our experiments were carried out with three representative 7-phosphanorbornadiene complexes **1–3** [5,6]. These complexes were found to undergo a

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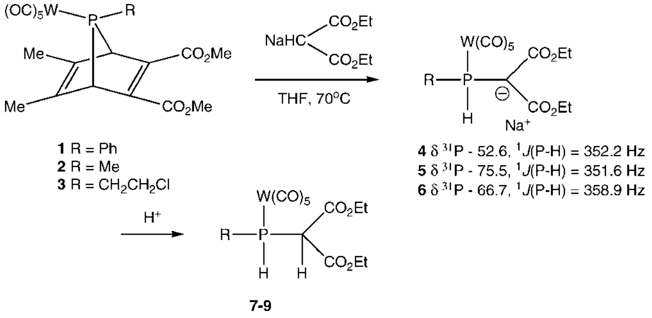
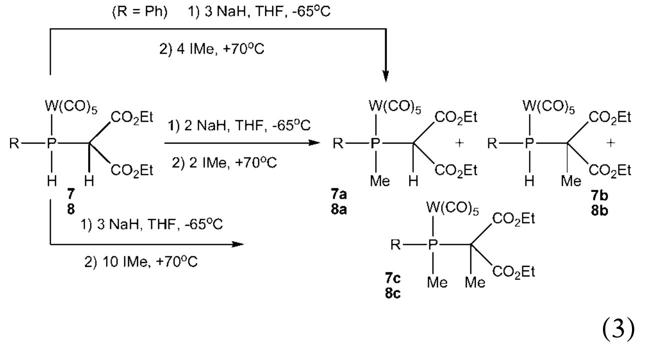
clean reaction with the malonate sodium derivative in THF at 70°C to give, after protonation, the functional secondary phosphine complexes **7–9** in excellent yields [Eq. (2)].



(2)

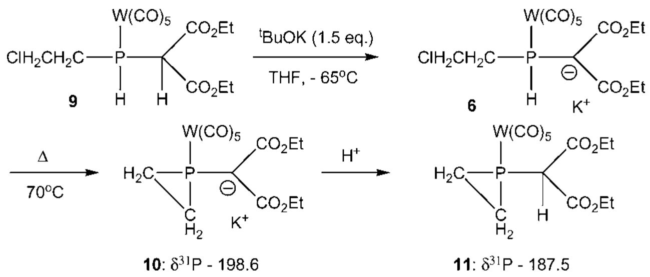
The primary products of the reaction are the phosphino-substituted carbanions **4–6** whose formation was monitored by ^{31}P NMR spectroscopy of the crude reaction mixtures. The presence of the P—H bonds was ascertained by the huge ^{1}J(P—H) coupling constants. Unfortunately, we were unable to get satisfactory crystals of one of these carbanions. Their formation demonstrates that the C—H are more acidic than the P—H protons in **7–9**. Upon hydrolysis, the carbanions **4–6** give the secondary phosphine complexes **7–9** which were fully characterized by NMR spectroscopy, mass spectrometry, and elemental analyses. As an example, we shall describe the main spectroscopic features of **7**. The ^{31}P resonance of **7** appears at lower field than the resonance of the corresponding carbanion **4**: δ ^{31}P–19.1 ppm (CH_2Cl_2), ^{1}J(P—H) = 361.8 Hz. The P—H proton appears as a doublet of doublet at 6.36 ppm ($CDCl_3$), ^{3}J(H—H) = 6.8 Hz, resulting from the coupling with the α-CH proton. The corresponding α-CH carbon resonates at 52.80 ppm ($CDCl_3$) with a ^{1}J(C—P) coupling of 14.3 Hz. The base peak on the mass spectrum (EI) (*m/z* 509) corresponds to the loss of three CO's. The mechanism leading to the formation of **4** and **7** remains open to discussion. Formally, **4** results from the nucleophilic attack of the malonate ion onto the transient phosphinidene complex [PhP-W(CO)$_5$]. But an alternative possibility would imply a direct nucleophilic attack at the phosphorus bridge of the precursor **1**, followed by a retro-McCormack cycloreversion. These cycloreversions are known to be extremely easy with pentacoordinate phosphorus derivatives, see for example [7,8].

A preliminary investigation of the chemistry of the highly functional secondary phosphine complexes **7–8** was then carried out. Their metalation by NaH in THF at low temperature exclusively gives the monoanions **4–5**, even when a large excess of NaH is used. With a two-fold excess of NaH, the subsequent methylation of these anions by two equivalents of methyl iodide at +70°C yields a mixture of the three possible monomethylated and dimethylated products as shown in Eq. (3).



(3)

We were unable to separate the products of the **a, b, c** mixtures, but, curiously, the almost exclusive formation of the P-methylated product **7a** was observed when using 3NaH + 4IMe, and, more logically, the exclusive formation of the dimethylated products **7c** and **8c** was observed when running the reactions with a threefold excess of NaH and a tenfold excess of IMe. In the case of complex **7**, methylated products **7a, 7b**, and **7c** are formed in a 2:1:2 ratio when using 2NaH + 2IMe. The minor product **7b** was easily identified through its P—H bond: δ ^{31}P +3.8 ppm ($CDCl_3$), ^{1}J(P—H) = 356.2 Hz. The P—H proton appears as a doublet at 6.16 ppm ($CDCl_3$) with no ^{3}J(H—H) coupling. On the ^{13}C spectrum ($CDCl_3$), the P-*C*Me carbon appears at 55.15 ppm with a ^{1}J(C—P) coupling of 15.8 Hz and the corresponding methyl resonates at 18.67 ppm with a ^{2}J(C—P) coupling of 6.1 Hz. The P-methylated product **7a** displays a ^{31}P resonance at −1.6 ppm ($CDCl_3$). The ^{13}C spectrum shows the P-Me at 13.69 ppm, ^{1}J(C—P) = 26.4 Hz and the P—CH at 54.02 ppm, ^{1}J(C—P) = 10.1 Hz. The carbanion corresponding to **7a** resonates at −12.8 ppm in THF (sodium derivative). The dimethylated product **7c** was also completely characterized. It displays a ^{31}P resonance at +8.8 ppm ($CDCl_3$). The ^{13}C spectrum shows the P-Me at 16.40 ppm, ^{1}J(C—P) = 26.7 Hz and the P-*C*Me at 57.29 ppm, ^{1}J(C—P) = 11.6 Hz. The P-C*Me* appears at 19.66 ppm, ^{2}J(C—P) = 4.8 Hz. In all these compounds, the two diastereotopic CO_2Et groups give two sets of well-separated resonances. In order to have a better insight into the mechanism of the reaction, we monitored the evolution of the reaction mixture by ^{31}P NMR spectroscopy. Upon addition of IMe to a THF solution of anion **4**, the first product to appear is the carbanion of **7a** at ca. −12.8 ppm, followed by the dimethylated product **7c** at 8.8 ppm. Our interpretation of these observations is as follows. The negative charge of the carbanion **4** is delocalized between C and P, so that phosphorus competes efficiently with the α-carbon as the initial methylation site. This situation is reminiscent of what is observed with bis(methoxycarbonyl)methylphosphines: metalation at the α-carbon, reaction of IMe at P [9]. But of course, in our case, there is no change of the coordination state of P upon methylation. Our proposal is fully supported by the following observation. The metalated derivative **6** (Li^+ or K^+) is quantitatively converted into the corresponding phosphirane derivative upon heating at 70°C in THF [Eq. (4)].



(4)

The high-field shift of the ^{31}P resonance is very characteristic of the 3-membered P—C heterocycles [10]. Phosphirane **11** has been fully characterized by NMR spectroscopy and mass spectrometry. The ^{13}C ring resonances ($\delta^{13}CH_2$ 14.43 ppm in $CDCl_3$) appear at high field as expected, and the exocyclic CH resonates as a singlet at 63.24 ppm. The mass spectrum shows the molecular peak at *m/z* 542 (^{184}W).

From this series of experiments, it appears quite clearly that the reaction of weak carbon nucleophiles with 7-phosphanorbornadiene complexes is a powerful method to create P—C bonds between the incoming nucleophiles and phosphinidene units. Synthetic applications are probably possible.

EXPERIMENTAL

NMR spectra were recorded on a multinuclear Bruker AVANCE 300 MHz spectrometer operating at 300.13 for ^1H, 75.47 for ^{13}C, and 121.50 MHz for ^{31}P. Chemical shifts are expressed in parts per million (ppm) downfield from internal tetramethylsilane (^1H and ^{13}C) and external 85% aqueous H_3PO_4(^{31}P). Mass spectra were obtained at 70 eV with an HP 5989B spectrometer by the direct inlet method.

Diethyl [(phenylphosphino)malonate]pentacarbonyltungsten **7**

A sample of 1.89 ml (12.5 mmol) of diethyl malonate in 5 ml of THF was added dropwise at room temperature to a solution of 300 mg (12.5 mmol) of NaH in 10 ml of THF, under inert atmosphere. The mixture was stirred in a closed Schlenk tube for 20 min. After decantation, 3.6 ml (3 mmol) of the above solution was added to 2 g (3 mmol) of 7-phenyl-7-phosphanorbornadiene complex **1** in solution in 10 ml of THF, under inert atmosphere of nitrogen in a closed Schlenk tube. The solution was then heated at 70°C for 2 h. The product was isolated after chromatography on silica gel (eluent: hexane 19/diethylether 1) as a white powder. Yield 69% (1.22 g).

^{31}P NMR ($CDCl_3$): $\delta = -18.46$ ($^1J_{P-W} = 241.1$ Hz, $^1J_{P-H} = 360.3$ Hz). ^1H NMR ($CDCl_3$): $\delta = 1.07$ and 1.20 (2t, 6H, $^3J_{H-H} = 7.1$ Hz, $OCH_2C\mathbf{H}_3$), 3.99 and 4.20 (2m, 4H, $OC\mathbf{H}_2CH_3$), 4.24 (m, 1H, P—C**H**), 6.43 (dd, 1H, $^1J_{P-H} = 360.3$ Hz, $^3J_{H-H} = 6.8$ Hz, P—**H**), 7.5 (m, 5H, $C_6\mathbf{H}_5$-P). ^{13}C NMR ($CDCl_3$): $\delta = 13.8$ and 14.0 (2s, $OCH_2\mathbf{C}H_3$), 54.3 (d, $^1J_{P-C} = 14.2$ Hz, P—**C**H), 62.7 and 63.0 (2s, $O\mathbf{C}H_2CH_3$), 131.1 (m, $\mathbf{C}_6H_5$-P), 165.3 and 165.7 (2s, **C**═O), 195.5 (d, $^2J_{P-C} = 6.8$ Hz, $^1J_{W-C} = 125.5$ Hz, **CO** cis), 198.3 (d, $^2J_{P-C} = 24.8$ Hz, **CO** trans). *m/z* (^{184}W): 593 (M^+, 1.5%), 564 (M − CO, 64.5%), 537 (M^+ − 2CO, 16.0%), 509 (M^+ − 3CO, 100%), 480 (M − 4CO, 5.5%), 453 (M^+−5CO, 89.5%). Anal calcd for $C_{18}H_{17}O_9PW$: C, 36.51; H, 2.89. Found: C, 36.52; H, 2.88.

Diethyl [(methylphosphino)malonate]pentacarbonyltungsten **8**

A sample of 0.85 ml (5.6 mmol) of diethyl malonate in 5 ml of THF was added dropwise at room temperature to a solution of 150 mg (6.25 mmol) of NaH in 15 ml of THF, under inert atmosphere. The mixture was stirred in a closed Schlenk tube for 20 min. After decantation, 2 ml (0.56 mmol) of the above solution was added to 300 mg (0.5 mmol) of 7-methyl-7-phosphanorbornadiene complex **2** in solution in 2 ml of THF, under inert atmosphere of nitrogen in a closed Schlenk tube. The solution was then heated at 70°C for 1 h. The product was isolated after chromatography on silica gel (eluent: hexane 9/diethylether 1) as a white oil. Yield 40.2% (110 mg).

^{31}P NMR ($CDCl_3$): $\delta = -48.9$ ($^1J_{P-W} = 239.9$ Hz, $^1J_{P-H} = 348.9$ Hz). ^1H NMR ($CDCl_3$): $\delta = 1.25$ (t, 6H, $^3J_{H-H} = 7.1$ Hz, $OCH_2C\mathbf{H}_3$), 1.79 (dd, 3H, $^2J_{P-H} = 7.6$ Hz, $^3J_{H-H} = 6.5$ Hz, P—C$\mathbf{H}_3$), 3.99 (dd, 1H, $^2J_{P-H} = 5.6$ Hz, $^3J_{H-H} = 4.2$ Hz, P—C**H**), 4.22 (q, 4H, $^3J_{H-H} = 7.1$ Hz, $OC\mathbf{H}_2CH_3$), 5.5 (ddq, 1H, $^1J_{P-H} = 348.9$ Hz, $^3J_{H-H} = 6.5$ Hz, $^3J_{H-H} = 4.2$ Hz, P—**H**). ^{13}C NMR ($CDCl_3$): $\delta = 12.5$ (d, $^1J_{P-C} = 44.9$ Hz, P—$\mathbf{C}H_3$), 15.4 and 15.5 (2s, $OCH_2\mathbf{C}H_3$), 52.9 (d, $^1J_{P-C} = 17.6$ Hz, P—**C**H), 64.3 and 64.4 (2s, $O\mathbf{C}H_2CH_3$), 167.3 and 167.4 (2s, $\mathbf{C}O_2C_2H_5$), 196.9 (d, $^2J_{P-C} = 7.0$ Hz, **CO** cis), 199.7 (d, $^{2}J_{\mathrm{P-C}} = 24.5$ Hz, **C**O trans). *m/z* (^{184}W): 530 (M, 1.7%), 503 (M^{+}−CO, 69.5%), 474 (M−2CO, 11.3%), 447 (M^{+} − 3CO, 100%), 419 (M^{+} − 4CO, 12.2%), 391 (M^{+} − 5CO, 27.0%).

Diethyl [(2-chloroethylphosphino)malonate]-pentacarbonyltungten **9**

A sample of 1.7 ml (11.2 mmol) of diethyl malonate in 5 ml of THF was added dropwise at room temperature to a solution of 300 mg (12.5 mmol) of NaH in 15 ml of THF, under inert atmosphere. The mixture was stirred in a closed Schlenk tube for 20 min. After decantation, 1.6 ml (0.9 mmol) of the above solution was added to 600 mg (0.9 mmol) of 7-(2-chloroethyl)-7-phosphanorbornadiene complex **3** in solution in 3 ml of THF, under inert atmosphere of nitrogen in a closed Schlenk tube. The solution was then heated at 70°C for 20 min. The product was isolated after chromatography on silica gel (eluent: hexane 9/diethylether 1) as a colorless oil. Yield 27.5% (142.5 mg).

^{31}P NMR (CDCl$_3$): $\delta = -43.28$ ($^{1}J_{\mathrm{P-W}} = 243.3$ Hz, $^{1}J_{\mathrm{P-H}} = 359.6$ Hz). ^{1}H NMR (CDCl$_3$): $\delta = 1.33$ and 1.34 (2t, 6H, $^{3}J_{\mathrm{P-H}} = 7.2$ Hz), 2.7 and 2.8 (2m, 2H, P—C**H**$_2$—CH$_2$—Cl), 3.8 (m, 2H, P—CH$_2$—C**H**$_2$—Cl), 4.22 (dd, 1H, $^{2}J_{\mathrm{P-H}} = 6.6$ Hz, $^{3}J_{\mathrm{H-H}} = 3.5$ Hz, P—C**H**), 4.30 and 4.31 (2q, 4H, $^{3}J_{\mathrm{H-H}} = 7.2$ Hz, OC**H**$_2$CH$_3$), 5.72 (dddd, $^{1}J_{\mathrm{P-H}} = 359.6$ Hz, $^{3}J_{\mathrm{H-H}} = 3.5$ Hz, $^{3}J_{\mathrm{H-H}} = 5.6$ Hz, $^{3}J_{\mathrm{H-H}} = 6.8$ Hz, P—**H**). ^{13}C NMR (CDCl$_3$): $\delta = 3.6$ and 3.7 (2s, OCH$_2$CH$_3$), 30.2 (d, $^{1}J_{\mathrm{P-C}} = 23.5$ Hz, P—**C**H$_2$—CH$_2$—Cl), 41.2 (s, P—CH$_2$—**C**H$_2$—Cl), 50.3 (d, $^{1}J_{\mathrm{P-C}} = 18.20$ Hz, P—**C**H), 63.5 (s, O**C**H$_2$CH$_3$), 165.8 and 166.2 (2s, **C**═O), 195.6 (d, $^{2}J_{\mathrm{P-C}} = 6.9$ Hz, **C**O cis), 197.8 (d, $^{2}J_{\mathrm{P-C}} = 25.5$ Hz, **C**O trans).

Diethyl [(methylphenylphosphino)malonate]-pentacarbonyltungsten **7a**

A sample of 200 mg (0.34 mmol) of **7** in 3 ml of THF was added dropwise at 65°C to a solution of 25 mg of NaH (1 mmol) in 2 ml of THF. The mixture was allowed to get to room temperature and then 0.085 ml (1.36 mmol) of CH$_3$I was added under inert atmosphere of nitrogen. The solution was heated at 70°C for 4 h in a closed Schlenk tube. The product was isolated after chromatography on silica gel (eluent: hexane 22/diethylether 1) as a white powder. Yield 83% (171 mg).

^{31}P NMR (CDCl$_3$): $\delta = -1.39$ ($^{1}J_{\mathrm{P-W}} = 249.2$ Hz). ^{1}H NMR (CDCl$_3$): $\delta = 0.9$ and 1.2 (2t, 6H, $^{3}J_{\mathrm{H-H}} = 7.1$ Hz, OCH$_2$C**H**$_3$), 2.3 (d, 3H, $^{2}J_{\mathrm{P-H}} = 6.3$ Hz, P—C**H**$_3$), 3.8 and 4.1 (2q, 4H, $^{3}J_{\mathrm{H-H}} = 7.1$ Hz, OC**H**$_2$CH$_3$), 4.2 (d, 1H, $^{2}J_{\mathrm{P-H}} = 4.8$ Hz, P—C**H**), 7.4 (m, 5H, C$_6$**H**$_5$-P). ^{13}C NMR (CDCl$_3$): $\delta = 11.7$ and 11.9 (2s, OCH$_2$**C**H$_3$), 13.7 (d, $^{1}J_{\mathrm{P-C}} = 26.4$ Hz, P—**C**H$_3$), 54.0 (d, $^{1}J_{\mathrm{P-C}} = 10.0$ Hz, P—**C**H), 60.2 and 60.7 (2s, O**C**H$_2$CH$_3$), 131.0 (m, C$_6$H$_5$-P), 162.9 and 163.1 (2s, **C**═O), 194.4 (d, $^{2}J_{\mathrm{P-C}} = 7.0$ Hz, **C**O cis), 196.7 (d, $^{2}J_{\mathrm{P-C}} = 24.0$ Hz, **C**O trans). *m/z* (^{184}W): 607 (M^{+}, 0.2%), 577 (M^{-}−CO, 19.4%), 549 (M^{-} − 2CO, 18.6%), 521 (M^{-} − 3CO, 100%), 493 (M^{-} − 4CO, 0.6%), 466 (M−5CO, 23.4%). Anal calcd for C$_{19}$H$_{19}$O$_9$PW : C, 37.65 ; H, 3.16. Found: C, 37.64; H, 3.28.

Diethyl [(methylphenylphosphino)(methyl)-malonate]pentacarbonyltungsten **7c**

A sample of 780 mg (1.3 mmol) of **7** in 3 ml of THF was added dropwise at 65°C to a solution of 94 mg of NaH (3.9 mmol) in 2 ml of THF. The mixture was allowed to get to room temperature and then 0.81 ml (13 mmol) of CH$_3$I was added under inert atmosphere of nitrogen. The solution was heated at 70°C for 2 h in a closed Schlenk tube. The product was isolated after chromatography on silica gel (eluent: hexane 19/diethylether 1) as a yellowish oil. Yield 98% (789 mg).

^{31}P NMR (CDCl$_3$): $\delta = 8.8$ ($^{1}J_{\mathrm{P-W}} = 250.4$ Hz). ^{1}H NMR (CDCl$_3$): $\delta = 1.1$ and 1.2 (2t, 6H, $^{3}J_{\mathrm{H-H}} = 7.2$ Hz, OCH$_2$C**H**$_3$), 1.6 (d, 3H, $^{3}J_{\mathrm{P-H}} = 14.0$ Hz, P—C—C**H**$_3$), 2.3 (d, 3H, $^{2}J_{\mathrm{P-H}} = 5.4$ Hz, P—C**H**$_3$), 4.1 (m, 4H, OC**H**$_2$CH$_3$), 7.5 (m, 5H, C$_6$**H**$_5$—P). ^{13}C NMR (CDCl$_3$): $\delta = 13.8$ and 14.8 (2s, OCH$_2$**C**H$_3$), 16.4 (d, $^{1}J_{\mathrm{P-C}} = 26.7$ Hz, P—**C**H$_3$), 19.7 (d, $^{2}J_{\mathrm{P-C}} = 4.8$ Hz, P—C—**C**H$_3$), 57.3 (d, $^{1}J_{\mathrm{P-C}} = 11.6$ Hz, P—C), 62.5 and 62.6 (2s, O**C**H$_2$CH$_3$), 131.0 (m, **C**$_6$H$_5$—P), 197.2 (d, $^{2}J_{\mathrm{P-C}} = 6.9$ Hz, $^{1}J_{\mathrm{W-C}} = 126.3$ Hz, **C**O cis), 199.0 (d, $^{2}J_{\mathrm{P-C}} = 25.2$ Hz, **C**O trans). *m/z* (^{184}W): 592 (M−CO, 7.2%), 564 (M − 2CO, 32.0%), 536 (M − 3CO, 100%), 508 (M − 4CO, 1.3%), 480 (M−5CO, 15.1%).

Synthesis of the Mixture **7a, 7b, 7c**

A sample of 200 mg (0.34 mmol) of **7** in 3 ml of THF was added dropwise at 65°C to a solution of 16.3 mg of NaH (0.68 mmol) in 2 ml of THF. The mixture was allowed to get to room temperature and then 0.043 ml (0.68 mmol) of CH$_3$I was added under inert atmosphere of nitrogen. The solution was heated at 70°C for 4 h in a closed Schlenk tube. The products were isolated after chromatography on silica gel (eluent: hexane 20/diethylether 1) as a white powder.

Diethyl [(dimethylphosphino)(methyl)-malonate]pentacarbonyltungsten **8c**

The product **8c** was formed in the same way as **7c**. Isolated as a yellowish powder. Yield 78.9% (572 mg).

^{31}P NMR (CDCl$_3$): $\delta = -2.5$ ($^1J_{\mathrm{P-W}} = 245.1$ Hz). ^{1}H NMR (CDCl$_3$): $\delta = 1.3$ (t, 6H, $^3J_{\mathrm{H-H}} = 7.2$ Hz, $\mathrm{OCH_2C\mathbf{H}_3}$), 1.6 (d, 3H, $^3J_{\mathrm{P-H}} = 14.4$ Hz, $\mathrm{P{-}C{-}C\mathbf{H}_3}$), 1.8 (d, 6H, $^2J_{\mathrm{P-H}} = 6.5$ Hz, $\mathrm{P(C\mathbf{H}_3)_2}$), 4.2 and 4.3 (2q, 4H, $^3J_{\mathrm{H-H}} = 7.2$ Hz, $\mathrm{OC\mathbf{H}_2CH_3}$). ^{13}C NMR (CDCl$_3$): $\delta = 14.1$ (s, $\mathrm{OCH_2\mathbf{C}H_3}$), 18.1 (d, $^1J_{\mathrm{P-C}} = 25.7$ Hz, $\mathrm{P{-}(\mathbf{C}H_3)_2}$), 18.6 (d, $^2J_{\mathrm{P-C}} = 5.7$ Hz, $\mathrm{P{-}C{-}\mathbf{C}H_3}$), 55.7 (d, $^1J_{\mathrm{P-C}} = 13.6$ Hz, $\mathrm{P{-}\mathbf{C}}$), 62.6 (s, $\mathrm{O\mathbf{C}H_2CH_3}$), 197.0 (d, $^2J_{\mathrm{P-C}} = 7.0$ Hz, $^1J_{\mathrm{W-C}} = 125.8$ Hz, **C**O cis), 199.35 (d, $^2J_{\mathrm{P-C}} = 23.9$ Hz, **C**O trans). *m*/*z* (^{184}W): 530 (M—CO, 32.8%), 502 (M−2CO, 43.5%), 474 (M−3CO, 100%), 447 (M$^+$ − 4CO, 17.9%), 417 (M−5CO, 46.4%). Anal calcd for $\mathrm{C_{15}H_{19}O_9PW}$: C, 32.28; H, 3.43. Found: C, 32.53; H, 3.46.

Diethyl [(phosphirano)malonate]pentacarbonyltungsten **11**

A sample of 200 mg (0.34 mmol) of 9 in 2 ml of THF was added dropwise to a solution of 56.7 mg (0.5 mmol) of ^{t}BuOK in 2 ml of THF at −65°C under inert atmosphere of nitrogen. The mixture was then allowed to get to room temperature, then was heated at 70°C for 13 h in a closed Schlenk tube. The product was isolated by chromatography on silica gel (eluent: hexane 17/diethylether 3) as a colorless oil. Yield: 38.2% (71 mg).

^{31}P NMR (CDCl$_3$): $\delta = -186.7$ ($^1J_{\mathrm{P-W}} = 272.0$ Hz). ^{1}H NMR (CDCl$_3$): $\delta = 1.32$ (m, 8H, $\mathrm{OCH_2C\mathbf{H}_3}$ + $\mathrm{P{-}C\mathbf{H}_2{-}C\mathbf{H}_2}$), 1.59 (m, 2H, $\mathrm{[P{-}C\mathbf{H}_2{-}C\mathbf{H}_2]}$), 3.24 (d, 1H $^2J_{\mathrm{P-H}} = 8.8$ Hz, $\mathrm{P{-}C\mathbf{H}}$), 4.28 (q, 4H, $^3J_{\mathrm{H-H}} = 7.2$ Hz, $\mathrm{OC\mathbf{H}_2CH_3}$). ^{13}C NMR (CDCl$_3$): $\delta = 9.79$ (d, $^1J_{\mathrm{P-C}} = 12.7$ Hz, $\mathrm{[P{-}\mathbf{C}H_2{-}\mathbf{C}H_2]}$), 14.3 (s, $\mathrm{OCH_2\mathbf{C}H_3}$), 55.1 (d, $^1J_{\mathrm{P-C}} = 2.3$ Hz, $\mathrm{P{-}\mathbf{C}H}$), 63.2 (s, $\mathrm{O\mathbf{C}H_2CH_3}$), 165.6 (s, $\mathrm{\mathbf{C}O_2C_2H_5}$), 195.3 (d, $^2J_{\mathrm{P-C}} = 9.2$ Hz, **C**O cis), 197.4 (d, $^2J_{\mathrm{P-C}} = 35.7$ Hz, **C**O trans). *m*/*z* (^{184}W): 542 (M, 2.8%), 514 (M−CO, 49.1%), 486 (M−2CO, 11.0%), 458 (M−3CO, 2.0%), 431 (M−4CO, 100%), 400 (M−5CO, 92.6%).

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