Chemical Communications

ELECTRONIC SUPPORTING INFORMATION

Halogenation of A-Frame μ-Carbido Complexes: A Diamagnetic Rhodium(II) Carbido Complex

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Harrison J. Barnett and Anthony F. Hill*

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 (^{1}H at 400.1 MHz, ^{31}P at 161.9 MHz, and ^{13}C at 100.5 MHz), Bruker Avance 600 (^{1}H at 600.1 MHz, ^{31}P at 242.9 MHz, and ^{13}C at 192.5 MHz) or Bruker Avance 700 (^{1}H at 700.1 MHz, ^{31}P at 283.5 MHz, and ^{13}C at 176.1 MHz) spectrometers. Chemicals shifts (δ) are reported in ppm and referenced internally to the solvent peak for ^{1}H and ^{13}C, and external H_3PO_4 reference for ^{31}P NMR. The couplings for multiplicities of the NMR resonances, $^{n}J_{AB}$, are reported in Hz. 2D ^{31}P-^{13}C{^{1}H} NMR studies were undertaken on a Bruker Avance 800.

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.

Cyclic voltammetry measurements were recorded using a ecorder 401 potentiostat system from eDaq Pty Ltd. Measurements were carried out at room temperature using Pt disc working-, Pt wire auxiliary- and Ag/AgCl or SCE reference electrodes, such that the ferrocene/ferrocenium redox couple was located at 0.46 V (CH_2Cl_2) relative to saturated calomel electrode (ipc/ipa = 1, DEp 0.09–0.12 V).[1] Scan rates were typically 100 mV s−1. Electrochemical solutions contained 0.1 M [NBu_4][PF_6] and ca 10−3 M complex in dried and distilled solvent. Solutions were purged and maintained under a nitrogen atmosphere.

Theoretical studies used the B3LYP and 6-31G*-LanL2Dζ levels of theory implemented within the Spartan18 suite of programs: *Spartan 18*® (2018) Wavefunction, Inc., 18401 Von Karman Ave., Suite 370 Irvine, CA 92612 U.S.A.[2]

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.

Synthesis of [Rh_2(μ-C)Cl_2(μ-dppf)$_2$] (4)

Rh_2(u-C)Cl_2(PPh_3)$_4$ (77.0 mg, 0.058 mmol) and dppf (104 mg, 0.188 mmol) were dissolved in dry CH_2Cl_2 (10 mL). The bright orange solution was stirred at room temperature for 24 hours. The solution was concentrated under reduced pressure. The mixture was subjected to a silica column with CH_2Cl_2 eluent, and an orange band collected. Ethanol was added, and an orange precipitate emerged upon removal of volatiles under reduced pressure. The precipitate was isolated *via* vacuum filtration, washed with ethanol, and dried *in vacuo*. Received 80 mg (0.057 mmol, 99 % yield) of orange product. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45-7.16 (4 x m, 40 H, PPh_2), 6.24 (br s, 3 H, Cp) 4.17, 4.12 (2 x s, 10 H, Cp), 3.74 (br s, 3 H, Cp). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ: 18.90 (br. d, $^{1}J_{RhP}$ = 191 Hz). ^{13}C NMR: 134.9 (br. s, C^{1}{C_6H_5}), 133.7 (s, C^{3,5}{C_6H_5}), 129.5 (s, C^{4}{C_6H_5}), 128.0 (t$^{v,\,2}J_{CP}$ = 5 Hz, C^{2,6}{C_6H_5}), 127.0 (t$^{v,\,2}J_{CP}$ = 4 Hz, C^{2,6}{C_6H_5}), 76.3 (t^{v}, J_{CP} = 23 Hz, C_a), 73.3 (s, C_b), 70.9 (s, C_y). IR ν_{max} (ATR, cm^{-1}): 3055, 1432, 693 (ν_{FeC}). Accurate mass (*m/z*): found 663.0049 [M–2Cl]$^{2+}$, Calc. for $C_{69}H_{56}Fe_2P_4Rh_2$: 663.0071. Anal found: C, 54.42; H, 3.96 %. Calc for $C_{69}H_{56}Cl_2Fe_2P_4Rh_2.2CH_2Cl_2$: C, 54.41; H, 3.86 %. Crystal data for $C_{69}H_{56}Cl_2Fe_2P_4Rh_2{\cdot}2(CH_2Cl_2)$: Mw = 1567.29, monoclinic, $P2_1/c$, a = 13.1742(3) Å, b = 26.8362(6) Å, c = 18.2963(3) Å, β = 90.747(2)°, V = 6468.0(2) Å^3, Z = 4, ρ_{calcd} = 1.609 Mg m^{-3}, T =

[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 1867970 and 1921282 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

150.00(10) K, red block, 0.31 × 0.18 × 0.11 mm, 13206 independent reflections, F^2 refinement, R = 0.048, wR = 0.109 for 10044 reflections with I > 2σ(I), θ_{max} = 26.4°, 794 parameters. CCDC 1867970.

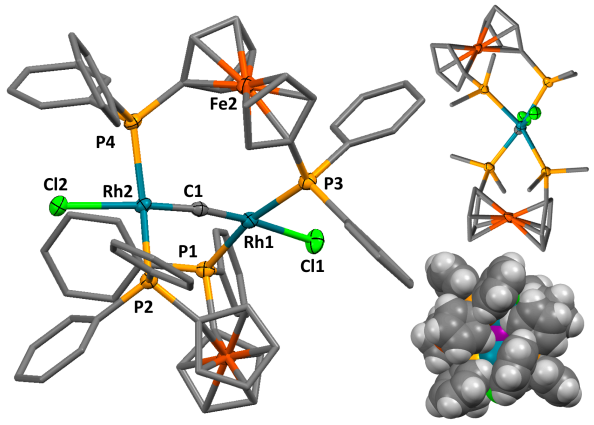

Figure S1. Molecular structures of **4** in a crystal of **4**.$(CH_2Cl_2)_2$ (50% displacement ellipsoids, solvent and hydrogen atoms omitted, phenyl and cyclopentadienyl groups simplified). Selected bond lengths (Å) and angles (°): Rh1–C1 1.782(4), Rh2–C1 1.767(4), Rh1–Cl1 2.3965(11), Rh2–Cl2 2.4262(12), P1–Rh1–P3 167.97(4), C1–Rh1–Cl1 175.22(14), C1–Rh2–Cl2 165.53(13), Rh2–C1–Rh1 168.4(3). Insets show views along inter-rhodium vector and the steric protection (space-filling representation) afforded the μ-carbido bridge (purple) by the bridging ligands.

Synthesis of $[Rh_2(\mu\text{-}C)Cl_4(\mu\text{-}dppf)_2]$ (5)

$[Rh_2(\mu\text{-}C)Cl_2(dppf)_2]$ (40 mg, 0.029 mmol) and $PhICl_2$ (17 mg, 0.062 mmol) were dissolved in CH_2Cl_2 (10 mL). The orange solution immediately turns darks green and was left stirring at room temperature for 15 hours. The solution was concentrated under reduced pressure and subjected to a silica column (CH_2Cl_2 eluent). A green/yellow band was isolated, *n*-hexane was added and the dark green product isolated *via* filtration and washed with ethanol and hexane. Received 34 mg (0.023 mmol, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.23 (br. s, 7 H, PPh_2), 7.53-7.48 (m, 13 H, PPh_2), 7.30 (br. s, 8 H, PPh_2), 7.10 (br. s, 4 H, PPh_2), 6.88 (br. s, 8 H, PPh_2), 5.69 (br. s, 4 H, dppf), 4.20 (br. s, 4 H, dppf), 4.01 (br. s, 4 H, dppf), 3.84 (br. s, 4 H, dppf). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ: 28.49 (d, $^1J_{RhP}$ = 95 Hz). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ: 137.6, 136.6, 133.8, 130.8, 130.4, 129.5, 128.0, 126.7 (8 x br. s, PPh_2), 81.7 (s, C_α), 73.1 (br. s, C_β), 71.9 (br. s, C_γ). IR ν_{max} (ATR, cm^{-1}): 3050, 1433, 688 (ν_{FeC}). MS-ESI(+): *m/z* = 1467.89 $[M]^+$. Accurate mass: found 1467.8862 $[M]^+$, Calc. for $C_{69}H_{56}P_4{}^{35}Cl_3{}^{37}Cl^{56}Fe_2{}^{103}Rh_2$: 1467.8866. Anal found: C, 53.22; H, 3.37 %. Calc for $C_{69}H_{56}Cl_4Fe_2P_4Rh_2.CHCl_3$: C, 52.95; H, 3.62 %. Crystal data for $0.5(C_{69}H_{56}Cl_4Fe_2P_4Rh_2)\cdot1.27(CHCl_3)$: Mw = 884.55, orthorhombic, *Fddd*, a = 13.1949(4) Å, b = 31.0550(6) Å, c = 40.4621(7) Å, α = β = γ = 90°, V = 16580.1(7) $Å^3$, Z = 16, ρ_{calcd} = 1.417 Mg m^{-3}, T = 150.00(10) K, dark green rhombohedral, 0.28 × 0.23 × 0.05 mm, 4177 independent reflections, F^2 refinement, R = 0.060, wR = 0.191 for 3806 reflections with I > 2σ(I), θ_{max} = 73.8°, 222 parameters, 24 restraints. CCDC 1921282.

Computational Details

Computational studies were performed by using the SPARTAN18® suite of programs.[1] Geometry optimisation (gas phase) was performed at the DFT level of theory using the Becke, 3-parameter, Lee–Yang–Parr exchange-correlation functional.[2] The Los Alamos effective core potential type basis set (LANL2DZ) of Hay and Wadt[3] was used for rhodium and iron; the Pople 6-31G* basis sets[4] were used for all other atoms. Frequency calculations were performed to confirm that the optimized structure was a minimum and also to identify vibrational modes of interest.

1 *Spartan 18*® (2018) Wavefunction, Inc., 18401 Von Karman Ave., Suite 370 Irvine, CA 92612 U.S.A.
2 (a) A. D. Becke, *Phys. Rev. A*., 1988, **38**, 3098–3100; (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*., 1988, **37**, 785–789; (c) J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822 – 8824. (d) Y. Yang, M. N. Weaver and K. M. Merz Jnr, *J. Phys. Chem. A*., 2009, **113**, 9843 – 9851.
3 (a) P. J. Hay and W.R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270-283. (b) W. R. Wadt and P. J. Hay, *J. Chem. Phys.,* 1985, **82**, 284-298. (c) P. J. Hay, W. R. Wadt, *J. Chem. Phys.,* 1985, **82**, 299-310.
4 W. J. Hehre, R. Ditchfeld and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257-2261.

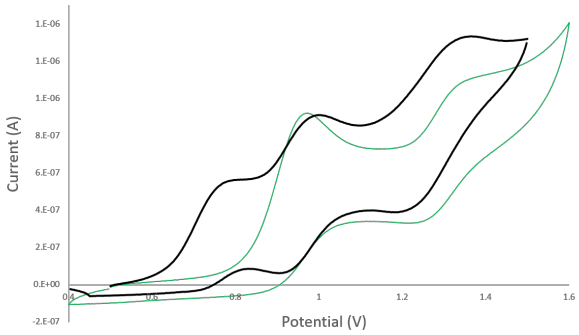

Figure S2. Cyclic voltammograms of $[Rh_2(\mu\text{-}C)Cl_2(PPh_3)_4]$ (**1**, green, 0.94, 1.3V) and $[Rh_2(\mu\text{-}C)Cl_2(\mu\text{-}dppf)_2]$ (**4**, black, 0.75, 0.96, 1.3V) at 100 mV/s under the conditions given in the ESI. Scale shown is relative to $E^0(Cp_2Fe)$ = 0.460 V (*cf.* Ag/AgCl).

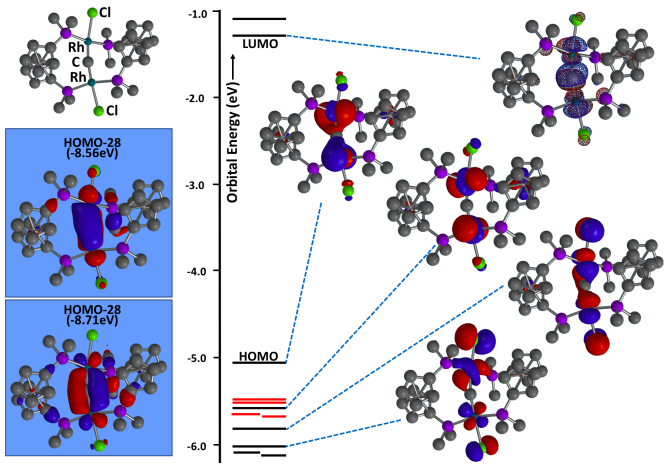

Figure S3. Optimised geometry and molecular orbitals of interest for the complex $[Rh_2(\mu\text{-}C)Cl_2(\mu\text{-}dmpf)_2]$ (**4'**) (DFT: B3LYP/6-31G*-LanL2Dζ, orbitals designated in red are primarily ferrocene-based). Insets = Conjugated fully π-bonding orbitals of Rh=C=Rh spine.

Table S1. Cartesian Coordinates for $[Rh_2(\mu\text{-}C)Cl_2(dmpf)_2]$ (4')

Atom	x	y	z
Rh	1.044186	0.752461	1.042755
Rh	-0.928642	-1.489828	-0.904579
Fe	-2.628977	1.017169	3.177117
Fe	2.738520	0.232175	-3.196526
Cl	1.899589	2.410437	2.739944
Cl	-2.364289	-3.363369	-1.799169
P	0.467653	-0.628718	2.891936
P	-2.993538	-0.755364	0.099011
P	1.898112	2.322207	-0.563095
P	0.716919	-2.455305	-2.360079
C	0.140585	-0.328830	-0.060803
C	-0.959534	-0.006160	3.844515
C	-2.162242	-0.704910	4.210790
H	-2.425167	-1.713589	3.922777
C	-2.952090	0.157276	5.024516
H	-3.923577	-0.078919	5.439731
C	-2.250139	1.390692	5.168284
H	-2.595277	2.260088	5.713463
C	-1.030704	1.298449	4.438670
H	-0.281856	2.070387	4.315982
C	-4.338453	0.949541	2.039759
H	-5.175984	0.285231	2.203552
C	-3.186272	0.671205	1.220418
C	-2.329758	1.820738	1.303839
H	-1.348674	1.903653	0.852935
C	-2.941873	2.781811	2.154586
H	-2.514999	3.735355	2.437336
C	-4.184530	2.245956	2.607609
H	-4.875104	2.725630	3.289888
C	3.194029	-1.085346	-1.680747
H	2.935328	-0.932030	-0.640350
C	2.354687	-1.710960	-2.662169
C	3.065418	-1.660698	-3.914785
H	2.710121	-2.035723	-4.864433
C	4.312565	-1.008529	-3.699596
H	5.060566	-0.804317	-4.455329
C	4.391159	-0.653216	-2.320393
H	5.214048	-0.137023	-1.843091
C	1.977310	1.935962	-2.342308
C	0.959001	1.258510	-3.092944
H	0.045255	0.848960	-2.680900
C	1.384426	1.168271	-4.449997
H	0.838144	0.695461	-5.256039
C	2.665974	1.786010	-4.555060
H	3.262317	1.867920	-5.454871
C	3.033352	2.262672	-3.264323
H	3.955572	2.772397	-3.020778
C	1.141757	-4.195928	-1.900459
H	0.209238	-4.753634	-1.780810
H	1.684424	-4.199130	-0.950560
H	1.765860	-4.663851	-2.669218
C	0.052617	-2.626658	-4.075185
H	-0.940895	-3.072976	-4.005637
H	0.701588	-3.256989	-4.692408
H	-0.032315	-1.637637	-4.533639
C	1.791339	-0.765811	4.174696
H	1.440099	-1.347678	5.033565
H	2.082294	0.237528	4.491179
H	2.665003	-1.256339	3.733255
C	0.068220	-2.404466	2.583274
H	0.986983	-2.900855	2.254791
H	-0.662965	-2.506140	1.775661
H	-0.291749	-2.900701	3.490273
C	0.991237	3.935525	-0.530859
H	-0.036718	3.787769	-0.875307
H	1.478730	4.676987	-1.172789
H	0.973316	4.289433	0.503894
C	3.628951	2.836751	-0.176649
H	4.307622	1.986878	-0.290253
H	3.648587	3.158547	0.866423
H	3.956612	3.656024	-0.825380
C	-4.160210	-0.300125	-1.266223
H	-4.235774	-1.145855	-1.954591
H	-3.765467	0.565396	-1.806240
H	-5.149208	-0.050885	-0.866167
C	-3.912336	-2.097764	0.975352
H	-3.925695	-2.971200	0.320445
H	-4.937273	-1.792263	1.209066
H	-3.397030	-2.357743	1.903453

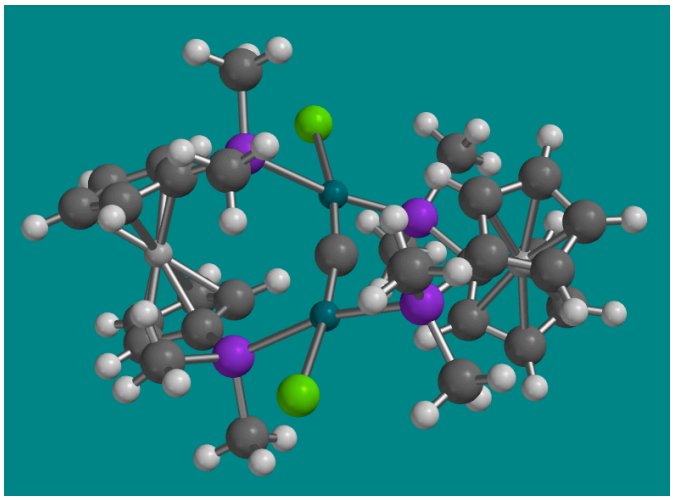

Table S2. Cartesian Coordinates for $[Rh_2(\mu\text{-}C)Cl_4(dmpf)_2]$ (5')

Atom	x	y	z
Rh	-1.716828	0.001335	0.001000
Fe	0.050326	0.009011	4.770119
Cl	-3.000126	1.898912	-1.068949
P	-2.016142	1.239430	2.041265
C	-1.681710	-0.842481	4.049222
H	-1.776667	-1.661229	3.350832
C	-1.621308	0.543853	3.678490
C	-1.648895	-0.929707	5.467585
H	-1.662644	-1.846958	6.042864
C	-1.558100	0.392417	5.994796
H	-1.485323	0.660254	7.041489
C	-1.539933	1.302181	4.899329
H	-1.466603	2.379565	4.975268
C	0.041829	0.004360	0.000556
Rh	1.850716	0.001146	-0.001184
Cl	2.622058	-2.092924	-1.038917
P	2.061128	-1.236797	2.073001
C	1.798215	0.866380	4.096684
H	1.884888	1.695095	3.410656
C	1.737348	-0.517863	3.713625
C	1.735532	0.942288	5.514199
H	1.741196	1.855048	6.096742
C	1.632977	-0.382664	6.030670
H	1.536294	-0.656931	7.073552
C	1.632134	-1.284109	4.929326
H	1.556003	-2.361629	5.000141
Fe	0.051927	-0.008882	-4.771998
Cl	-2.995940	-1.896732	1.074636
P	-2.012559	-1.239460	-2.038112
C	-1.679137	0.842615	-4.046119
H	-1.773189	1.660427	-3.346576
C	-1.618189	-0.544082	-3.676710
C	-1.648205	0.931305	-5.464379
H	-1.663963	1.847408	-6.041366
C	-1.558867	-0.391100	-5.993331
H	-1.487538	-0.657063	-7.040618
C	-1.537919	-1.300898	-4.898479
H	-1.462916	-2.378084	-4.976096
Cl	2.625751	2.093176	1.037230
P	2.063766	1.236560	-2.076084
C	1.798580	-0.866869	-4.098052
H	1.886700	-1.695598	-3.412360
C	1.739402	0.517708	-3.716477
C	1.736795	-0.943582	-5.515559
H	1.735907	-1.857456	-6.096329
C	1.633062	0.381201	-6.032778
H	1.540929	0.656150	-7.075948
C	1.636147	1.283572	-4.932122
H	1.561535	2.361063	-5.003627
C	-1.201594	2.883404	1.977769
H	-1.527535	3.365493	1.052429
H	-0.115872	2.757384	1.944796
H	-1.481627	3.507693	2.832366
C	-3.815064	1.583233	2.244182
H	-4.175391	2.127752	1.369345
H	-3.988582	2.159271	3.159015
H	-4.336458	0.624099	2.307576
C	3.813159	-1.789264	2.247079
H	4.111304	-2.308667	1.333690
H	3.922134	-2.449812	3.113658
H	4.446417	-0.908148	2.385259
C	1.068920	-2.783943	2.009546
H	1.400793	-3.349842	1.136483
H	0.011431	-2.535539	1.881530
H	1.197179	-3.391330	2.911106
C	3.815854	1.787870	-2.250993
H	3.924399	2.449931	-3.116482
H	4.448606	0.906738	-2.391486
H	4.115028	2.305486	-1.337004
C	1.072461	2.784165	-2.012879
H	1.201550	3.390891	-2.914610
H	1.404889	3.349711	-1.139807
H	0.014779	2.536528	-1.884892
C	-1.196348	-2.882782	-1.971852
H	-1.474174	-3.507472	-2.826861
H	-1.523899	-3.364595	-1.046866
H	-0.110936	-2.755224	-1.936478
C	-3.811191	-1.585102	-2.243000
H	-3.983144	-2.160321	-3.158607
H	-4.332973	-0.626150	-2.305920
H	-4.172561	-2.130822	-1.369199