Chemical Communications



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Halogenation of A-Frame μ -Carbido Complexes to Afford μ_2 -Halocarbynes

Harrison J. Barnett and Anthony F. Hill*

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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, 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. Chemicals shifts (δ) are reported in ppm and referenced internally to the solvent peak for ¹H and ¹³C, and external H₃PO₄ reference for ³¹P NMR. The couplings for multiplicities of the NMR resonances, ⁿJ_{AB}, are reported in Hz. For ³¹P NMR environments which were second order in nature, both the observed and simulated (in parentheses) coupling constants are presented. Simulations were run using gNMR.

ATR solid state spectra were obtained with a PerkinElmer FT-IR Spectrometer. Elemental microanalytical data were provided by 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 Checkcif-validated .cif files are available on request from the Cambridge Crystallographic Data Centre. The known compound $[Rh_2(u-C)Cl_2(PPh_3)_4]$ was prepared as described in the literature, and remaining reagents were obtained from commercial sources.

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Synthesis of [Rh₂(µ-C)Cl₂(dppm)₂] (5a)

[Rh₂(µ-C)Cl₂(PPh₃)₄] (100.0 mg, 0.075 mmol) and dppm (150 mg, 0.390 mmol) were dissolved in dry DCM (10 mL). The red solution was stirred at room temperature for 24 hours. The solution was concentrated under reduced pressure, and nhexane added until a red precipitate formed. The precipitate was isolated via vacuum filtration, washed with cold hexane and ether, and dried in vacuo. Received 77 mg (0.073 mmol, 97% yield) of yellow product. ¹H NMR (400 MHz, CDCl₃) δ_{H} = 7.78 (br. s, 15 H, Ph), 7.31 - 7.25 (m, 25 H, Ph), 2.90 (s, 4 H, CH₂). ³¹P{¹H} NMR (162 MHz, CDCl₃) δ_P = 19.12 (m, ¹J_{RhP} = 191 (150) Hz, ²J_{RhP} = 38 (40) Hz, ${}^{4}J_{PP}$ = (2.3) Hz). ${}^{13}C$ NMR (192.5 MHz, CDCl₃) δ_{C} = 134.2 [br., C^{2,6}(C₆H₅)], 132.2 [m, C¹(C₆H₅)], 130.5 [C^{3,5}(C₆H₅)], 128.4 [C⁴(C₆H₅)], 22.0 (t, ¹J_{PC} = 11 Hz, CH₂). IR ν_{max} (ATR, cm⁻¹): 2935, 999 (vas Rh=C=Rh). ESI-MS(+): m/z = 1099.04 [M+H+MeCN]⁺. Accurate mass: Found 1099.0352 $[M+H+MeCN]^{\scriptscriptstyle +},\ Calcd.\ for\ C_{53}H_{48}{}^{35}Cl_2NP_4Rh_2{\rm :}\ 1098.0224.$ Anal Found: C, 57.98; H, 4.25%. Calcd. for C₅₁H₄₅Cl₂P₄Rh₂: C, 57.92; H, 4.19%. Crystal data for C₅₁H₄₄Cl₂P₄Rh₂·1.27(CH₂Cl₂): M_w = 1162.77, tetragonal, P4₁, a = b = 21.2680(4) Å, c = 14.3108(4) Å, V = 6473.2(3) $Å^3$, Z = 4, $D_{calcd.}$ = 1.193 Mg m⁻³, T = 150.0(1) K, orange needle, 0.70 × 0.21 × 0.15 mm, 13,165 independent reflections, F^2 refinement, $R_1 = 0.059$, $wR_2 = 0.182$ for 10,739 reflections with $l > 2\sigma(l)$, $\theta_{max} = 26.4^{\circ}$, Flack = [-0.018(13)], 587 parameters, CCDC 1867971.

Synthesis of $[Rh_2(\mu_2-C)(MeCN)_2(dppm)_2](OTf)_2(6)$

 $[Rh_2(\mu-C)Cl_2(dppm)_2]$ (100 mg, 0.095 mmol) and AgOTf (50 mg, 0.195 mmol) were dissolved in acetonitrile (10 mL). The red solution was stirred at room temperature for two hours. ³¹P NMR monitoring confirmed 100% *in situ* conversion. Toluene (10 mL) was added, and the solution concentrated under reduced pressure. Red crystals of the product were isolated and washed with ether. Isolated 13 mg (0.010 mmol, 11%) of red

^{a.} Research School of Chemistry, Australian National University, Canberra, Australian Capital Territory, ACT 2601, Australia.

⁺Corresponding author: Email: a.hill@anu.edu.au

Electronic Supplementary Information (ESI) available: Synthetic procedures, spectroscopic and crystallographic data. See DOI: 10.1039/x0xx00000x. CCDC 1867971 and 1880641 - 1880643 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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crystals. ¹H NMR (400 MHz, CD₃CN) δ_{H} = 7.67 - 7.66 (m, 14 H, PPh₂), 7.43 - 7.40 (m, 14 H, PPh₂), 7.37 - 7.32 (m, 14 H, PPh₂), 1.95 - 1.93 (br.m, MeCN). ${}^{31}P{}^{1}H{}$ NMR (162 MHz, CDCl₃) δ_{P} = 24.13 (m, ${}^{1}J_{RhP}$ = 184 Hz), (162 MHz, CD₃CN) δ_{P} = 23.83 (m, ${}^{1}J_{RhP}$ = 184 (142) Hz, ${}^{3}J_{RhP}$ = 44 (43.5) Hz, ${}^{4}J_{PP}$ = (1.5) Hz). ${}^{13}C{}^{1}H$ NMR (101 MHz, CD₃CN) δ_{C} = 134.4 [br., C^{2,6}(C₆H₅)], 132.4 [br., C^{3,5}(C₆H₅)], 131.5 [m, C¹(C₆H₅)], 129.9 [br., C⁴(C₆H₅)], 122.2 (q, ${}^{1}J_{CF}$ = 321 Hz, CF₃), 119.0 (CN), 19.7 (t, ${}^{1}J_{PC}$ = 14 Hz, CH₂), CH₃ obscured by solvent. IR ν_{max} (ATR, cm $^{-1}$): 2284, 1246, 1224, 1160, 1027. ESI-MS(+): *m/z* = 493.02 [M–2MeCN]²⁺. Accurate mass: found 493.0245 [M-2MeCN]²⁺, Calcd. for C₅₁H₄₄P₄Rh₂: 493.0252. Inadequate amounts of analytically pure sample could be isolated for elemental analysis. Crystal data for $C_{55}H_{50}N_2P_4Rh_2 \cdot 2(CF_3O_3S) \cdot 2(C_7H_8)$: $M_w = 1551.07$, monoclinic, $P2_1/c$, a = 11.7284(3) Å, b = 23.9123(7) Å, c = 12.0420(3) Å, $\beta =$ 95.506(3)°, V = 3370.89(16) Å³, Z = 2, D_{calcd.} = 1.528 Mg m⁻³, T = 150.0(1) K, red needle, 0.20 × 0.11 × 0.07 mm, 5,954 independent reflections, F^2 refinement, $R_1 = 0.098$, $wR_2 = 0.270$ for 5,146 reflections with $l > 2\sigma(l)$, $\theta_{max} = 66.6^{\circ}$, 423 parameters, CCDC 1880641.

Synthesis of [Rh₂(µ₂-CCl)(µ₂-Cl)Cl₄(dppm)₂] (9a)

[Rh₂(µ-C)Cl₂(dppm)₂] (30 mg, 0.028 mmol) and PhICl₂ (30.8 mg, 0.112 mmol) were dissolved in dry DCM (10 mL). The orange solution immediately turned yellow and was stirred at room temperature for 15 hours. The solution was concentrated under reduced pressure and purified by chromatography using a silica gel column (DCM eluent). A yellow band was collected and diluted with n-hexane. Slow removal of the dichloromethane under reduced pressure afforded yellow crystals that were isolated by filtration and dried in vacuo. Received 27 mg (0.022 mmol, 80%). ¹H NMR (400 MHz, CDCl₃) δ_{H} = 7.91 (br. s, 7 H, C₆H₅), 7.52 (br. s, 8 H, C₆H₅), 7.36-7.31 (m, 7 H, C₆H₅), 7.18 (t^v, J = 7 Hz, 3 H, C₆H₅), 7.03 (t^v, J = 7 Hz, 7 H, C₆H₅), 3.56 (d, ${}^{2}J_{HP}$ = 17 Hz, 2 H, CH₂), 3.20 (d, ²J_{PH} = 12 Hz, 2 H, CH₂). ³¹P{¹H} NMR (162 MHz, CDCl₃) δ_P = 3.38 (m, ¹J_{RhP} = 95 (81) Hz, ³J_{RhP} = (14) Hz, ⁴J_{PP} = (2.3) Hz).¹³C{¹H} NMR (192.5 MHz, CDCl₃) δ_{C} = 135.9, 132.1, 131.1, 130.7, 128.1, 127.9 (C₆H₅), 24.88 (t^{, 1}J_{CP} = 10 Hz, CH₂). IR ν_{max} (ATR, cm⁻¹): 3060, 2987, 1434, 852 (ν_{CCl}). ESI-MS(+): *m/z* = 1162.89 [M-Cl]⁺. Accurate mass: found 1162.8861 [M-Cl]⁺, Calcd. for C₅₁H₄₄³⁵Cl₅P₄Rh₂: 1162.8911. Anal Found: C, 49.77; H, 3.76%. Calcd. for C₅₁H₄₄Cl₆P₄Rh₂.0.5(CH₂Cl₂): C, 49.65; H, 3.76%. Crystal data for C₅₁H₄₄Cl₆P₄Rh₂·CHCl₃: M_w = 1318.63, triclinic, P-1 (No. 2), *a* = 10.9452(5) Å, *b* = 14.1036(7) Å, *c* = 23.4931(8) Å, $\alpha = 81.467(4)^{\circ}, \beta = 76.544(3)^{\circ}, \gamma = 69.731(4)^{\circ}, V = 3299.5(3) \text{ Å}^3$ Z = 2, $D_{calcd} = 1.327$ Mg m⁻³, T = 150.0(1) K, red plate, 0.89×0.41 \times 0.29 mm, 16,211 independent reflections, F² refinement, R₁ = 0.080, $wR_2 = 0.223$ for 9,963 reflections with $l > 2\sigma(l)$, $\theta_{max} =$ 29.4°, 592 parameters, CCDC 1880642.

Synthesis of $[Rh_2(\mu_2-CBr)(\mu_2-Br)Br_4(dppm)_2]$ (9b)

 $[Rh_2(\mu\text{-}C)Cl_2(dppm)_2]$ (78 mg, 0.074 mmol) and AgOTf (46.8 mg, 0.182 mmol) were dissolved in dry DCM (10 mL). The orange solution was stirred at room temperature for one hour, during

which time a white precipitate formed. Excess KBr (61.5 mg, 0.517 mmol) was added, and the solution stirred for a further half hour. The solution was cannula filtered into a dry Schlenk tube, and pyridinium tribromide (63.0 mg, 0.197 mmole) added to the filtrate. The red solution was stirred for 15 hours at room temperature. Ethanol was added, resulting in the deposition of an orange precipitate upon removal of DCM under reduced pressure. The orange precipitate was isolated via vacuum filtration and dried in vacuo. Received 72.0 mg (0.049 mmol, 67%). ¹H NMR (400 MHz, CDCl₃) δ_{H} = 7.94 (br., 9 H, C₆H₅), 7.55 (br., 11 H, C₆H₅), 7.33 (br., 12 H, C₆H₅), 7.15 (t^v, J = 7 Hz, 9 H, C₆H₅), 7.00 (br., 9 H, C₆H₅), 3.18, 3.13 (br.s. x 2, 2 H x 2, CH₂). ³¹P{¹H} NMR (162 MHz, CDCl₃) $\delta_P = -5.73$ (m, ¹J_{RhP} = 96 (86) Hz, ${}^{3}J_{RhP} = (10) Hz$, ${}^{4}J_{PP} = (2.3) Hz$). ${}^{13}C{}^{1}H{} NMR (192.5 MHz, CDCl_{3}) \delta_{C}$ = 136.3, 134.3, 132.2, 131.1, 130.8, 130.7, 128.0, 127.9, 127.8 (C_6H_5) , 24.88 $(t^{,1}J_{CP} = 10 \text{ Hz}, \text{CH}_2)$. IR v_{max} (ATR, cm⁻¹): 3053, 2963, 1433. ESI-MS(+): $m/z = 1386.63 [M-Br]^+$, 652.86 [M-2Br]⁺⁺. Accurate mass: found 1386.6341 [M-Br]+, Calcd. for $C_{51}H_{44}Br_5P_4Rh_2$: 1386.6370. Anal Found: C, 41.62; H, 3.10%. Calcd. for C₅₁H₄₄Br₆P₄Rh₂: C, 41.78; H, 3.03%. Crystal data for $C_{51}H_{44}Br_6P_4Rh_2$: $M_w = 1466.02$, tetragonal, $P4_32_12$, a = b =15.3383(2) Å, c = 25.9466(5) Å, V = 6104.3(2) Å³, Z = 4, $D_{calcd} =$ 1.595 Mg m⁻³, T = 150.0(1) K, red prism, 0.16 × 0.13 × 0.07 mm, 5,390 independent reflections, F^2 refinement, $R_1 = 0.094$, $wR_2 =$ 0.322 for 3,779 reflections with $l > 2\sigma(l)$, $\theta_{max} = 66.6^{\circ}$, Flack = -0.032(12), 366 parameters, 414 restraints, CCDC 1880643.

¹H NMR Spectrum of [Rh₂(μ -C)Cl₂(dppm)₂] (5a)







 $^{13}\text{C}\{^{1}\text{H}\}$ NMR Spectrum of $[\text{Rh}_{2}(\mu\text{-C})\text{Cl}_{2}(\text{dppm})_{2}]$ (5a)



¹H NMR Spectrum of [Rh₂(µ-C)(MeCN)₂(dppm)₂](OTf)₂ (wet d³-MeCN) (6)







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^{13}C NMR Spectrum of [Rh₂(μ -C)(MeCN)₂(dppm)₂](OTf)₂ (6)



¹H NMR Spectrum of [Rh₂(μ_2 -CCI)(μ_2 -CI)Cl₄(dppm)₂] (9a)



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 $^{31}P\{^{1}H\}$ NMR Spectrum of [Rh_2(µ_2-CCI)(µ_2-CI)Cl_4(dppm)_2] (9a) with simulated second order coupling



¹³C NMR Spectrum of [Rh₂(μ_2 -CCI)(μ_2 -CI)Cl₄(dppm)₂] (low solubility) (9a)



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¹H NMR Spectrum of [Rh₂(μ_2 -CBr)(μ_2 -Br)Br₄(dppm)₂] (crystallised with ethanol) (9b)



³¹P{¹H} NMR Spectrum of [Rh₂(μ_2 -CBr)(μ_2 -Br)Br₄(dppm)₂] (9b) with simulated second order coupling



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1 H- 1 H COSY NMR Spectrum of [Rh₂(μ_{2} -CCI)(μ_{2} -CI)Cl₄(dppm)₂] (9a), focussed on the methylene environments of dppm

