Electronic Supporting Information for:
A Heterobimetallic Cumulenic µ-Carbido Complex

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CCDC 1959089 and 1959090 contain the supplementary crystallographic data for this paper, and are available free of charge from The Cambridge Crystallographic Data Centre.
COMMUNICATION

Experimental

General Considerations

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

NMR spectra were obtained on a Bruker Avance 400 (1H at 400.1 MHz, 13C at 100.6 MHz) or a Bruker Avance 700 (1H at 700.0 MHz, 13C at 176.1 MHz) spectrometers at the temperatures indicated. Chemical shifts (δ) are reported in ppm with coupling constants given in Hz and are referenced to the solvent peak, or external references (PhSe)₂ for 77Se. 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 77Se, 79Se, or 183W satellites. 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. The abbreviation ‘pz’ is used to refer to the pyrazolyl rings on the hydrotrois(3,5-dimethylpyrazol-1-yl)borate (Tp*) ligand. Spectra provided generally correspond to samples obtained directly from chromatography and may contain residual solvent as recrystallised samples often display reduced solubility.

Infrared spectra were obtained using a PerkinElmer 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 provided by the London Metropolitan University. High-resolution electrospray ionisation mass spectrometry (ESI-MS) was performed by the ANU Research School of Chemistry mass spectrometry service with acetonitrile or methanol as the matrix.

Data for X-ray crystallography were collected with an Agilent Xcalibur CCD diffractometer using Mo-Kα radiation (λ = 0.71073 Å) and the CrysAlis PRO software.² The structures were solved by direct or Patterson methods and refined by full-matrix least-squares on F² using the SHELXS and SHELXL programs.² Hydrogen atoms were located geometrically and refined using a riding model. Diagrams were produced using the CCDC visualisation program Mercury.³

The synthesis of the tungsten selenocarbonylate [W(CSe)(CO)₅(Tp*)]NEt₃ [1]NEt₃ has been described previously.⁴

Synthesis of [W(CSe)(CO)(NO)(Tp*)] (2). A solution of [1]NEt₃ (400 mg, 0.527 mmol) and N-methyl-N-nitroso-4-toluenesulphonamide (Diazald®, 118 mg, 0.551 mmol) in MeCN (30 mL) was stirred for 3.5 h, gradually turning dark green. After removing volatiles under reduced pressure, the product was extracted with benzene (15 mL) and filtered through a pad of diatomaceous earth (2 x 8 cm), washing with benzene until the filtrate ran clear. Volatiles were again removed under reduced pressure and the solid was then loaded onto a silica gel column with CH₂Cl₂, eluting the first green band with petroleum spirits (40–60 °C). Volatiles were removed under reduced pressure to give a light green solid. Yield: 241 mg (0.38 mmol, 72%). IR (CH₂Cl₂, cm⁻¹): 1992s, 1665br vNO, 1088s vCSe, IR (cm⁻¹): 1972s vCO, 1657s vNO, 1078s vCSe. 1H NMR (700 MHz, CDCl₃, 298 K): δH = 5.91, 5.83, 5.82 (3 x s, 1H x 3, pzCH₂), 2.70, 2.64, 2.42, 2.39, 2.36, 2.35 (6 x s, 3H x 6, pzCH₃). 13C(1H) NMR (176 MHz, CDCl₃, 298 K): δC = 367.2 (δC= 176, WCSe), 215.9 (δC= 158, WCO), 153.9, 153.5, 152.5, 145.4, 145.2, 144.9 (pzCH₃), 107.3, 107.1, 106.8 (pzCH₂), 16.0, 14.9, 14.8, 13.0, 12.7, 12.6 (pzCH₃). 77Se NMR (134 MHz, CDCl₃, 298 K): δSe = 1188. MS (ESI, +ve ion, m/z): Found: 631.0593. Calcd for C₁₁H₂₂BN₃O₆Se₁₈¹⁸ wast [M⁺]: 631.0595. Anal. Found: C, 32.49; H, 3.22; N, 15.40. Calcd for C₁₁H₂₂BN₃O₆Se₁₈¹⁸W: C, 32.41; H, 3.52; N, 15.56%.

Synthesis of [WRe(μ-η-C₅H₅)(CO)₄(η-C₅H₅)] (5). A colourless solution of [Re(CO)₅(η-C₅H₅)] (150 mg, 0.446 mmol) in THF (50 mL) was photolysed at 0 °C using an unfiltered mercury lamp until conversion was complete as determined by IR spectroscopy. The resultant light yellow [Re(CO)₅(THF) (η-C₅H₅)] solution was added dropwise to a green solution of 2 (70 mg, 0.11 mmol) in THF (10 mL) and stirred for 3.5 hours during which time the mixture slowly turned yellow brown. After removing the volatiles under reduced pressure, the solid was dissolved in minimal CH₂Cl₂ and loaded onto a silica gel column (3 x 20 cm) and eluted with 100% petroleum spirits to collect a green band. The eluent was slowly changed to 30% CH₂Cl₂ in petroleum spirits (40–60 °C) to collect a yellow/green band then a dark yellow-brown band of pure 5. Yield: 12 mg (0.014 mmol, 13%), IR (CH₂Cl₂, cm⁻¹): 1998s, 1944s, 1915s vCO, 1634s vNO, IR (cm⁻¹): 2022w, 1993m, 1949m, 1891s vCO, 1636s vNO, 968m vC=C. 1H NMR (400 MHz, CDCl₃, 298 K): δH = 5.88, 5.81, 5.74 (3 x s, 1H x 3, pzCH), 5.59 (5H, Cp), 2.70, 2.64, 2.42, 2.39, 2.36, 2.35 (6 x s, 3H x 6, pzCH₂). 13C(1H) NMR (176
MHz, CDCl3, 298 K): δc = 508.8 (WCre), 224.7 (WCO), 202.0, 199.4 (ReCO), 152.9, 152.8, 152.2, 145.0, 144.6, 144.6 (pzCCH), 106.9, 106.6, 106.4 (pzCH), 88.4 (Cp), 16.6, 15.4, 14.9, 13.1, 12.9, 12.5 (pzCH). MS (ESI, +ve ion, m/z): Found: 859.12787. Calcd for C49H82BrO18S18Se: 859.12789.

Crystals suitable for structural determination were grown by slow diffusion of n-hexane into a CH2Cl2 solution at -20 °C. Crystal Data for C39H32BrCl2O2Re2, 185g/mol: monoclinic, space group P21/n (no. 14), a = 8.049(4), b = 21.8669(10), c = 17.3220(7) Å, β = 95.2214(4), V = 3053.2(2) Å³, Z = 4, T = 150.0(1) K, μ(Mo Kα) = 7.944 mm⁻¹, Dcalc = 2.052 Mg.m⁻³, 3177 reflections measured (6.546° ≤ 2θ ≤ 52.736°), 6229 unique (Rint = 0.0664, Rgmin = 0.0578) which were used in all calculations. The final R1 was 0.0360 (I > 2σ(I)) and wR2 was 0.0651 (all data) for 380 refined parameters with 0 restraints, CCDC 1959089.

Isolation of [Re2(μ-Se)(CO)3(η-C5H5)]2 (6). From the column above, elution of 5 was followed by an orange band which could not be unambiguously identified, followed closely by elution of a green band of pure 6. Yield 8 mg (0.012 mmol, 10 % based on 2). IR (CH2Cl2, cm⁻¹): 1955s, 1907m, V(OH) M (400 MHz, CDCl3, 298 K): δc = 5.44 (Cp). 13C(H) NMR (176 MHz, CDCl3, 298 K): δc = 201.5, 131(CO). 88.4 (Cp). MS (ESI, +ve ion, m/z): Found: 693.8823. Calcd for C39H32BrO2Re2Se: 693.8835.

Crystals suitable for structural determination were grown by slow diffusion of n-hexane into a CH2Cl2 solution at -20 °C. Crystal Data for C39H32BrCl2O2Re2Se (Mw = 693.58 g/mol): triclinic, space group P-1 (no. 2), α = 7.4306(5), β = 7.9327(6), γ = 13.4641(11) Å, a = 103.629(6), δ = 95.575(6), γ = 104.678(6), V = 735.66(10) Å³, Z = 2, T = 150.0(1) K, μ(Mo Kα) = 18.924 mm⁻¹, Dcalc = 3.131 Mg.m⁻³, 5879 reflections measured (6.734° ≤ 2θ ≤ 52.74°), 2872 unique (Rint = 0.0378, Rgmin = 0.0554) which were used in all calculations. The final R1 was 0.0310 (I > 2σ(I)) and wR2 was 0.0504 (all data) for 190 refined parameters with 0 restraints, CCDC 1959090.

Computational Details

Computational studies were performed by using the SPARTAN18® suite of programs.5 Geometry optimisation (gas phase) was performed at the DFT level of theory using either (i) the wB97X-D range separated hybrid generalized gradient approximation functional with empirical corrections for long-range non-bonded (dispersive) interactions,6 or (ii) the Minnesota functional M06-2.7 The Los Alamos effective core potential type basis set (LANL2DZ) of Hay and Wadt8 was used for tungsten and rhenium; the Pople 6-31G* basis sets9 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.
References


Calculated Infrared Spectrum of [WRe(µ-C)(CO)3(NO)(Tp)] with location of primarily $\nu_{as}(W=C=Re)$ at 984 cm$^{-1}$ (Obs.: 968 cm$^{-1}$).
IR (CH₂Cl₂, cm⁻¹) for [W(CSe)(CO)₂(Tp*)]NEt₄ (2)
IR (ATR, cm$^{-1}$) for [W(CSe)(CO)$_2$(Tp*)]NEt$_4$ (2)
$^1$H NMR (700 MHz, CDCl$_3$, 298 K) for [W(CSe)(CO)$_2$(Tp*)]NEt$_4$ (2)
$^{13}$C{($^1$H)} NMR (176 MHz, CDCl$_3$, 298 K) for [W(CSe)(CO)$_2$(Tp*)]NEt$_4$ (2)
$^{77}$Se NMR (134 MHz, CDCl$_3$, 298 K) for [W(CSe)(CO)$_2$(Tp*)]NEt$_4$ (2)
IR (CH$_2$Cl$_2$, cm$^{-1}$) for [WRe(μ-C)(CO)$_3$(NO)(Tp*)(η-η-C$_5$H$_5$)] (5)
IR (ATR, cm$^{-1}$) for [WRe($\mu$-C)(CO)$_3$(NO)(Tp*)($\eta$-C$_5$H$_5$)] (5)
Difference IR (ATR, cm⁻¹) of \([W(CSe)(CO)_2(Tp^*)]NEt_4\) (2) and \([WRe(\mu-O)(CO)_3(NO)(Tp^*)(η-C_5H_5)]\) (5)
$^1$H NMR (400 MHz, CDCl$_3$, 298 K, δ) for [WRe(μ-C)(CO)$_3$(NO)(Tp*){(η-C$_5$H$_5$)}] (5)
$^{13}$C($^1$H) NMR (176 MHz, CDCl$_3$, 298 K) for [WRe($\mu$-C)(CO)$_3$(NO)]($\eta$-$\text{C}_5\text{H}_5$)](5)
IR (CH$_2$Cl$_2$, cm$^{-1}$) for [Re$_2$(μ-Se)(CO)$_4$(η-C$_5$H$_5$)$_2$] (6)
$^1$H NMR (400 MHz, CDCl$_3$, 298 K) for [Re$_2$(µ-Se)(CO)$_4$(η-$C_5$H$_5$)$_2$] (6)
$^{13}$C($^1$H) NMR (176 MHz, CDCl$_3$, 298 K) for [Re$_2$(μ-Se)(CO)$_4$(η-C$_5$H$_5$)$_2$] (6)