Rearrangement of Bis(alkylidynyl)phosphines to Phosphaacyls

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SUPPORTING INFORMATION

General Considerations

Unless otherwise stated, experimental work was carried out at room temperature under a dry and oxygen-free nitrogen atmosphere using standard Schlenk, vacuum line and inert atmosphere (argon) drybox techniques with dried and degassed solvents.

NMR spectra were obtained at 25°C on Varian Mercury 300 (1H at 300.1 MHz, 13C at 75.47 MHz, 31P at 121.5 MHz), Varian Inova 300 (1H at 299.9 MHz, 13C at 75.42 MHz, 31P at 121.4 MHz), Varian MR 400 (1H at 399.9 MHz, 13C at 100.5 MHz, 31P at 161.9 MHz), Bruker Avance 400 (1H at 400.1 MHz, 31P at 162.0 MHz), Varian Inova 500 (1H at 500.0 MHz, 13C at 125.7 MHz), Bruker Avance 600 (1H at 600.0 MHz, 13C at 150.9 MHz) or Bruker Avance 800 (1H at 800.1 MHz, 13C at 201.2 MHz) spectrometers. Chemical shifts (δ) are reported in ppm and referenced to the solvent peak (1H, 13C) or external 85% H3PO4 (31P) with coupling constants given in Hz. The multiplicities of NMR resonances are denoted by the abbreviations s (singlet), d (doublet), t (triplet), m (multiplet), br (broad) and combinations thereof for more highly coupled systems. Where applicable, the stated multiplicity refers to that of the primary resonance exclusive of 133W satellites. Whilst 13C{1H} signals for carbon nuclei of PPh and PCy groups could be routinely observed, their narrow spectral range and comparable JPC values on occasion precluded unequivocal assignment, in which case they are designated as 'C2,3,5,6(PPh)' or 'C2,3,5,6(Cy)'. In some cases, distinct peaks were observed in the 1H and 13C{1H} NMR spectra, but to the level of accuracy that is reportable (i.e. 2 decimal places for 1H NMR, 1 decimal place for 13C NMR) they are reported as having the same chemical shift.

Infrared spectra were obtained using a Perkin-Elmer Spectrum One FT-IR spectrometer. The strengths of IR absorptions are denoted by the abbreviations vs (very strong), s (strong), m (medium), w (weak), sh (shoulder) and br, (broad). Elemental microanalytical data were obtained from the ANU Research School of Chemistry microanalytical service. Electrospray ionisation mass spectrometry (ESI-MS) was performed by the ANU Research School of Chemistry mass spectrometry service with acetonitrile as the matrix. Data for X-ray crystallography were collected with a Agilent Xcalibur CCD, Agilent SuperNova CCD or Nonius Kappa CCD diffractometers and structures solved with the assistance of Dr Tony Willis whose help is gratefully acknowledged.

The complexes [M=ClBr(CO)x(Tp*)] have been described previously.1

Synthesis of [Mo=Cl(1BuPh)(CO)x(Tp*)] (1a) and PhP{C=Mo(CO)x(Tp*)}2 (1b)

The complex [Mo=ClBr(CO)x(Tp*)] (0.40 g, 0.74 mmol) was dissolved in THF (20 mL) and the solution was cooled in a dry ice/acetone bath for 20 minutes before n-butyllithium (1.6 M in n-hexane, 0.74 mmol) was added slowly by syringe. The initially bright yellow solution turned to pale orange immediately. After 30 minutes of stirring, PPhCl2 (0.05 mL, 0.37 mmol) was injected slowly by syringe. This reaction mixture was then stirred for one hour at −78 °C before being gradually warmed to room temperature over one hour. The mixture was re-cooled to −78°C and a second equivalent of n-butyllithium (0.74 mmol) was then injected into the resulting red-orange solution, and the resulting yellow-orange solution was stirred at low temperature for one hour before being allowed to warm to room temperature. After being freed of volatiles, the oily crude product was chromatographed over silica gel using a 10% DCN/n-hexane solution mixture at −15 °C. After a very faint yellow band, a peach- yellow band was collected, which yielded [Mo=Cl(1BuPh)(CO)x(Tp*)] (2) as an oily yellow residue. A small amount of red-orange solid from the
latter fraction was also isolated, which was identified as PhP[C=Mo(CO)₂(Tp*)]₂ (1a).

Data for 2: IR (C₆H₅): 1995s, 1916/1912s (split) νᵣ CO cm⁻¹. ¹H NMR (C₆D₆): δ₀ = 0.81 (t, 3 H, CH₂CH₃), δ₂ = 7.32 (m, 2 H, CH₂Me), δ₃ = 8.67 (s, 1 H, PCH₂), δ₄ = 4.20 (t, 2 H, PCH₂), δ₅ = 2.58 (s, 12 H, pzCH₂), δ₆ = 1.98 (s, 6 H, CH₃). The resulting light brown solution was stirred for 50 minutes. Nevertheless, partial spectroscopic data are as follows. IR (C₆H₅): 1995s, 1916/1912s (split) νᵣ CO cm⁻¹. ¹H NMR (C₆D₆): δ₀ = 0.81 (t, 3 H, CH₂CH₃), δ₂ = 7.32 (m, 2 H, CH₂Me), δ₃ = 8.67 (s, 1 H, PCH₂), δ₄ = 4.20 (t, 2 H, PCH₂), δ₅ = 2.58 (s, 12 H, pzCH₂), δ₆ = 1.98 (s, 6 H, CH₃). The resulting light brown solution was stirred for 50 minutes.

Data for 1a: An analytically pure sample of this compound could not be obtained as it degraded during cryostatic chromatography. Nevertheless, partial spectroscopic data are as follows. IR (C₆H₅): 1995s, 1916/1912s (split) νᵣ CO cm⁻¹. ¹H NMR (C₆D₆): δ₀ = 0.81 (t, 3 H, CH₂CH₃), δ₂ = 7.32 (m, 2 H, CH₂Me), δ₃ = 8.67 (s, 1 H, PCH₂), δ₄ = 4.20 (t, 2 H, PCH₂), δ₅ = 2.58 (s, 12 H, pzCH₂), δ₆ = 1.98 (s, 6 H, CH₃). The resulting light brown solution was stirred for 50 minutes.

Synthesis of CyP{C=W(CO)₂(Tp*)}₂ (1b)
A solution of [W(≡CBr)(CO)₂(Tp*)] (1.000 g, 1.60 mmol) and [Pd(PPh₃)₂] (0.088 g, 0.076 mmol, 5 mol% - not optimised) in benzene (40 mL) was treated with triethylamine (0.26 mL, 1.9 mmol) and phenylphosphine (1.25 mL, 0.63 M in hexane, 0.788 mmol) and the reaction mixture was heated to reflux. After 18 hours the dark brown solution was allowed to cool and the solvent was removed under reduced pressure. The crude mixture was chromatographed on silica gel using hexane as the eluent initially, then increasing the polarity to 2:1 toluene:hexane. The initial yellow and brown fractions were collected and discarded, and the following major red-orange band containing the product was collected. The solvent was removed under reduced pressure and the residue was dissolved in CH₂Cl₂. Ethanol was added and the solution was concentrated on the rotary evaporator to afford 1b as an orange powder. Crystals suitable for crystallographic analysis were grown from a solution of 1b in benzene/Et₂O/pentane at ~20°C. Yield 0.640 g (0.531 mmol, 67%). IR (Nujol): 2549w ν₅H, 2010sh, 1970s, 1913s, 1905sh, 1887s. N.B.: Upon standing in solution in air, 2 cleanly decomposed to a second compound, presumably to be the phosphine oxide [Mo≡C=P(Bu)₆] (CO)₂(Tp*) which was however not pursued further. ¹H NMR (C₆D₆): δ₀ = 0.81 (t, 3 H, CH₂CH₃), δ₂ = 7.32 (m, 2 H, CH₂Me), δ₃ = 8.67 (s, 1 H, PCH₂), δ₄ = 4.20 (t, 2 H, PCH₂), δ₅ = 2.58 (s, 12 H, pzCH₂), δ₆ = 1.98 (s, 6 H, CH₃). The resulting light brown solution was stirred for 50 minutes.

ESI-MS (+) m/z: 627.19 [M⁺H⁺], 645.18 [M⁺OH⁺].

Synthesis of CyP{C=W(CO)₂(Tp*)}₂ (1c)
A solution of [W(≡CBr)(CO)₂(Tp*)] (0.250 g, 0.40 mmol) in THF (10 mL) was cooled to ~70°C and treated with nBuLi (2.5 M in hexanes, 0.16 mL, 0.40 mmol). The resulting light brown solution was stirred for 50
minutes and then treated with PCl₃Cy (1.0 M in THF, 0.20 mL, 0.20 mmol). The solution instantly turned red and was stirred for a further 30 minutes then allowed to warm to room temperature. Volatiles were removed under reduced pressure. The residue was chromatographed on silica gel using hexane as the eluent. The polarity was gradually increased to 2:1 hexane:THF. The first yellow band (containing [W(=CBr)(CO)₅(Tp⁺)]) was discarded, and the second (orange) band containing the product was collected. The solvent was removed under reduced pressure to afford 1c as a red-orange powder. Crystals suitable for crystallographic analysis were grown from a solution of 1c in benzene/hexane at 12°C. Yield 0.136 g (0.121 mmol, 57%). IR (Nujol): 2546 w, 2006 sh, 1969s, 1905s, 1891s, 1883 s cm⁻¹. IR (THF): 2548 w, 1980m, 1969s, 1988 s, 1833 s cm⁻¹. 1H NMR (C₆D₆) δ₁H = 5.45 (s, 4 H, pzH), 5.32 (s, 2 H, pzH), 2.63 (s, 12 H, pzCH₃), 2.37 (s, 6 H, pzCH₃), 2.26 - 2.11 (m, 2 H, C₆H₄), 2.08 (s, 12 H, pzCH₃), 2.01 (s, 6 H, pzCH₃), 1.68 - 1.13 (m, 9 H, C₆H₃). 13C{1H} NMR (C₆D₆) δc = 291.1 (d, Wc = 80.3, JPC = 190.1), 227.1 (br, CO), 152.6 (4 C), 152.5 (2 C), 144.8 (2 C), 143.7 (4 C) [C(3-5)(pz)], 107.0 (2 C), 106.7 (4 C) [C(6)(pz)], 41.2 (d, C₆H₁₁), JPC = 11.2), 31.3 (d, C₆H₁₁, JPC = 12.2), 27.4 (d, C₆H₁₁, JPC = 11.8 Hz), 26.6 [C(4)(C₆H₁₁)], 17.0 (4 C), 15.2 (2 C), 12.5 (4 C), 12.3 (2 C) (pzCH₃). 31P{1H} NMR (C₆D₆) δp = 89.9 (JWP = 67.5). 31P{1H} NMR (CDCl₃) δp = 87.8 (JWP = 68.0). ESI-MS (+): m/z 1213.3 [M + H⁺]. Accurate mass: found 1213.3494 [M + H⁺]. Calcd. for C₆₂H₅₈N₂₁O₁₅P₁₈₄W₂: 1213.3490. Anal. found: C, 41.79; H, 4.67; N, 13.62%. Calcd. for C₄₀H₄₅B₂N₁₂O₄P₁₈₄W₂: C, 41.61; H, 4.57; N, 13.86%. Crystal data for C₆₂H₅₈B₂N₁₂O₄PW₂C₆H₄: Mw = 1290.39, monoclinic, P2₁/c, a = 24.2055(3), b = 10.4092(1), c = 25.5107(3) Å, β = 105.9841(6)°, V = 6179.17(12) Å³, Z = 4, ρcalcd = 1.387 Mg m⁻³, μ(Mo Kα) = 3.79 mm⁻¹, T = 200(2) K, orange plate, 0.19 × 0.18 × 0.09 mm, 14148 independent reflections. F⁻² refinement, R = 0.038, wR = 0.100 for 10493 reflections (I > 2σ(I), 2θmax = 55°), 622 parameters.

**Synthesis of CIP{W(CO)₅(Tp⁺)}₂ (1d)**

A solution of [W(=CBr)(CO)₅(Tp⁺)] (0.100 g, 0.159 mmol) in THF (5 mL) was cooled to –78°C and treated with nBuLi (0.45 M in hexanes, 0.42 mL, 0.19 mmol). The resulting light brown solution was stirred for 30 minutes and then treated with PCl₃ (0.30 M in hexane, 0.27 mL, 0.081 mmol). The solution instantly turned dark red and was stirred for a further 30 minutes then allowed to warm to room temperature. Volatiles were removed under reduced pressure. The residue was extracted with benzene (5 mL), filtered, and the solvent was removed under reduced pressure to afford crude 1d as a dark red solid (ca 72% 1d and ca 12% 3d by 31P{1H} NMR spectroscopy). Combined yield 0.083 g (0.071 mmol, 90%). IR (THF): 2550 w, 1996s, 1866s, 1906s νCO cm⁻¹. 1H NMR (C₆D₆) δ₁H = 5.48 (s, 4 H, pzH), 5.32 (s, 2 H, pzH), 2.69 (s, 6 H, pzCH₃), 2.54 (s, 6 H, pzCH₃), 2.31 (s, 6 H, pzCH₃), 2.09 (s, 12 H, pzCH₃), 2.02 (s, 6 H, pzCH₃). 13C{1H} NMR (C₆D₆) δc = 280.0 (d, Wc = 97.9, JPC = 194.0), 226.4 (CO, JWC = 164.5), 225.0 (CO, JWC = 166.0), 152.8 (2 C), 152.6 (2 C), 152.2 (2 C), 145.4 (2 C), 144.4 (2 C), 144.3 (2 C) [C(3,5)(pz)], 107.4 (2 C), 106.9 (4 C) [C(4)(pz)], 17.3 (2 C), 17.0 (2 C), 15.2 (2 C), 12.6 (4 C), 12.5 (2 C) (pzCH₃). 31P{1H} NMR (C₆D₆) δp = 124.9 (JWP = 66.4). The complex could not be purified due to hydrolytic sensitivity precluding chromatography and its gradual conversion to 3d, which had similar solubility.

**Synthesis of (μ-PhPCC){W(CO)₅(Tp⁺)}₂ (3b)**

A solution of 1b (0.192 g, 0.16 mmol) in toluene (15 mL) was heated under reflux for 42 hours. The dark purple suspension was filtered and the volatiles were removed under reduced pressure. The solid was extracted with benzene (5 mL) and filtered, then layer with hexane (5 mL) and cooled to 4°C. The resulting purple precipitate was isolated by filtration and found to contain 3b as the major product (ca 65% by 31P{1H} NMR spectroscopy). Crystals suitable for crystallographic analysis were grown from a solution of 3b in a mixture of benzene and hexane at –12°C. IR (toluene): 2548 vw, 1970m, 1941vs, 1876vs, 1858s νCO cm⁻¹. 1H NMR (C₆D₆) δ₁H = 8.19 (m, 2 H, C₆H₄), 7.34 (m, 3 H, C₆H₃), 5.69, 5.66 (s x 2, 1 H x 2, pzH), 5.46, 5.24 (s x 2, 2 H x 2, pzH), 2.67, 2.62, 2.53, 2.26, 2.24 (s x 5, 5 H x 5, pzCH₃), 2.17 (s, 6 H, pzCH₃), 2.15, 2.13, 2.01, 1.94 (s x 4, 3 H x 4, pzCH₃), 1.72 (s, 3 H, pzCH₃). 31P{1H} NMR (C₆D₆) δp = –74.5 (br.). ESI-MS (+): m/z 1207.3 [M + H⁺]. Accurate mass: found 1207.3021 [M + H⁺]. Calcd. for C₆₂H₅₈B₂N₁₂O₄PW₂C₆H₄: Mw = 1284.34, orhombic, Pca₂₁, a = 24.8643(5), b = 10.7400(2), c = 19.2900(4) Å, V = 5151.3(2) Å³, Z = 4, ρcalcd = 1.656 Mg m⁻³, μ(Mo Kα) = 4.55 mm⁻¹, T = 200(2) K, dark purple block, 0.10 × 0.07 × 0.06 mm, 8997 independent reflections. F² refinement, R = 0.043, wR = 0.089 for 6669 reflections (I > 2σ(I), 2θmax = 55°), 623 parameters.

**Synthesis of (μ-CIPCC){W(CO)₅(Tp⁺)}₂ (3d)**

A solution of 1d (0.083 g, 0.071 mmol) in C₆D₆ (0.5 mL) was heated to 50°C. After 13 hours 31P{1H} NMR spectroscopy of the dark magenta solution indicated formation of 3d as the major product (ca 75% by
$^{31}$P($^1$H) NMR spectroscopy. Crystals suitable for crystallographic analysis were grown by slow diffusion of $n$-pentane into a solution of 3d in CH$_2$Cl$_2$ at −15°C. 

$^1$H NMR (C$_6$D$_6$) $\delta$H = 5.51, 5.48, 5.47, 5.34, 5.32, 5.29 (s x 6, 1 H x 6, pzH), 2.74, 2.68, 2.54, 2.51, 2.30, 2.24 (s x 6, 3 H x 6, pzCH$_3$), 2.11 (s, 9 H, pzCH$_3$), 2.08 (s, 6 H, pzCH$_3$), 2.01 (s, 3 H, pzCH$_3$). $^{31}$P($^1$H) NMR (C$_6$D$_6$) $\delta$P = 92.7 (br., h.h.w. ≈ 50 Hz). Crystal data for C$_{36}$H$_{44}$B$_2$ClN$_{12}$O$_4$PW$_2$·(CH$_2$Cl$_2$)$_2$: $M_w$ = 1334.44, monoclinic, $P2_1/c$, $a$ = 22.1833(6), $b$ = 10.5501(3), $c$ = 23.1940(4) Å, $\beta$ = 114.4551(14)$^\circ$, $V$ = 4941.2(2) Å$^3$, $Z$ = 4, $\rho_{calc}$ = 1.794 Mg m$^{-3}$, $\mu$(Mo K$\alpha$) = 5.01 mm$^{-1}$, $T$ = 200(2) K, dark red block, 0.09 × 0.06 × 0.04 mm, 8702 independent reflections. $F^2$ refinement, $R$ = 0.096, $wR$ = 0.242 for 6928 reflections ($I > 2\sigma(I)$, $2\theta_{\text{max}}$ = 50$^\circ$), 576 parameters.
Optimized Geometry of trimethylphosphirene
(DFT: B3LYP-6-311++G**)

Optimized Geometry of trimethylazirene
(DFT: B3LYP-6-311++G**)

Solution Infrared (THF) Spectrum of 1b
Solid State (Nujol) Infrared Spectrum of 1b
$^1$H NMR Spectrum (400 MHz) of 1b in C$_6$D$_6$
$^{13}\text{C}^\text{1H} \text{ NMR (150.9 MHz) Spectrum of 1b in C}_6\text{D}_6$

$^{1}\text{H} \text{ NMR Spectrum (161.9 MHz) of 1b in C}_6\text{D}_6$
Solution Infrared (THF) Spectrum of 1c
Solid State (Nujol) Infrared Spectrum of 1c
$^1$H NMR Spectrum (400 MHz) of 1c in CDCl$_3$

$^{31}$P{$^1$H} NMR Spectrum (161.9 MHz) of 1c in CDCl$_3$
Solution Infrared (THF) Spectrum of 1d

$^{31}P\{^1H\}$ NMR Spectrum (161.9 MHz) of 1d in CDCl$_3$
$^{13}$C($^1$H) NMR Spectrum (150.9 MHz) of 1d in CDCl$_3$

$^1$H NMR Spectrum (400 MHz) of 1d in CDCl$_3$
Solution Infrared (toluene) Spectrum of 3b

Solid State (Nujol) Infrared Spectrum of 3b
$^1$H NMR Spectrum (300 MHz) of 3b in C$_6$D$_6$

$^{31}$P{$^1$H} NMR Spectrum (121.5 MHz) of crude reaction mixture for 1b-3b Conversion (42 hours @ 110°C)

Unidentified side products and Decomposition products of 3b (increase with time)