Electronic Supporting Information

Bis(alkylidynyl)telluride and Ditellurides
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EXPERIMENTAL ......................................................... 2
General Considerations ............................................. 2
Synthesis of [Et₄N][Mo(≡CMe)(CO)₂(Tp*)] Et₄N[2a] ................. 2
Synthesis of [Et₄N][W≡CMe)(CO)₂(Tp*)] Et₄N[2b] ..................... 2
Formation of [W≡CMeLi][CO)₂(Tp*)] in situ Li[2b] .................. 3
Synthesis of Mo[≡CPh][CO)₂(Tp*)] 3a .................................. 3
Synthesis of W[≡CPh][CO)₂(Tp*)] (3b) ................................. 3
Synthesis of Mo[≡C≡Me(C₂H)₂]CO)[CO)₂(Tp*)] 4a ...................... 4
Synthesis of W[≡C≡Me(C₂H)₂]CO)[CO)₂(Tp*)] 4b ...................... 4
Synthesis of Mo[≡C≡Ph(C₂H)₂]CO)[CO)₂(Tp*)] (5a) ................... 4
Synthesis of W[≡C≡Ph(C₂H)₂]CO)[CO)₂(Tp*)] (5b) ................... 4
Synthesis of [(Tp*)][CO)₂Mo≡C]₂Te (6a) .............................. 5
Synthesis of [(Tp*)][CO)₂W≡C]₂Te (6b) .............................. 5
Synthesis of [(Tp*)][CO)₂Mo≡C]₂Te₂ (7a) ............................ 5
Synthesis of [(Tp*)][CO)₂W≡C]₂Te₂ (7b) ............................ 5

X-RAY CRYSTALLOGRAPHY ........................................ 5
Refinement details ................................................... 6
Table S1. X-ray Structure Summary ................................. 8

NOTES AND REFERENCES ........................................... 8

SPECTRA ............................................................... 9
¹H NMR Spectrum of Et₄N[2b] ........................................... 9
¹²⁵Te[¹H] NMR Spectrum of Et₄N[2b] .............................. 9
¹H NMR Spectrum of 3a ............................................. 10
¹³C[¹H] NMR Spectrum of 3a ...................................... 11
¹²⁵Te[¹H] NMR Spectrum of 3a ...................................... 11
¹H NMR Spectrum of 3b ........................................... 12
¹³C[¹H] NMR Spectrum of 3b ...................................... 12
¹²⁵Te[¹H] NMR Spectrum of 3b ...................................... 13
¹H NMR Spectrum of 4b ........................................... 13
¹³C[¹H] NMR Spectrum of 4b ...................................... 14
¹²⁵Te[¹H] NMR Spectrum of 4b ...................................... 14
¹H NMR Spectrum of 5a ........................................... 15
¹³C[¹H] NMR Spectrum of 5a ...................................... 15
¹²⁵Te[¹H] NMR Spectrum of 5a ...................................... 15
¹H NMR Spectrum of 6a ........................................... 16
¹³C[¹H] NMR Spectrum of 6a ...................................... 16
¹²⁵Te[¹H] NMR Spectrum of 6a ...................................... 17
¹H NMR Spectrum of 6b ........................................... 17
¹³C[¹H] NMR Spectrum of 6b ...................................... 18
¹²⁵Te[¹H] NMR Spectrum of 6b ...................................... 18
¹H NMR Spectrum of 7a ........................................... 19
¹³C[¹H] NMR Spectrum of 7a ...................................... 20
¹²⁵Te[¹H] NMR Spectrum of 7a ...................................... 20
¹H NMR Spectrum of 7b ........................................... 21
¹³C[¹H] NMR Spectrum of 7b ...................................... 21
¹²⁵Te[¹H] NMR Spectrum of 7b ...................................... 22
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 at 25°C on Bruker Avance 400 (1H at 400.1 MHz, 13C [1H] at 100.6 MHz, 125Te [1H] at 126.3 MHz) or Bruker Avance 700 (1H at 700.0 MHz, 13C at 150.9 MHz) spectrometers. Chemical shifts (δ) are reported in ppm and referenced to the solvent peak (1H, 1H2O) or externally referenced to diphenyl distilulurite (125Te, δTe = 422), 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 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 hydridotris(3,5-dimethylpyrazol-1-yl)borate (Tp*) ligand.

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 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) or an Agilent SuperNova CCD diffractometer using Cu-Kα radiation (λ = 1.54184 Å) using the CrystAlis PRO software. A summary of the X-ray crystal structure data for compounds all compounds described in this work is provided in Table S1. The structures were solved by direct or Patterson methods and refined by full-matrix least-squares on F2 using the SHELXS and SHELXL programs, or with the CRYSTALS software. Hydrogen atoms were located geometrically and refined using a riding model. Diagonals were produced using the CCDC visualisation program Mercury.

The complexes [Mo(C≡Br)(CO)2(Tp*)] (1a) and [W(C≡Br)(CO)2(Tp*)] (1b) have been described previously. Synthesis of [Et₄N][Mo(C≡CTe)(CO)₂(Tp*)] Et₄N[2a]

This salt has been described previously from the reaction of the chlorocarbonyl complex [Mo(C≡Cl)(CO)(Tp*)] and an aqueous/methanol solution of ‘Na₂Te’ however, no experimental details were provided and only limited spectroscopic data (νCO, νCTe) were reported. The following high yield synthesis involves

anhydrous conditions and the use of Li₂Te. Further characterisational data are also included.

To a solution of elemental tellurium (59.1 mg, 0.463 mg/atom) in THF (5 mL) at ~78 °C was added lithium triethylborohydride (463 μL, 1.0 M in THF, 0.46 mmol). The mixture was stirred at reduced temperature for 1 h before being warmed to room temperature and stirred for a further 1 h. After this time the solution was transferred by cannula into a solution of 1a (250 mg, 0.463 mmol) in THF (10 mL) at ~78 °C. The mixture was warmed to room temperature and stirred for 1 h, during which time the mixture turned light brown. After this time, Et₄NBr (97.3 mg, 0.463 mmol) was added as a solid and the mixture was stirred for 4 h, during which time a yellow precipitate formed. The precipitate was collected by filtration, washed with THF (3 x 10 mL), deionized water (3 x 10 mL) and diethyl ether (5 x 10 mL), and dried in vacuo to give pure Et₄N[2a] (268 mg, 0.373 mmol, 81%) as a yellow (sometimes yellow-green) solid. IR (CHCl₃, cm⁻¹): 1927s, 1843s (CO). 1H NMR (CDCl₃, δ): 1.15 (t, JHH = 7.2 Hz, 12 H, CH₂CH₃), 2.22 [s, 6 H, pz(CH₃)], 2.28 [s, 6 H, pz(CH₃)], 2.62 [s, 6 H, pz(CH₃)], 3.19 (q, JHH = 6.9 Hz, 8 H, NCH₂), 5.70 (s, 1 H, pzH), 5.83 (s, 2 H, pzH). Satisfactory 13C (1H) NMR have not been acquired due to the very poor solubility in a range of common deuterated organic solvents. 125Te NMR (126 MHz, DMSO, 298 K, δ): 1248. MS (ESI, -ve ion, m/z): Caled for C₂Hp₂Te₂BMoTe: C, 38.9; H, 6.02; N, 13.57%. Found: C, 41.65; H, 6.02; N, 13.57%.

Synthesis of [Et₄N][W(C≡CTe)(CO)₂(Tp*)] Et₄N[2b]

To a solution of 1b (100 mg, 0.159 mmol) in THF (10 mL) was added Li₂Te (2.02 mL, 0.078 M in THF, 0.158 mmol, prepared as described above) and the resulting mixture was stirred at room temperature overnight, during which time the solution turned light brown. After this time, Et₄NBr (33.6 mg, 0.160 mmol) was added as a solid and the mixture stirred at 0 °C for 4 h, during which time a yellow precipitate formed. The solvent was removed by cannula filtration and the precipitate was collected by filtration, washed with deionized water (2 x 10 mL) and diethyl ether (5 x 10 mL), and dried in vacuo to give pure 2b (109 mg, 0.135 mmol, 85%) as a yellow (sometimes yellow-green) solid. A crystal suitable for X-ray crystallographic analysis was grown by slow evaporation of an acetonitrile solution at ~20 °C.

IR (CHCl₃, cm⁻¹): 1978, 1891 νCO, (KBr, cm⁻¹): 1971, 1885 νCO, 1912s, 1923s νCO, 982s νCTe. 1H NMR (600 MHz, CD₂CN, 298 K, δ): 1.18 (t, JHH = 7.2 Hz, 12 H, CH₂CH₃), 2.31 [s, 3 H, pz(CH₃)], 2.37 [s, 3 H, pz(CH₃)], 2.77 [s, 6 H, pz(CH₃)]. 3.10 (q, JHH = 7.2 Hz, 8 H, NCH₂), 5.73 (s, 1 H, pzH), 5.86 (s, 2 H, pzH). 13C (1H) NMR (150 MHz, CD₂CN/toluene-d₈, 298 K, δ): 7.6 (CH₂CH₃), 12.7 15.6 16.5 (pzCH₃), 52.9 (NCH₂), 106.6, 106.8 (C₂pz), 145.0 154.9 152.7 153.8 (C≡Te), 227.7 (CO), 302.3 (W≡CTe). Low solubility.
Formation of [W(≡CTeLi)(CO)3]  in situ Li[2b].

A yellow solution of [W≡CB(CN)(pz)2] (1b: 0.472 g, 0.795 mmol) in tetrahydrofuran (20 mL) was treated with Li2Te in tetrahydrofuran (0.048 M, 16.6 mL, 0.799 mmol) and was stirred for 17 hours to yield a clear dark brown solution of [W≡CTeLi](CO)3] Li[2b]. IR (KBr, cm−1): 1960, 1879 νCO. IR (THF, cm−1): 1906, 1819 νCO. 1H NMR (600 MHz, acetone-δ6, 298 K, δ): 2.41 [s, 3 H, pz(CH3)], 2.42 [s, 3 H, pz(CH3)], 2.48 [s, 6 H, pz(CH3)], 2.86 [s, 6 H, pz(CH3)], 5.85 (s, 1 H, pzH), 5.97 (s, 2 H, pzH). 13C [1H] NMR (150 MHz, acetone-δ6, 298 K, δ): 34.6, 34.7, 35.6, 35.8. 125Te NMR (126 MHz, CD2CN), 298 K, δ): 1031. MS (ESI, −ve ion, m/z): Caled for C32H32N2O2Te: M+ [M + H]+: 677.0460. Found: 677.0466. Anal. Caled for C32H32N2O2TeW: C, 38.70; H, 5.25; N, 12.15%. Found: C, 38.64; H, 5.12; N, 12.06%.

Synthesis of Mo(≡CTeBu)(CO)2(Tp*) 3a

To a solution of tellurium (35.4 mg, 0.277 mmol) in THF (5 mL) at −78 °C was added nBuLi (173 μL, 1.6 M in hexanes, 0.277 mmol) and the mixture was stirred at this temperature for 30 min. After this time, the solution was transferred by cannula into a solution of 1a (100 mg, 0.185 mmol) in THF (5 mL) at −78 °C, causing the initially yellow solution to turn dark green. Stirring was continued for 30 min at reduced temperature before the solution was warmed to room temperature and the solvents removed in vacuo. The residue was subjected to column chromatography (10 x 3 cm silica gel column), eluting first with n-hexane followed by 20% v/v CH2Cl2-n-hexane. An orange band was collected and the solvents were removed under reduced pressure to afford pure 3a (89.1 mg, 0.138 mmol, 75%) as orange microcrystals.

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Chemical Communications

precluded the measurement of 1JW,CH and 1JTeC. This resonance is tentatively attributed to the tellurocarbonyl ligand, however it is to higher frequency than might be expected and is unusually broad when compared to the rest of the spectrum. We suggest that this reflects a dynamic process that possibly involves the solvent or ion pairing, in which case the apparent chemical shift may well represent a weighted average. In any event, the assignment of this resonance should be taken as speculative.
Synthesis of Mo(≡CTeMe)(CO)₂(Tp*) 4a

This synthesis of this complex has been described previously, via the reaction of [Mo≡Cl(O)₂(Tp*)] with tellurium and iodomethane. The following procedure provides comparable yields.

To a solution of tellurium (35.4 mg, 0.277 mg.atom) in THF (5 mL) at −78 °C was added MeLi (173 µL, 1.6 M in diethyl ether, 0.277 mmol) and the mixture was stirred at reduced temperature for 1 h. After this time, the solution was transferred by cannula into a solution of 1a (100 mg, 0.185 mmol) in THF (5 mL) at −78 °C, causing the initially yellow solution to turn bright orange. The mixture was slowly warmed to room temperature and stirring was continued for 1 h. The solvents were then removed in vacuo and the residue was subjected to column chromatography (10 x 3 cm silica gel column, eluting first with n-hexane followed by 20% v/v CH₂Cl₂/n-hexane. An orange band was collected and the solvents were removed under reduced pressure to afford pure 4a (96.6 mg, 0.160 mmol, 86%) as an orange solid. The characterization data for this species matched those reported in the literature.

Synthesis of W(≡CTeMe)(CO)₂(Tp*) 4b

Method a. A solution of 1b (0.050 g, 0.0795 mmol) in tetrahydrofuran (20 mL) was treated with a solution of Li₂Te in tetrahydrofuran (0.047 M, 1.89 mL, 0.089 mmol) and was left to stir for 17 hours to yield a clear dark brown solution of Li[2b] (vide supra). To the brown solution 1 drop of MeI (excess) was added and the mixture was left to stir for 17 hours turning the solution slightly red. The solvent was concentrated to a few mL under reduced pressure. Hexane was then added to the concentrate which was left to stand for 24 hours producing microcrystals of 4b. The crystals were washed with ether and hexane. Yield 0.0397g (0.057 mmol, 72%).

Method b. To a solution of tellurium (30.4 mg, 0.239 mg.atom) in THF (5 mL) at −78 °C was added MeLi (149 µL, 1.6 M in diethyl ether, 0.239 mmol) and the mixture was stirred at reduced temperature for 1 h. After this time, the solution was transferred by cannula into a solution of 1b (100 mg, 0.159 mmol) in THF (5 mL) at −78 °C, causing the initially yellow solution to turn orange-brown. The mixture was slowly warmed to room temperature and stirring was continued for 1 h. The solvents were then removed in vacuo and the residue was subjected to column chromatography (10 x 3 cm silica gel column, eluting first with n-hexane followed by 20% v/v CH₂Cl₂/n-hexane. An orange band was collected and the solvents were removed under reduced pressure to afford pure 4b (79.8 mg, 0.115 mmol, 73%) as an orange solid. IR (CH₂Cl₂, cm⁻¹): 1977s, 1886s vCO. (KBr, cm⁻¹): 1968s, 1877s vCO-¹H NMR (700 MHz, CDCl₃, 298 K, δ): 2.30 [s, 3 H, pz(CH₃)], 2.35 [s, 6 H, pz(CH₃)], 2.36 [s, 3 H, pz(CH₃)], 2.39 [s, 3 H, TeCH₃], 2.59 [s, 6 H, pz(CH₃)], 5.74 (s, 1 H, pzH), 5.90 (s, 2 H, pzH). ¹³C¹H NMR (176 MHz, CDCl₃, 298 K, δ): −16.1 (TeCH₃), 12.8 15.4 16.8 (pzCH₃), 106.7 106.8 [C≡C(pz)], 144.6 145.4 152.1 152.7 [C≡C(pz)]; 224.3 (CO, 1JCO = 85.0 Hz), 250.8 (W≡CTe). ¹²⁵Te¹H NMR (126 MHz, CDCl₃, 298 K, δ): 634. MS (ESI, +ve ion, m/z): Calcd for C₁₀H₈N₂O₂TeW [M+H⁺]: 693.0768. Found: 693.0763. Anal. Calcd for C₁₀H₈N₂O₂TeW: C, 32.99; H, 3.64; N, 12.15%. Found: C, 33.06; H, 3.63; N, 12.04 %.

Synthesis of Mo(≡CTePh)(CO)₂(Tp*) (5a)

To a solution of tellurium (35.4 mg, 0.277 mg.atom) in THF (5 mL) at −78 °C was added PhLi (146 µL, 1.9 M in di-n-butyl ether, 0.277 mmol) and the mixture was stirred at reduced temperature for 30 min. After this time, the solution was transferred by cannula into a solution of 1a (100 mg, 0.185 mmol) in THF (5 mL) at −78 °C, causing the initially yellow solution to turn dark green. Stirring was continued for 30 min at reduced temperature before the solution was warmed to room temperature and the solvents were removed in vacuo. The residue was extracted with n-hexane (2 x 10 mL), the solvent volume was reduced to ca. 2 mL and subjected to column chromatography (10 x 1 cm silica gel column, eluting first with n-hexane followed by 20% v/v CH₂Cl₂/n-hexane. An orange band was collected and the solvents were removed under reduced pressure to afford pure 5a (76.0 mg, 0.991 mmol, 62%) as red microcrystals. IR (CH₂Cl₂, cm⁻¹): 1988s, 1911s vCO-¹H NMR (700 MHz, CDCl₃, 298 K, δ): 2.30 [s, 3 H, pz(CH₃)], 2.33 [s, 3 H, pz(CH₃)], 2.34 [s, 6 H, pz(CH₃)], 2.40 [s, 6 H, pz(CH₃)], 5.70 (s, 1 H, pzH), 5.81 (s, 2 H, pzH), 7.26–7.37 [m, 3 H, H₁(Ph)], 7.92 [d, JHH = 7.5 Hz, 2 H, H₂(Ph)]. ¹³C¹H NMR (176 MHz, CDCl₃, 298 K, δ): 12.8 12.8 14.8 15.9 (pzCH₃), 106.4 106.5 [C≡C(pz)], 114.9 [C≡C(Ph)], 128.5 [C(Ph)], 129.7 [C≡C(Ph)], 138.9 [C≡C(Ph)], 144.6 145.3 151.5 151.6 [C≡C(pz)], 226.1 (CO), 262.0 (Mo≡CTe). ¹²⁵Te¹H NMR (126 MHz, CDCl₃, 298 K, δ): 1108. MS (ESI, +ve ion, m/z): Calcd for C₁₉H₁₇N₂O₂BMoTeNa [M + Na⁺]: 691.0286. Found: 691.0332. Anal. Calcd for C₁₉H₁₇N₂O₂BMoTeC: C, 43.29; H, 4.09; N, 12.62%. Found: C, 43.30; H, 3.98; N, 12.52 %.

Synthesis of W(≡CTePh)(CO)₂(Tp*) (5b)

To a solution of tellurium (30.4 mg, 0.239 mg.atom) in THF (5 mL) at −78 °C was added PhLi (126 µL, 1.9 M in di-n-butyl ether, 0.239 mmol) and the mixture was stirred at reduced temperature for 30 min. After this time, the solution was transferred by cannula into a solution of 1b (100 mg, 0.195 mmol) in THF (5 mL) at −78 °C, causing the initially yellow solution to turn dark green. Stirring was continued for 30 min at reduced temperature before the solution was warmed to room temperature and the solvents removed in vacuo. The residue was extracted with n-hexane (2 x 10 mL), the solvent volume was reduced to ca. 2 mL and subjected to column chromatography (10 x 1 cm silica gel column, eluting first with n-hexane followed by 20% v/v CH₂Cl₂/n-hexane. An orange band was collected and the solvents were removed under reduced pressure to afford pure 5b (65.3 mg, 0.0866 mmol, 54%) as orange crystals. IR (CH₂Cl₂, cm⁻¹): 1980s, 1890s vCO-¹H NMR (400 MHz, CDCl₃, 298 K, δ): 2.30 [s, 3 H, pz(CH₃)], 2.34 [s, 6 H,
Synthesis of \([\text{Tp}^*]({\text{CO}})_2{\text{Mo(=C})]_2\text{Te} (6a)\)

To a solution of 1a (100 mg, 0.185 mmol) in THF (10 mL) was added a solution of Li₂Te in THF (2.35 mL, 0.078 M, 0.19 mmol) and the resulting mixture was stirred for 3 h, during which time the solution turned brown. After this time, additional 1a (100 mg, 0.185 mmol) was added as a solid and the mixture was stirred for a further 48 h. After this time, the solvent was removed in vacuo and the residue was subjected to column chromatography (20 x 1 cm silica gel column), eluting initially with n-hexane followed by 10% v/v CH₂Cl₂/n-hexane. An orange-red band was collected and the solvents were removed under reduced pressure to give pure 6a (121 mg, 0.115 mmol, 31%) as an orange solid. IR (CHCl₃, cm⁻¹): 1992, 1916 VS, CO₂.¹H NMR (400 MHz, CDCl₃, 298 K, δ): 2.30 [s, 6 H, pz(CH₃)], 2.31 [s, 6 H, pz(CH₃)], 2.35 [s, 12 H, pz(CH₃)], 2.39 [s, 12 H, pz(CH₃)], 5.70 (s, 2 H, pzH), 5.72 (s, 4 H, pzH).¹³C¹H NMR (101 MHz, CDCl₃, 298 K, δ): 12.8 12.8 14.7 15.2 (pzCH₂), 106.3 106.6 [C²(pz)], 144.2 145.4 151.6 151.8 [C³(pz)], 226.0 (CO), 252.3 (Mo=CTe).¹²⁵Te¹H NMR (126 MHz, CDCl₃, 298 K, δ): 1426. MS (ESI, +ve ion, m/z): Calcd for C₅₃H₇₈N₂O₆Te₂Mo₂Te [M⁺]: 1050.9980. Found: 1050.1000. Anal. Calcd for C₅₃H₇₈N₂O₆Te₂Mo₂Te: C, 41.18; H, 4.22; N, 16.01%. Found: C, 41.09; H, 4.30; N, 15.76%.

Synthesis of \([\text{Tp}^*]({\text{CO}})_2{\text{W(=C})]_2\text{Te} (6b)\)

To a solution of 1b (100 mg, 0.159 mmol) in THF (10 mL) at −78 °C was added Li₂Te (2.35 mL, 0.078 M in THF, 0.19 mmol). The solution was warmed to room temperature and stirring continued for 2 h, during which time the solution turned light brown. After this time, additional 1b (100 mg, 0.159 mmol) was added as a solid and the mixture was stirred for a further 48 h. After this time, the solvent was removed in vacuo and the residue was subjected to column chromatography (20 x 1 cm silica gel column), eluting initially with n-hexane followed by 10% v/v CH₂Cl₂/n-hexane. An orange-red band was collected and the solvents were removed under reduced pressure to give pure 6b (155 mg, 0.126 mmol, 40%) as an orange solid. A crystal suitable for X-ray structure determination was grown by slow evaporation of a CHCl₃/ethanol mixture. IR (CHCl₃, cm⁻¹): 1975, 1892 VS, CO₂.¹H NMR (400 MHz, CDCl₃, 298 K, δ): 2.31 [s, 6 H, pz(CH₃)], 2.37 [s, 18 H, pz(CH₃)], 2.40 [s, 12 H, pz(CH₃)], 5.75 (s, 2 H, pzH), 5.76 (s, 4 H, pzH).¹³C¹H NMR (101 MHz, CDCl₃, 298 K, δ): 12.6 15.4 16.5 (s, pzCH₃), 106.5 106.8 [C²(pz)], 144.0 145.4 152.7 [C³(pz)], 244.1 (CO).¹²⁵Te¹H NMR (126 MHz, CDCl₃, 298 K, δ): 1181. MS (ESI, +ve ion, m/z): Calcd for C₄₅H₄₁N₂O₅B₂W₂Te₂ [M⁺]: 1226.1863. Found: 1226.1857. Anal. Calcd for C₄₅H₄₁N₂O₅B₂W₂Te₂: C, 35.28; H, 3.62; N, 13.71%. Found: C, 35.19; H, 3.60; N, 13.53%.

Synthesis of \([\text{Tp}^*]({\text{CO}})_2{\text{Mo(=C})]_2\text{Te} (7a)\)

To a flask containing Et₄N[2a] (50.0 mg, 0.070 mmol) and ferrocenium hexafluorophosphosphate (23.0 mg, 0.070 mmol) was added MeCN (10 mL) and the suspension was stirred vigorously for 2 h, during which time a dark purple precipitate formed. The mixture was filtered and the purple solid was washed with a large volume (10 x 10 mL) of MeCN then dried in vacuo to give pure 7a (22.4 mg, 0.0190 mmol, 55%) as a dark purple powder. IR (CHCl₃, cm⁻¹): 1995s, 1916s VS, CO₂.¹H NMR (400 MHz, CDCl₃, 298 K, δ): 2.30 [s, 6 H, pz(CH₃)], 2.33 [s, 6 H, pz(CH₃)], 2.35 [s, 12 H, pz(CH₃)], 2.50 (s, 2 H, pzH), 5.78 (s, 4 H, pzH).¹³C¹H NMR (101 MHz, CDCl₃, 298 K, δ): 12.8 12.8 14.8 16.3 (pzCH₂), 106.4 106.5 [C²(pz)], 144.5 145.3 151.7 151.8 [C³(pz)], 225.9 (CO), 248.9 (Mo=CTe).¹²⁵Te¹H NMR (126 MHz, CDCl₃, 298 K, δ): 992. MS (ESI, +ve ion, m/z): Calcd for C₄₅H₄₁N₂O₅B₂Mo₂Te₂ [M⁺ + H⁺]: 1180.0082. Found: 1180.0062. Anal. Calcd for C₄₅H₄₁N₂O₅B₂Mo₂Te₂: C, 36.7; H, 3.77; N, 14.27%. Found: C, 36.80; H, 3.64; N, 14.18%.

Synthesis of \([\text{Tp}^*]({\text{CO}})_2{\text{W(=C})]_2\text{Te} (7b)\)

To a flask containing Et₄N[2b] (50.0 mg, 0.062 mmol) and ferrocenium hexafluorophosphosphate (20.5 mg, 0.062 mmol) was added MeCN (10 mL) and the suspension was stirred vigorously for 2 h, during which time a dark purple precipitate formed. The mixture was filtered and the purple solid was washed with a large volume (10 x 10 mL) of MeCN then dried in vacuo to give pure 7b (19.2 mg, 0.0142 mmol, 46%) as a dark purple powder. The crystal selected for X-ray structure determination was grown by slow evaporation of a diethyl ether solution. IR (CHCl₃, cm⁻¹): 1978s, 1894s VS, CO₂.¹H NMR (400 MHz, CDCl₃, 298 K, δ): 2.31 [s, 6 H, pz(CH₃)], 2.36 (s, 12 H, pz(CH₃)], 2.38 (s, 6 H, pz(CH₃)], 2.55 (s, 12 H, pz(CH₃)], 5.73 (s, 2 H, pzH), 5.85 (s, 4 H, pzH).¹³C¹H NMR (101 MHz, CDCl₃, 298 K, δ): 12.8 (2 C, coincident) 15.4 17.1 (pzCH₃), 106.7 106.8 [C²(pz)], 144.4 145.4 152.7 152.8 [C³(pz)], 224.2 (CO), 236.0 (W≡CTe).¹²⁵Te¹H NMR (126 MHz, CDCl₃, 298 K, δ): 851. MS (ESI, m/z): Calcd for C₄₅H₄₁N₂O₅B₂W₂Te₂ [M⁺ + H⁺]: 1355.0988. Found: 1355.1069. Anal. Calcd for C₄₅H₄₁N₂O₅B₂W₂Te₂: C, 31.95; H, 3.28; N, 12.42%. Found: C, 35.01; H, 3.28; N, 12.41%. NB: The crystallographic analysis suggested solvent accessible voids which may account for the low %carbon value.

X-Ray Crystallography
Refinement details

The crystal structure determination of 4b was complicated by significant positional disorder characteristics. Two molecules of 4b were present per asymmetric unit. One of these molecules was fairly well defined, although the tellurium atom was located over two positions and was refined to a relative ratio of ca 92:8, the minor component was treated isotropically. In the second molecule, the C–Te–Me moiety was heavily disordered and was modelled over four positions and was refined to a relative ratio of ca. 57:20:8:6 with the liberal use of distance and thermal parameter restraints. There was also a small amount of full-molecule disorder (ca. 10%) for which only the heavy W and Te atoms could be located in the difference map. These disorder characteristics were present in four distinct data sets for which crystals were obtained from different solvent combinations. For this reason, we have included this structure only as evidence of the connectivity, but eschew more detailed interpretation.

The crystal of 4b was found to contain two parent molecules per asymmetric unit. In one of these molecules a carbonyl group and the phenyltellurocarbyne exhibited positional disorder, the components of which were refined to a relative ratio of ca 89:11. The minor component was refined with restrained, isotropic thermal parameters. Hydrogen atoms were not located for the minor component.

The crystal of 6b was grown by slow evaporation of a chloroform/ethanol solution and was found to contain regions of highly disordered solvent which could not be modelled effectively. The SQUEEZE algorithm was invoked, the calculations for which indicated that the two solvent accessible voids contained approximately 237 electrons, consistent with four molecules of chloroform (232 electrons), or two molecules of chloroform of solvation per molecule of 6b. The data precision is less than ideal and so is not suitable for distance and angle comparisons, but is included as confirmation of the atom connectivity.

The crystal of 7b, grown by slow evaporation of a diethyl ether solution, was found to contain a region of significantly disordered solvent which could not be modelled effectively and so the SQUEEZE algorithm was invoked. The calculations determined that the two solvent accessible voids in the unit cell contained approximately 244 electrons each, consistent with 6 diethyl ether molecules (252 electrons) in total, or 1.5 molecules of diethyl ether per molecule of 7b.
### Table S1. X-ray Structure Summary

<table>
<thead>
<tr>
<th>formula</th>
<th>Et₄N(2b)</th>
<th>4b</th>
<th>5b</th>
<th>6b 2.5C₈H₁₂</th>
<th>7b</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₆BN₂O₂TeW</td>
<td>2.627, 0.222</td>
<td>0.032 x 0.043 x 0.155</td>
<td>3.672, 25.027</td>
<td>0.0343, 0.0568</td>
<td>0.0681, 0.1168</td>
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</tbody>
</table>

**Notes and references**

Spectra

$^1$H NMR Spectrum of Et$_4$N[2b]

$^{13}$C($^1$H) NMR Spectrum of Et$_4$N[2b]

See caveat discussed in experimental procedure regarding tentative observation of $\delta$(CTe).
$^{125}$Te{¹H} NMR Spectrum of Et₄N[2b]

$^1$H NMR Spectrum of 3a
\(^{13}\text{C}^\text{\textit{H}}\) NMR Spectrum of 3a

\(^{125}\text{Te}^\text{\textit{H}}\) NMR Spectrum of 3a
$^1$H NMR Spectrum of 3b

$^{13}$C($^1$H) NMR Spectrum of 3b
$^{125}\text{Te}[^1\text{H}]$ NMR Spectrum of 3b

$^1\text{H}$ NMR Spectrum of 4b
$^{13}$C{$_1^1$H} NMR Spectrum of 4b

$^{125}$Te{$_1^1$H} NMR Spectrum of 4b
$^1$H NMR Spectrum of 5a

$^{13}$C($^1$H) NMR Spectrum of 5a
$^{125}\text{Te}[^1\text{H}]$ NMR Spectrum of 5a

$^1\text{H}$ NMR Spectrum of 6a
$^{13}$C{\textit{t}H} NMR Spectrum of 6a

$^{125}$Te{\textit{t}H} NMR Spectrum of 6a
$^1$H NMR Spectrum of 6b

$^{13}$C($^1$H) NMR Spectrum of 6b
$^{125}\text{Te}{ }^1\text{H}} NMR Spectrum of 6b

$^1\text{H}} NMR Spectrum of 7a
$^{13}$C($^1$H) NMR Spectrum of 7a

$^{125}$Te($^1$H) NMR Spectrum of 7a
$\textbf{1}^H\text{NMR Spectrum of 7b}$

$\textbf{13}^{C(1)}\text{NMR Spectrum of 7b}$
$^{125}\text{Te}^1\text{H}$ NMR Spectrum of 7b