Simple Generation of a Dirhodium μ-Carbido Complex via Thiocarbonyl Reduction

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General Considerations

All reactions involving air-sensitive compounds were carried out under a dry and oxygen-free nitrogen atmosphere using standard Schlenk and vacuum line techniques, with the use of dried and degassed solvents.

NMR spectra were obtained at 298 K with Bruker Avance 400 (1H at 400.1 MHz, 31P at 161.9 MHz, 11B at 128.4 MHz, 19F at 376.5 MHz and 13C at 100.5 MHz), Bruker Avance 600 (1H at 600.1 MHz, 31P at 242.9 MHz, and 13C at 192.5 MHz) or Bruker Avance 700 (1H at 700.1 MHz, 31P at 283.5 MHz, and 13C at 176.1 MHz) spectrometers. Chemical shifts (δ) are reported in ppm and referenced internally to the solvent peak for 1H and 13C, an external H3PO4 reference for 31P NMR, an external BF3·OEt2 reference for 11B NMR, and an external CFC13 (δs = 0.00 ppm) reference for 19F NMR. The couplings for multiplicities of the NMR resonances, JAB, are reported in Hz. Virtual triplet 13C resonances characteristic of trans-bis(PPh3) ligands are denoted t with the apparent coupling constant given.

Solution and Nujol Infrared spectra were obtained using a Perkin-Elmer Spectrum One FT-IR spectrometer, and ATR solid state spectra were obtained with a Perkin-Elmer FT-IR Spectrometer. Elemental microanalysis was performed at the London Metropolitan University. High- and Low-Resolution Electrospray Ionisation Mass Spectrometry (ESI-MS) was performed by the ANU Research School of Chemistry mass spectrometry service, using acetonitrile for the matrix.

Data for the X-ray crystallography analysis were obtained on either an Oxford Diffraction Xcalibur or Oxford Diffraction SuperNova diffractometer and processed using the Olex suite of software. The Check cif -validated .cif files are available on request from the Cambridge Crystallographic Data Centre. The known compounds [RhCl(PPh3)3] and [RhCl(CS)(PPh3)] were prepared as described below in accordance with the literature, and remaining reagents were obtained from commercial sources.

Synthesis of [Rh2(μ-C)Cl2(PPh3)4] (2)

The complex RhCl(CS)(PPh3)2 (1: 550 mg, 0.778 mmol) was partially dissolved in dry benzene (40 mL). A solution of H2Cat in THF (8.0 mL, 0.30 M, 2.4 mmol) was added and the solution stirred with heating at 50°C for fifteen hours. The solution was concentrated under reduced pressure and the orange product 2 which precipitated by addition of benzene (20 mL) was isolated via cannula filtration and dried in vacuo. Yield 214 mg (0.160 mmol, 41%). 1H NMR (CDCl3, 400 MHz) δH = 7.13-7.17 [m, 1H, 24 H, H2(C6H5)], 7.27-7.30 [m, 12 H, H4(C6H5)], 7.39-7.44 [m, 24 H, H3(C6H5)]. 13C NMR (CDCl3, 176 MHz) δC = 42.4.0 (t.br, μ-C, JN=C not resolved), 134.9 [t', C(H6)], J = 6], 133.1 [t', C2H(C6H5), J = 22], 129.4 [t', C3H(C6H5), J = 5 Hz], 127.9 [C(C6H5)J] NMR (CDCl3, 162 MHz) δC = 21.61 (dd, J= 6, J= 180, J= 7 Hz), IR (ATR, cm⁻1) νmax = 1011 (ν357-CR6). MS-ESI(+) m/z = 1301.14 [M+Cl]⁺, 1039.05 [M+Cl-PPh]⁺. Accurate mass: found 1301.1438 [M+Cl+H]⁺. Calc. for C73H50Cl4P4Rh2: 1301.1444. Anal. found: C, 62.90%; H, 4.62%. Calcd. for C73H50Cl4P4Rh2: C, 62.47; H, 4.39%. The compound was structurally characterized as a dichloromethane monosolvate through single crystal X-ray crystallography. Crystal data for C73H50Cl4P4Rh2: Mr = 1422.73, triclinic, P-1 (No. 2), a = 12.5983(2), b = 13.8742(3), c = 20.5650(4) Å, α = 85.461(2), β = 84.238(1), γ = 75.285(1)°, V = 3453.74(12) Å⁴, Z = 2, μ(Cu Kα) = 6.47 mm⁻¹, T = 150.0(1) K, red block 0.27 × 0.14 × 0.09 mm, 13,963 independent reflections, F² refinement, R₁ = 0.0345, wR₂ = 0.090 for 12,988 reflections (l > 2σ(l)), 2θ max = 147.6°), 757 parameters. The asymmetric cell contained one molecule of Rh2(μ-C)Cl2(PPh3)4, a molecule of DCM and what was believed to be an additional two heavily disordered DCM molecules. No sensible disordered model could be formulated for the unknown solvates which would match the observed

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Synthesis of [Rh₂(μ-C)(PPh₃)₂(H₂B(pzMe₂)₂)] (5a)

Complex 2 (116 mg, 0.0867 mmol) and K[HB(pz)] (62 mg, 0.33 mmol) were dissolved in dry dichloromethane (20 mL). The orange solution was stirred with heating at reflux for 12 hours. The red solution was concentrated under reduced pressure then diluted with ethanol (10 mL). The red compound was recovered. The formula weight, density etc. listed above do not include any correction for the missing solvate.

Synthesis of [Rh₂(μ-C)(PPh₃)₂(H₂B(pzMe₂)₂)] (5b)

The complex 2 (150 mg, 0.112 mmol) and K[HB(pzMe₂)] (100 mg, 0.413 mmol) were dissolved in dry dichloromethane (20 mL). The solution was stirred with heating at reflux for three hours, turning red in colour. The solution was concentrated under reduced pressure, and ethanol (10 mL) added to precipitate the orange product, which was isolated via vacuum filtration and dried in vacuo. Yield: 42 mg (0.037 mmol, 33%). 1H NMR (400 MHz, CDCl₃) δH = 1.43, 2.00, 2.31 [s x 3, 23 H, pZCH₂], 3.33 [br. d, 2 H, BH₂], 5.02, 5.85 [s x 2, 4 H, H₁(Pz)], 6.93, 7.14, 7.29 [m x 3, 30 H, CH₃]. 31P(1H) NMR (162 MHz, CDCl₃) δP = 38.62 (d, JHH = 222 Hz). 31B{1H} NMR (128 MHz, CDCl₃) δB = −12.5 (br.). 13C{1H} NMR (151 MHz, CDCl₃) δC = 148.6, 148.0, 143.1 [C₃{(C₃Pz)}], 134.7 [d, C(CH₂), JHH = 12], 132.5 [d, C₃{(C₃Pz)}], JHH = 25 Hz], 129.2 [br. d, C₅{(C₃H₄)}, JHH = 50 Hz], 127.3 [d, C₃{(C₃H₄)}, JHH = 9 Hz], 106.0, 104.7 [C{(Hz)}], 13.8, 12.9, 12.0 (pzCH₃). IR (ATR, cm⁻¹) vmax = 2458 (vBH), 1538 (vCeC), 1373 (vCeN), 1159 (vCeN), 978 (vα=C-α). Accurate mass: found 1117.07132 [M-pz* + MeCN + Na⁺]. Calcd. for C₉₀H₂₁₁B₃N₂Na₂P₉Rh₂: 1117.2423. The compound was structurally characterised through single crystal X-ray crystallography of a hexane solvate. Crystal data for C₉₀H₂₁₁B₃N₂P₉Rh₂·C₆H₆: Mw = 1234.69, monoclinic, I2/a, a = 18.7605(7), b = 13.5447(6), c = 23.3266(10), β = 99.55(4), V = 5851.9(4) Å³, Z = 4, ρcalc = 1.401 Mgm⁻³, μ(Mo Kα) = 0.67 mm⁻¹, T = 150.0(1) K, red plate, 0.48 × 0.36 × 0.24 mm, 5971 independent reflections, F² refinement, R1 = 0.047, wR2 = 0.128 for 4551 reflections (I > 2o(I), 20max = 26.4°), 361 parameters, no restraints. The asymmetric cell contained one molecule of Rh₂(μ-C)(Bp*)₂(PPh₃)₁ with one solvent molecule of n-hexane present.

Synthesis of [Rh₂(μ-C)(PPh₃)₂(HB(pz)] (6a)

The complex 2 (150 mg, 0.112 mmol) and K[HB(pz)] (102 mg, 0.409 mmol) were dissolved in dry dichloromethane (25 mL). The orange solution was stirred at room temperature for 16 hours, turning red in colour. The solution was concentrated under reduced pressure and then diluted with ethanol (10 mL) before the remaining DCM was removed slowly. The red product precipitated in the ethanol solution, and was isolated via vacuum filtration. The product was washed with cold ethanol and dried in vacuo. Yield 62 mg (0.053 mmol, 48%). 1H NMR (400 MHz, CDCl₃) δH = 4.53 (br., BH), 5.82 [s x 6, 1 H, H₃(pz)], 6.88, 7.13, 7.24, 7.51, 7.66 [m x 5, 42 H, CH₃ and H₃(pz)]. 31P{1H} NMR (162 MHz, CDCl₃) δP = 42.64 (d, JHH = 214 Hz). 13B{1H} NMR (128 MHz, CDCl₃) δB = −3.16 (br.). 13C{1H} NMR (151 MHz, CDCl₃) δC = 135.6, 135.5 [C{(C₃Pz)}], 135.2 [d, C(CH₂), JHH = 9 Hz], 132.3 [d, C₅{(C₃H₄)}, JHH = 10], 132.1, 132.0 [C{(C₃Pz)}], 130.9 [d, C₅{(C₃H₄)}, JHH = 14], 128.6 [d, C(CH₂), JHH = 12], 106.6, 105.5 [C{(Hz)}]. IR (ATR, cm⁻¹) vmax = 2458 (vBH), 1530 (vCeC), 1260 (vCeN), 1111 (vα=C-α). Accurate mass: found 1169.2139 [M⁺H]. Calcd. for C₆₀H₁₂₁B₃N₂P₉Rh₂: 1169.4544. Anal. found: C, 52.29; H, 4.27; N, 11.40%. Calcd. for C₆₀H₁₂₁B₃N₂P₉Rh₂(CH₃Cl₂)₁₂: C, 52.33; H, 4.20; N, 12.96%. The compound was structurally characterised through single crystal X-ray crystallography.

Synthesis of [Rh₂(μ-C)(μ-C₆H₄PPh₃)₂(HB(pz-Me₂)] (7)

The complex 2 (150 mg, 0.112 mmol) and K[HB(pzMe₂)] (75 mg, 0.22 mmol) were dissolved in dry dichloromethane (20 mL)

The program identified solvent accessible voids totalling 454.6 Å³ and 133.8 electrons per unit cell were recovered. The formula weight, density etc. listed above do not include any correction for the missing solvate.
and the solution was stirred at room temperature for three hours, turning dark red in colour. The solution was concentrated under reduced pressure, and dry ethanol added to precipitate the dark red product, which was washed with cold ethanol and dried in vacuo. Yield 82 mg (0.061 mmol, 54%). $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta_H =$ -12.86 (ddd, 1 H, RhH, $\delta_{J_{Rh}} = 29$, $\delta_{J_{Rh}} = 25$, $\delta_{J_{Net}} = 3$ Hz), 7.85, 7.47, 7.43, 7.28, 7.09, 7.03, 6.85, 6.73 [m x 8, 14 H, C$_6$H$_2$, and C$_7$H$_7$], 5.66 (2H), 5.64, 5.60, 5.44, 5.42 [s x 5, 6 H, H$_2$(pz)], 4.46 (s v.br, 1 H, BH), 2.69, 2.38, 2.33, 2.29, 2.26, 2.22, 2.19, 2.09, 1.72, 1.67, 1.56, 1.02 (pzCH$_3$). $^{31}$P($^{1}$H) NMR (162 MHz, CDCl$_3$) $\delta_P =$ 60.70 (dd, $\delta_{J_{BH}} = 226$, $\delta_{J_{BH}} = 35$ Hz). $^{13}$B($^{1}$H) NMR (128 MHz, CDCl$_3$) $\delta_B =$ -9.06 (br. Not resolved). $^{13}$C($^{1}$H) NMR (151 MHz, CDCl$_3$) $\delta_C =$ 15C NMR (151 MHz, CDCl$_3$) 447.2 [ddd, $\delta_{J_{BH}}C =$ 50.3, 39.9, $\delta_{J_{PC}}C =$ 19.6, HMBC with $\delta_H =$ -12.7; Rh=C=Rh], 165.4 [HMBC with $\delta_H =$ -12.7, C$_2$(PC$_6$H$_4$:Rh)], 151.6, 151.2, 150.4, 149.7, 149.5, 148.8 [C(pz)], 145.0, 144.9, 143.4, 143.3, 143.0, 143.0 [C(pz)], 140.6 [d, $\delta_{J_{PC}}C =$ 18.2, C$_2$(PC$_6$H$_4$:Rh)], 137.1 [d, $\delta_{J_{PC}}C =$ 11.2, C$_2$(C$_6$H$_5$)], 135.6 [d, $\delta_{J_{PC}}C =$ 11.2, C$_2$(PC$_6$H$_4$:Rh)], 132.4 [d, $\delta_{J_{PC}}C =$ 55.1, C$_2$(C$_6$H$_5$)], 131.70 [d, $\delta_{J_{PC}}C =$ 37.9, C$_2$(C$_6$H$_5$)], 131.1 [d, $\delta_{J_{PC}}C =$ 13.7, C$_2$(PC$_6$H$_4$:Rh)], 127.84 [d, C$_2$(C$_6$H$_5$), $\delta_{J_{PC}}C =$ 10.0], 127.73, [d, C$_2$(C$_6$H$_5$), $\delta_{J_{PC}}C =$ 11.0], 126.7 [C$_2$(PC$_6$H$_4$:Rh)], 112.3 [d, $\delta_{J_{PC}}C =$ 8.3 Hz, C$_2$(PC$_6$H$_4$:Rh)], 106.3, 106.2, 105.6(2C), 105.3, 105.1 [C(pz)], 16.6, 15.7, 15.4, 14.8, 14.7, 14.4, 13.9, 13.1, 12.91, 12.85, 12.8, 12.7 [pzCH$_3$]. The quaternary resonance for the ortho bridging carbon (expected to be a ddd) was unable to be unambiguously identified in the 1-D $^{13}$C($^{1}$H) NMR spectrum due to multiplicity and poor signal/noise. It could however be identified via a HMBC $^{1}$H-$^{13}$C experiment at 165.4 ppm through correlation to the hydride resonance. IR (ATR, cm$^{-1}$): 2521 (v$_{NO}$), 2076 (v$_{RhH}$), 1544 (v$_{C-C}$), 1382 (v$_{CN}$), 1203 (v$_{CN}$), 1003 (v$_{Rh-C}$-Rh). MS-ESI(+)$: m/z = 1075.31 [M+H]$^+$. Accurate mass: found 1075.3123 [M+H]$^+$. Calcd. for C$_{36}$H$_{46}$O$^{+}$: C, 45.82; H, 4.25; N, 9.17%. Calcd. for C$_{36}$H$_{48}$B$_{2}$N$_{2}$PRh$_{2}$: C, 46.98; H, 4.93; N, 12.64%. The compound was structurally characterised through single crystal X-ray crystallography. Crystal data for C$_{36}$H$_{48}$B$_{2}$N$_{2}$PRh$_{2}$: M$_{w}$ = 1074.49, monoclinic, C2/c, a = 26.2284(10), b = 10.6335(4), c = 38.1123(13) Å, β = 97.948(4)*, V = 10527.6(7) Å$^3$, Z = 8, $\rho_{calcd} = 1.356$ Mgm$^{-3}$, $T = 150.0(1)$ K, red needle, 0.30 × 0.09 × 0.06 mm, 9,285 independent reflections, $F^2$ refinement, $R_1 = 0.059$, $wR_2 = 0.126$ for 6,797 reflections ($I > 2\sigma(I)$, $2\theta_{max} = 25.0^\circ$), 611 parameters, 1 restraint.
$^1$H NMR Spectrum of [Rh$_2$(µ-C)Cl$_2$(PPh$_3$)$_4$] (2)
$^{31}\text{P}^{1\text{H}}$ NMR Spectrum of $[\text{Rh}_2(\mu-\text{C})\text{Cl}_2(\text{PPh}_3)_4]$ (2)
$^{13}$C{$^{1}$H} NMR Spectrum of [Rh$_2$(μ-C)Cl$_2$(PPh$_3$)$_4$] (2)(Inset: Carbido atom ca 50% $^{13}$C enriched, originating from enriched $^{13}$CS$_2$)
$^1$H NMR Spectrum of [Rh$_2$(µ-C)(Bp)$_2$(PPh$_3$)$_2$] (5a)
$^{31}\text{P}^{1\text{H}}$ NMR Spectrum of [Rh$_2$(μ-C)Cl$_2$(PPh$_3$)$_4$] (5a)
$^{11}\text{B}^{1}H\text{ NMR Spectrum of } [\text{Rh}_2(\mu\text{-C})(\text{Bp})_2(\text{PPh}_3)_2] \text{ (5a)}$
$^{13}\text{C}^1\text{H}$ NMR Spectrum of $[\text{Rh}_2(\mu-C)(\text{Bp})_2(\text{PPh}_3)_2]$ (5a)
$^1$H NMR Spectrum of [Rh$_2$(µ-C)(Bp*)(PPh$_3$)$_2$] (5b)
$^{31}$P$^{1}$H NMR Spectrum of [Rh$_2$(µ-C)(Bp*)$_2$(PPh$_3$)$_2$] (5b)
$^{11}$B$^{1}H$ NMR Spectrum of $[\text{Rh}_2(\mu-C)(\text{Bp}^*)(\text{PPh}_3)_2] \ (5b)$
$^{13}$C{¹H} NMR Spectrum of [Rh$_2$(µ-C)(Bp*)$_2$(PPh$_3$)$_2$] (5b) (Poorly soluble)
$^1$H NMR Spectrum of [Rh$_2$(µ-C)(Tp)$_2$(PPh$_3$)$_2$] (6a)
$^{31}\text{P}^{1\text{H}}$ NMR Spectrum of $[\text{Rh}_2(\mu-\text{C})(\text{Tp})_2(\text{PPh}_3)_2]$ (6a)
$^{11}$B$^{1}{\text{H}}$ NMR Spectrum of [Rh$_2$(μ-C)(Tp)$_2$(PPh$_3$)$_2$] (6a)
$^{13}\text{C}^1\text{H}$ NMR Spectrum of \([\text{Rh}_2(\mu-C)(\text{Tp})_2(\text{PPh}_3)_2]\) (6a) [Poor solubility]
$^{1}H$ NMR Spectrum of $[\text{Rh}_2(\mu-\text{C})\text{H(Tp}^*\text{)}]_2(\text{C}_6\text{H}_4\text{PPh}_2-2)$] (7)
$^{31}$P\(^{1}H\) NMR Spectrum of [Rh\(_2\)(µ-C)H(Tp\(^{*}\))\(_2\)(C\(_6\)H\(_4\)PPh\(_2\)-2)] (7)


$^{11}\text{B}^{[1\text{H}]} \text{NMR Spectrum of } [\text{Rh}_2(\mu-\text{C})\text{H}(\text{Tp}^*)_2(\text{C}_6\text{H}_4\text{PPh}_2-2)]$ (7)
$^{13}$C$^1$H NMR Spectrum of [Rh$_2$(µ-C)H(Tp$^*$)$_2$(C$_6$H$_4$PPh$_2$-2)] (7) [50% $^{13}$C enriched at Rh$_2$C]
$^{13}\text{C}-^1\text{H}$ HMBC NMR Spectrum of $[\text{Rh}_2(\mu-\text{C})\text{H}({\text{Tp}^*})_2(\text{C}_6\text{H}_4\text{PPh}_2-2)]$ (7) showing weak correlation between hydride and carbide/aryl resonances (magnitude phased, f2).
High frequency (hydride region) $^1$H NMR spectrum of [Rh$_2$(μ-C)H(Tp*)(C$_6$H$_4$PPh$_2$-2)] (7)