Chemical Communications

Supporting Information

An Anionic Nucleophilic d^4 Carbyne Complex

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General Considerations

All manipulations of air-sensitive compounds were carried out at room temperature under a dry oxygen-free nitrogen atmosphere using standard Schlenk, vacuum line, or inert atmosphere (argon) glovebox techniques with dried and degassed solvents. NMR spectra were obtained on a Bruker Avance 400 (^{1}H at 400.1 MHz, ^{13}C at 100.5 MHZ, ^{31}P at 162.0 MHz), Bruker Avance 700 (^{1}H at 700.1 MHz, ^{13}C at 176.1 MHz, ^{31}P at 283.5 MHz), or Bruker Avance 800 with cryoprobe (^{1}H at 800.1 MHz, ^{13}C at 200.2 MHz) spectrometer. Chemicals shifts (δ) are reported in ppm and referenced to the solvent peak (^{1}H, ^{13}C) or external 85% H_3PO_4. The multiplicities of NMR resonances are denoted by the abbreviations s (singlet), d (doublet), t (triplet), sep (septet), m (multiplet), and combinations thereof for more highly coupled systems and $^nJ_{ab}$ reported in Hz. Assignments of phenyl ring resonances are denoted C_i for *ipso*, C_o for *ortho*, C_m for *meta* and C_p for *para* carbon environments. Whilst $^{13}C\{^1H\}$ for carbon nuclei of the $(C_6H_{11})_2P(CH_2CH_2)P(C_6H_{11})_2$ ligand were observed, their narrow spectral range precluded unequivocal assignment for the dcpe carbon environments. Similarly, proton environments within the dcpe ligand could not be uniquely identified due to the complex multiplicities and similar chemical shifts encountered. Infrared spectra were obtained using a Perkin-Elmer Spectrum One FT-IR spectrometer. Elemental microanalysis has been performed at the London Metropolitan University. 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 on either an Oxford Diffraction SuperNova or Oxford Diffraction Xcalibur diffractometer.

Synthesis of $W(\equiv C^tBu)(SnMe_3)(dcpe)(CO)_2$

To a yellow solution of $W(\equiv CH)(Br)(dcpe)(CO)_2$ (151 mg, 0.200 mmol) in THF (10 mL) at -78°C (dry ice/acetone), 0.38 mL of a 1.6 M solution of ^{t}BuLi in hexanes (0.60 mmol) was added *via* syringe. The resultant dark red solution was allowed to stir for 30 minutes at this temperature before 0.60 mL of a 1.0 M solution of $SnMe_3Cl$ in THF (0.60 mmol) was added *via* syringe. The reaction was allowed to stir at this temperature for a further 30 minutes before removal of the cooling bath. THF was removed *in vacuo* and the product was extracted using toluene (2 x 10 mL) *via* cannula filtration from the insoluble LiBr precipitate. Removal of the toluene *in vacuo* followed by washing with Et_2O (2 x 5mL) afforded the product as a yellow powder. Yield: 54 mg, 30%. IR (toluene) ν/cm^{-1}: 1961 (CO), 1899 (CO). IR (Nujol) ν/cm^{-1}: 1951 (CO), 1886 (CO). ^{1}H NMR (C_6D_6, 25°C): δ_H 2.09 (m, 2H, CH in dcpe), 2.01-1.87 (m, 4 H, $P(C\underline{\mathbf{H_2}})_2P$), 1.79-1.04 (m, 42 H, 21 x CH_2, 1.30 (s, 9 H, $C(C\mathbf{H_3})_3$), 0.44 (s, $^2J_{SnH}$ = 27.2, 9 H, $Sn(C\underline{\mathbf{H_3}})_3$). ^{13}C NMR ($C_6D_6$, 25°C): δ_C 317.2 (t, $W\equiv\underline{\mathbf{C}}$, $^2J_{CP}$ = 7.47 Hz), 219.5 (dd, $^2J_{CP(cis)}$ = 7.00 Hz, $^2J_{CP(trans)}$ = 26.2, $W(\underline{\mathbf{C}}O)_2$), 53.3 pm ($\underline{\mathbf{C}}(CH_3)$), 42.0 (d, $\underline{\mathbf{C}}H[C_6H_{11}]$, J_{CP} = 21.0), 40.8 (d, $\underline{\mathbf{C}}H[C_6H_{11}]$, J_{CP} = 18.7), 30.8 ($\underline{\mathbf{C}}H_2[C_6H_{11}]$), 30.0 ($\underline{\mathbf{C}}H_2[C_6H_{11}]$), 29.3 (d, J_{CP} = 4.1, $\underline{\mathbf{C}}H_2[C_6H_{11}]$), 28.8 ($\underline{\mathbf{C}}H_2[C_6H_{11}]$), 28.7 ($C(\underline{\mathbf{C}}H_3)_3$), 27.7 (d, J_{CP} = 8.0, $\underline{\mathbf{C}}H_2[C_6H_{11}]$), 27.6 (d, J_{CP} = 4.2) $\underline{\mathbf{C}}H_2[C_6H_{11}]$), 27.5 (d, J_{CP} = 11.22, $\underline{\mathbf{C}}H_2[C_6H_{11}]$), 27.2 (d, J_{CP} = 11.0, $\underline{\mathbf{C}}H_2[C_6H_{11}]$), 26.3. ($\underline{\mathbf{C}}H_2[C_6H_{11}]$), 26.0 ($\underline{\mathbf{C}}H_2[C_6H_{11}]$), 23.6 (dd, $^1J_{CP}$ = 22.7, $^2J_{CP}$ = 13.4, $P(\underline{\mathbf{C}}H_2)_2P$), -3.7 ($^1J_{C^{119}Sn}$ = 91.4, $^1J_{C^{117}Sn}$ = 88.4, $Sn\underline{\mathbf{C}}H_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 25°C): δ_P 51.7 ($^1J_{PW}$ = 220, $^2J_{P^{119}Sn}$ = 151, $^2J_{P^{117}Sn}$ = 145). Crystals suitable for crystallographic analysis were obtained slow evaporation of a solution in benzene under a nitrogen atmosphere. MS-ESI(+): 731.36 $[M-SnMe_3]^+$. Accurate mass: found 731.3367 $[M-SnMe_3]$. Calcd for $C_{33}H_{57}O_2P_2{}^{184}W$ 731.3343. Anal. found: C, 48.18; H, 7.50; N, 0.00%. Calcd. for $C_{36}H_{66}O_2P_2SnW$: C, 48.29; H, 7.43; N, 0.00%.

Crystal data for $C_{36}H_{66}O_2P_2SnW$: M_w = 895.41 , triclinic, space group $P\bar{1}$ (no. 2), a = 9.1646(3) Å, b = 12.5454(5) Å, c = 17.8461(3) Å, α = 87.399(2)°, β = 77.495(2)°, γ = 75.600(3)°, V = 1940.14(3) Å^3, Z = 2, T = 150(2) K, μ(Cu Kα) = 11.499 mm^{-1}, ρ_{calc}

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= 1.533 Mgm^{-3}, 36372 reflections measured (8.91° ≤ 2Θ ≤ 144.81°), 7638 unique (R_{int} = 0.043) which were used in all calculations. The final R_1 was 0.0322 (I>2.0σ(I)) and wR_2 was 0.0838 (all data). CCDC 1515542

Synthesis of W(≡C^{t}Bu)(Br)(dcpe)(CO)$_2$

To a yellow solution of W(≡CH)(Br)(dcpe)(CO)$_2$ (151 mg, 0.200 mmol) in THF (10 mL) at -78°C (dry ice/acetone), 0.38 mL of a 1.6 M solution of ^{t}BuLi in hexanes (0.60 mmol) was added *via* syringe. The resultant dark red solution was allowed to stir for 30 minutes at this temperature before 0.30 mL of neat ^{t}BuBr (0.366 g, 2.7 mmol) was added *via* syringe. The reaction was allowed to stir at -78°C for a further 30 minutes before removal of the cooling bath. THF was removed *in vacuo* and the product was extracted using DCM (2x 10 mL) *via* filtration through a glass frit from the insoluble LiBr precipitate. Removal of the DCM *in vacuo* followed by washing with a mixture of pentane and ether (5:1, 2x 5mL) afforded the product as a beige powder. Yield: 152 mg, 94%. IR (CH_2Cl_2) ν/cm^{-1}: 1978 (CO), 1908 (CO). IR (Nujol) ν/cm^{-1}: 1985 (CO), 1913 (CO) ^{1}H NMR ($CDCl_3$, 25^{o}C): δ_H 2.25-2.10 (m, 4 H, dcpe), 2.03-1.96 (m, 2 H, dcpe), 1.93-1.20 (m, 42 H, dcpe, 1.08 (s, 9 H, C(C**H$_3$**)$_3$). ^{13}C NMR ($CDCl_3$, 25^{o}C): δ_C 290.4 (t, W≡$\underline{\mathbf{C}}$, $^{2}J_{CP}$ = 7.47 Hz), 213.9 (dd, W($\underline{\mathbf{C}}$O)$_2$, $^{2}J_{CP(cis)}$ = 7.00 Hz, $^{2}J_{CP(trans)}$ = 26.2 Hz), 51.2 pm (d, $^{2}J_{WC}$ = 35.3, $\underline{\mathbf{C}}$(CH$_3$)$_3$), 40.4 (d, J_{CP} = 20.5, $\underline{\mathbf{C}}$H[C_6H_{11}], 34.8 (d, J_{CP} = $\underline{\mathbf{C}}$H[C_6H_{11}]), 30.4 ($\underline{\mathbf{C}}$H$_2$[C_6H_{11}]), 29.8 ($\underline{\mathbf{C}}$H$_2$[C_6H_{11}]), 29.3 ($\underline{\mathbf{C}}$H$_2$[C_6H_{11}]), 29.3 ($\underline{\mathbf{C}}$H$_2$[C_6H_{11}]), 28.6 (C($\underline{\mathbf{C}}$H$_3$)$_3$), 27.7 (d, J_{CP} = 12.4 Hz $\underline{\mathbf{C}}$H$_2$[C_6H_{11}]), 27.6 (d, J_{CP} = 13.8, $\underline{\mathbf{C}}$H$_2$[C_6H_{11}]), 27.4 (d, J_{CP} = 11.1, $\underline{\mathbf{C}}$H$_2$[C_6H_{11}]), 27.4 (d, J_{CP} = 9.34 Hz, $\underline{\mathbf{C}}$H$_2$[C_6H_{11}]), 26.3 ($\underline{\mathbf{C}}$H$_2$[C_6H_{11}]), 26.1 ($\underline{\mathbf{C}}$H$_2$[C_6H_{11}]), 22.2 (dd, $^{1}J_{CP}$ = 21.9, $^{2}J_{CP}$ = 11.9, P($\underline{\mathbf{C}}$H$_2$)$_2$P. ^{31}P{^{1}H} NMR ($CDCl_3$, 25^{o}C): δ_P 42.37 ($^{1}J_{PW}$ = 222). MS-ESI(+): 1541.5686 [2M-Br]$^+$, 835.2462 [M+Na]$^+$, 731.3343 [M-Br]$^+$. Accurate mass: found 731.3344 [M-Br]$^+$. Calcd for $C_{33}H_{57}O_2P_2{}^{184}W$ 731.3343. Anal. found: C, 48.59; H, 7.24; N: 0.00%. Calcd. for $C_{33}H_{57}BrO_2P_2W$: C, 48.84; H, 7.08; N, 0.00%. Crystals suitable for crystallographic analysis were obtained via diffusion of pentane into a concentrated solution of **3** in DCM at -20^{o}C.

Crystal Data for $C_{33}H_{56}BrO_2P_2W$: M_w =810.47, monoclinic, space group $P2_1/n$ (no. 14), a = 10.8206(5) Å, b = 14.4920(5) Å, c = 22.3551(9) Å, β = 96.561(4)°, V = 3482.6(2) Å^3, Z = 4, T = 150(2) K, μ(Mo Kα) = 4.583 mm^{-1}, ρ_{calc} = 1.546 Mgm^{-3}, 51350 reflections measured (6.71° ≤ 2Θ ≤ 50.05°), 6134 unique (R_{int} = 0.1066) which were used in all calculations. The final R_1 was 0.0410 (I > 2σ(I)) and wR_2 was 0.1091 (all data). CCDC 1515560.

Synthesis of W(≡C^{t}Bu)(Cl)(dcpe)(CO)$_2$

To a yellow solution of W(≡CH)(Br)(dcpe)(CO)$_2$ (151 mg, 0.200 mmol) in THF (10 mL) at -78°C (dry ice/acetone), 0.38 mL of a 1.6 M solution of ^{t}BuLi in hexanes (0.60 mmol) was added *via* syringe. The resultant dark red solution was allowed to stir for 30 minutes at -78°C before the addition of 0.30 mL of neat ^{t}BuCl (0.25g, 2.7 mmol) was added *via* syringe. The reaction was allowed to stir at -78°C for a further 30 minutes before removal of the cooling bath. THF was removed *in vacuo* and the product was extracted using DCM (2x 10mL) *via* filtration through a glass frit from the insoluble LiCl precipitate. Recrystallization of this product *via* vapour diffusion of pentane into DCM afforded the product as large orange crystals. Yield: 56 mg, 37%. IR (CH_2Cl_2) ν/cm^{-1}: 1991 (CO), 1915 (CO). IR (Nujol) ν/cm^{-1}: 1984 (CO), 1913 (CO). ^{1}H NMR ($CDCl_3$, 25^{o}C): δ_H 2.23-1.17 (m, 48 H, dcpe), 1.05 (s, 9 H, C(CH$_3$)$_3$). ^{13}C NMR ($CDCl_3$, 25^{o}C): δ_C 289.5 (t, W≡$\underline{\mathbf{C}}$, $^{2}J_{CP}$ = 7.64 Hz), 219.5 (dd, W($\underline{\mathbf{C}}$O)$_2$, $^{2}J_{CP(cis)}$ = 6.78 Hz, $^{2}J_{CP(trans)}$ = 41.6 Hz), 52.0 ($^{2}J_{CW}$ = 35.7, $\underline{\mathbf{C}}$(CH$_3$)$_3$, 39.9 (d, $^{1}J_{CP}$ = 21.3, $\underline{\mathbf{C}}$H[C_6H_{11}]), 33.9 (d, $^{1}J_{CP}$ = 18.39, $\underline{\mathbf{C}}$H[C_6H_{11}]), 30.4 ($\underline{\mathbf{C}}$H$_2$[C_6H_{11}]), 29.6 ($\underline{\mathbf{C}}$H$_2$[C_6H_{11}]), 29.4 ($\underline{\mathbf{C}}$H$_2$[C_6H_{11}]), 29.3 ($\underline{\mathbf{C}}$H$_2$[C_6H_{11}]), 28.77 (WCC$\underline{\mathbf{C}}$H$_3$), 27.76 (d, J_{CP} = 12.4 Hz $\underline{\mathbf{C}}$H$_2$[C_6H_{11}]), 27.6 (d, J_{CP} = 12.0, $\underline{\mathbf{C}}$H$_2$[C_6H_{11}]), 27.5 (d, J_{CP} = 9.18, $\underline{\mathbf{C}}$H$_2$[C_6H_{11}]), 27.4 (d, J_{CP} = 9.32, $\underline{\mathbf{C}}$H$_2$[C_6H_{11}]), 26.3. ($\underline{\mathbf{C}}$H$_2$[C_6H_{11}]), 26.1 ($\underline{\mathbf{C}}$H$_2$[C_6H_{11}]), 22.1 (dd, $^{1}J_{CP}$ = 22.2, $^{2}J_{CP}$ = 12.0, Cy$_2$P($\underline{\mathbf{C}}$H$_2$)$_2$PCy$_2$). ^{31}P{^{1}H} NMR ($CDCl_3$, 25^{o}C): δ_P 46.01 ($^{1}J_{PW}$ = 224 Hz). MS-ESI(+): 1555.5898 [2M+Na]$^+$, 791.2923 [M+Na]$^+$, 731.3340 [M-Cl]$^+$ Accurate mass: found 731.3340 [M-Cl]$^+$. Calcd for $C_{33}H_{57}O_2P_2{}^{184}W$ 731.3343. Anal. found: C, 50.69; H, 7.66; N, 0.00. Calcd. for $C_{33}H_{57}ClO_2P_2W$: C, 51.67; H, 7.49; N, 0.00%. NB: Calcd. for $C_{33}H_{57}ClO_2P_2W.(CH_2Cl_2)_{0.25}$: C, 50.66; H, 7.35; N, 0.00%.Crystals suitable for crystallographic analysis were obtained *via* diffusion of pentane into a solution of **4** in DCM at -20^{o}C.

Crystal Data for $C_{33}H_{57}ClO_2P_2W$: (M =767.02 g/mol): monoclinic, space group P2$_1$/n (no. 14), a = 10.90249(14) Å, b = 14.24490(18) Å, c = 22.5025(3) Å, β = 97.8393(13)°, V = 3462.09(8) Å^3, Z = 4, T = 150.(2) K, μ(Cu Kα) = 7.962 mm^{-1}, ρ_{calc} = 1.472 Mgm^{-3}, 45483 reflections measured (7.36° ≤ 2Θ ≤ 144.89°), 6760 unique (R_{int} = 0.0442) which were used in all calculations. The final R_1 was 0.0613 (I > 2σ(I)) and wR_2 was 0.1507 (all data). CCDC 1515559.

Synthesis of W(≡C^{t}Bu)(SPh)(CO)$_2$(dcpe)

To a yellow solution of W(≡CH)(Br)(dcpe)(CO)$_2$ (151 mg, 0.200 mmol) in THF (10 mL) at -78°C (dry ice/acetone), 0.38 mL of a 1.6 M solution of ^{t}BuLi in hexanes (0.60 mmol) was added *via* syringe. The resultant dark red solution was allowed to stir for 30 minutes at -78°C before the addition of PhSSPh (0.131 mg, 0.600 mmol) as a solid under a positive flow of nitrogen. The reaction was allowed to stir at -78°C for a further 30 minutes before removal of the cooling bath. THF was removed *in vacuo* and the product was extracted using DCM (2 x 10mL) *via* filtration through a glass frit from the insoluble lithium salt precipitate. The DCM was removed *in vacuo* and the subsequent residue washed with a mixture of Et_2O and pentane (2 x 5 mL, 1:10) to afford the product as a fine yellow powder. Yield: 120 mg, 71%. %. IR (CH_2Cl_2) ν/cm^{-1}: 1997 (CO), 1928 (CO). IR (Nujol) ν/cm^{-1}: 1993 (CO), 1928 (CO). ^{1}H NMR ($CDCl_3$, 25^{o}C): δ_H 7.50 (d, 2 H, $^{3}J_{HH}$ = 7.7, C$_o$H in SC$_6$H$_5$), 7.07 (d, 2 H, $^{3}J_{HH}$ = 8.0, $^{3}J_{HH}$ = 7.3, 2xC$_m$H in SC$_6$H$_5$), 6.91 (t, 1 H, $^{3}J_{HH}$ = 7.3, C$_p$H), 2.21 (m, 6 H, dcpe), 2.00 (m, 2 H, dcpe), 1.92-1.19 (m, 40 H, dcpe), 1.09 (s, 9 H, C(CH$_3$)$_3$). ^{13}C NMR ($CDCl_3$, 25^{o}C): δ_C 297.3 (t, $^{2}J_{CP}$ = 9.2, W≡$\underline{\mathbf{C}}$), $^{1}J_{WC}$ = 176.14), 216.3 (dd, $^{cis}J_{CP}$ = 7.7 $^{trans}J_{CP}$ = 37.3, W($\underline{\mathbf{C}}$O)$_2$), 147.4 (t, $^{3}J_{CP}$ = 2.86, C$_i$ in SC$_6$H$_5$), 134.5 (C$_m$ in SC$_6$H$_5$), 127.4 (C$_o$ in SC$_6$H$_5$), 122.5 (C$_p$ in SC$_6$H$_5$), 52.4 ($^{2}J_{CW}$ = 34.2, $\underline{\mathbf{C}}$(CH$_3$)$_3$), 40.9 (d, $^{1}J_{CP}$ = 19.3 Hz, $\underline{\mathbf{C}}$H[C_6H_{11}]) 34.4 (d, $^{1}J_{CP}$ = 18.5 Hz, $\underline{\mathbf{C}}$H[C_6H_{11}]), 30.5

($\underline{\mathbf{C}}H_2[C_6H_{11}]$), 30.1 ($\underline{\mathbf{C}}H_2[C_6H_{11}]$), 29.4 ($\underline{\mathbf{C}}H_2[C_6H_{11}]$), 29.3 (d, J_{CP} = 3.0, $\underline{\mathbf{C}}H_2[C_6H_{11}]$), 28.9 ($W{\equiv}CC\underline{\mathbf{C}}H_3$), 27.9 (d, J_{CP} = 12.3, $\underline{\mathbf{C}}H_2[C_6H_{11}]$), 27.8 (d, J_{CP} = 11.5, $\underline{\mathbf{C}}H_2[C_6H_{11}]$), 27.6 (d, J_{CP} = 5.3, $\underline{\mathbf{C}}H_2[C_6H_{11}]$), 27.6 (d, J_{CP} = 4.6, $\underline{\mathbf{C}}H_2[C_6H_{11}]$), 26.5 ($\underline{\mathbf{C}}H_2[C_6H_{11}]$), 26.3 ($\underline{\mathbf{C}}H_2[C_6H_{11}]$), 22.3 (dd, $^{1}J_{CP}$ = 22.2, $^{2}J_{CP}$ = 11.9, $P(\underline{\mathbf{C}}H_2)_2P$). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 25°C): δ_P 41.18 ($^{1}J_{PW}$ = 218 Hz). MS-ESI(+): 840.3453 $[M]^+$, 731.3386 $[M\text{-}SPh]^+$. Accurate mass: found 888.3453 $[M]^+$. Calcd for $C_{39}H_{62}O_2P_2S^{184}W$ 840.3455. Anal. found: C, 55.66; H, 7.53; N, 0.00%. Calcd. for $C_{39}H_{62}O_2P_2SW$: C, 55.71; H, 7.43; N, 0.00%. Crystals suitable for crystallographic analysis were obtained *via* diffusion of pentane into a solution of the complex in DCM at -20°C.

Crystal Data for $C_{39}H_{62}O_2P_2SW$: M_w =840.73, monoclinic, space group $P2_1/c$ (no. 14), a = 21.70419(20) Å, b = 20.77394(16) Å, c = 18.14956(16) Å, β = 106.3363(10)°, V = 7852.92(12) Å^3, Z = 8, T = 150(2) K, μ(Cu Kα) = 6.946 mm^{-1}, ρ_{calc} = 1.422 Mgm^{-3}, 158756 reflections measured (6.00° ≤ 2Θ ≤ 148.20°), 15875 unique (R_{int} = 0.0715) which were used in all calculations. The final R_1 was 0.0478 ($I > 2\sigma(I)$) and wR_2 was 0.1094 (all data). CCDC 1515561.

Synthesis of $W(\equiv C^tBu)(SePh)(dcpe)(CO)_2$

To a yellow solution of $W(\equiv CH)(Br)(dcpe)(CO)_2$ (151 mg, 0.200 mmol) in THF (10 mL) at -78°C (dry ice/acetone), 0.38 mL of a 1.6 M solution of ^tBuLi in hexanes (0.60 mmol) was added *via* syringe. The resultant dark red solution was allowed to stir for 30 minutes at -78°C before the addition of PhSeSePh (0.085 g, 0.27 mmol) was added *via* syringe. The reaction was allowed to stir at -78°C for a further 30 minutes before removal of the cooling bath. THF was removed *in vacuo* and the product was extracted using DCM (2x 10mL) *via* filtration through a glass frit from the insoluble LiCl precipitate. The DCM was removed *in vacuo* and the subsequent product washed with a mixture of ether and pentane (2 x 5 mL, 1:10) to afford the product as an off-white powder. Yield: 71 mg, 40%. IR (C_6H_6) ν/cm^{-1}: 1984 (CO), 1915 (CO). IR (Nujol) ν/cm^{-1}: 1977 (CO), 1908 (CO). ^{1}H NMR ($CDCl_3$, 25°C): δ_H 7.71 (d, $^{3}J_{HH}$ = 7.8, 2 H, C_oH in SeC_6H_5), 7.08-7.01 (m, 3 H, 2 x C_mH, 1 x C_pH in SeC_6H_5), 2.26-2.13 (m, 6 H, dcpe), 2.04-2.00 (m, 2H, dcpe), 1.94-1.25 (m, 40 H, dcpe), 1.13 (s, 9 H, $C(C\mathbf{H_3})_3$). ^{13}C NMR ($CDCl_3$, 25°C): δ_C 298.8 (t, $^{2}J_{CP}$ = 8.73, $W{\equiv}\underline{\mathbf{C}}$, $^{1}J_{WC}$ = 176.1), 216.3 (dd, $^{cis}J_{CP}$ = 7.2 $^{trans}J_{CP}$ = 36.5, $W(\underline{\mathbf{C}}O)_2$), 136.3 ($C_o$ in SC_6H_5), 136.0 (t, $^{3}J_{CP}$ = 2.92, C_i in SeC_6H_5), 127.4 (C_o in SC_6H_5), 123.5 (C_p in SC_6H_5), 52.2 ($^{2}J_{CW}$ = 33.6, $\underline{\mathbf{C}}(CH_3)_3$), 41.1 (d, $^{1}J_{CP}$ = 19.5, $\underline{\mathbf{C}}H[C_6H_{11}]$) 34.4 (d, $^{1}J_{CP}$ = 18.7 Hz, $\underline{\mathbf{C}}H[C_6H_{11}]$), 30.4 ($\underline{\mathbf{C}}H_2[C_6H_{11}]$), 30.1 ($\underline{\mathbf{C}}H_2[C_6H_{11}]$), 29.2 ($\underline{\mathbf{C}}H_2[C_6H_{11}]$), 29.1 (d, J_{CP} = 3.9, $\underline{\mathbf{C}}H_2[C_6H_{11}]$), 28.6 ($C(\underline{\mathbf{C}}H_3)_3$), 27.9 (d, J_{CP} = 12.3, $\underline{\mathbf{C}}H_2[C_6H_{11}]$), 27.7 (d, J_{CP} = 12.8, $\underline{\mathbf{C}}H_2[C_6H_{11}]$), 27.4 (d, J_{CP} = 9.4, $\underline{\mathbf{C}}H_2[C_6H_{11}]$), 27.6 (d, J_{CP} = 8.4, $\underline{\mathbf{C}}H_2[C_6H_{11}]$), 26.3 ($\underline{\mathbf{C}}H_2[C_6H_{11}]$), 26.1 ($\underline{\mathbf{C}}H_2[C_6H_{11}]$), 22.6 (dd, $^{1}J_{CP}$ = 22.5, $^{2}J_{CP}$ = 12.0). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 25°C): δ_P 41,18 ($^{1}J_{PW}$ = 218 Hz). MS-ESI(+): 888.2941 $[M]^+$, 731.3422 $[M\text{-}SePh]^+$. Accurate mass: found 888.2941 $[M]^+$. Calcd for $C_{39}H_{62}O_2P_2{}^{80}Se^{184}W$ 888.2900. Anal. found: C, 52.64; H, 7.11; N, 0.00%. Calcd. for $C_{39}H_{62}O_2P_2TeW$: C, 52.77; H, 7.04; N, 0.00%. Crystals suitable for crystallographic analysis were obtained *via* slow evaporation of a solution of the complex in Et_2O at -20°C.

Crystal Data for $C_{39}H_{62}O_2P_2SeW$: M_w =887.63: monoclinic, space group $P2_1/n$ (no. 14), a = 10.5933(3) Å, b = 15.6299(5) Å, c = 24.1696(6) Å, β = 99.630(3)°, V = 3945.44(19) Å^3, Z = 4, T = 150(2) K, μ(Cu Kα) = 7.473 mm^{-1}, ρ_{calc} = 1.494 Mgm^{-3}, 61798 reflections measured (6.76° ≤ 2Θ ≤ 147.67°), 7980 unique (R_{int} = 0.0725) which were used in all calculations. The final R_1 was 0.0473 ($I > 2\sigma(I)$) and wR_2 was 0.1163 (all data). CCDC 1515557.

Synthesis of $W(\equiv C^tBu)(TePh)(dcpe)(CO)_2$

To a yellow solution of $W(\equiv CH)(Br)(dcpe)(CO)_2$ (151 mg, 0.200 mmol) in THF (10 mL) at -78°C (dry ice/acetone), 0.38 mL of a 1.6 M solution of ^tBuLi in hexanes (0.60 mmol) was added *via* syringe. The resultant dark red solution was allowed to stir for 30 minutes at -78°C before the addition of PhTeTePh (0.10 g, 0.27 mmol). The reaction was allowed to stir at -78°C for a further 30 minutes before removal of the cooling bath. THF was removed *in vacuo* and the product was extracted using DCM (2x 10mL) *via* filtration through a glass frit from the insoluble LiCl precipitate. The DCM was removed *in vacuo* and the subsequent product washed with a mixture of ether and penatne (2x5mL, 1:10) to afford the product as an orange powder. Yield 112 mg, 60%. IR (C_6H_6) ν/cm^{-1}: 1981 (CO), 1914 (CO). IR (Nujol) ν/cm^{-1}: 1973 (CO), 1907 (CO). ^{1}H NMR ($CDCl_3$, 25°C): δ_H 8.37 (d, $^{3}J_{HH}$ = 7.5, 2 H, C_oH in TeC_6H_5), 7.07 (t, 1 H, $^{3}J_{HH}$ = 7.2, C_pH in TeC_6H_5), 7.01 (dd, $^{3}J_{HH}$ = 7.5, $^{3}J_{HH}$ = 7.2, 2 H, 2xC_mH in TeC_6H_5), 2.54-2.49 (m, 2 H, dcpe), 2.19-2.11 (m, 4 H, dcpe) 1.88-1.02 (m, 40 H, dcpe), 1.19 (s, 9 H, $C(C\underline{\mathbf{H_3}})_3$). ^{13}C NMR ($CDCl_3$, 25°C): δ_C 301.4 (t, $^{2}J_{CP}$ = 8.36, $W{\equiv}\underline{\mathbf{C}}$), 215.0 (dd, $^{cis}J_{CP}$ = 7.3 $^{trans}J_{CP}$ = 34.5, $W(\underline{\mathbf{C}}O)_2$), 141.1 ($C_m$ in TeC_6H_5), 128.0 (C_o in TeC_6H_5), 125.3 (C_p in SC_6H_5), 108.5 (t, $^{3}J_{CP}$ = 3.00, C_i in TeC_6H_5), 51.8 ($^{2}J_{CW}$ = 35.5, $W{\equiv}C\underline{\mathbf{C}}CH_3$), 41.7 (d, $^{1}J_{CP}$ = 19.2, $\underline{\mathbf{C}}H[C_6H_{11}]$), 38.0 (d, $^{1}J_{CP}$ = 19.2, $\underline{\mathbf{C}}H[C_6H_{11}]$), 30.8 ($\underline{\mathbf{C}}H_2[C_6H_{11}]$), 30.2 ($\underline{\mathbf{C}}H_2[C_6H_{11}]$), 29.4 (d, J_{CP} = 3.74, $\underline{\mathbf{C}}H_2[C_6H_{11}]$), 29.1 ($\underline{\mathbf{C}}H_2[C_6H_{11}]$), 28.4 ($W{\equiv}CC\underline{\mathbf{C}}H_3$), 27.6 (d, J_{CP} = 12.0, $\underline{\mathbf{C}}H_2[C_6H_{11}]$), 27.5 (d, J_{CP} = 13.2, $\underline{\mathbf{C}}H_2[C_6H_{11}]$), 27.3 (d, J_{CP} = 6.0, $\underline{\mathbf{C}}H_2[C_6H_{11}]$), 27.3 (d, J_{CP} = 4.2, $\underline{\mathbf{C}}H_2[C_6H_{11}]$), 26.3 ($\underline{\mathbf{C}}H_2[C_6H_{11}]$), 26.0 ($\underline{\mathbf{C}}H_2[C_6H_{11}]$), 23.1 (dd, $^{1}J_{CP}$ = 22.4 $^{2}J_{CP}$ = 12.5, $P(\underline{\mathbf{C}}H_2)_2P$). $^{31}P\{1H\}$ NMR ($CDCl_3$, 25°C): δ_P 37.99 ($^{1}J_{PW}$ = 218 Hz). MS-ESI: 731.3342 $[M\text{-}TePh]^+$. Accurate mass: found 731.3342 $[M\text{-}TePh]^+$. Calcd for $C_{33}H_{57}O_2P_2{}^{184}W$ 731.3343. Anal. found: C, 49.92 ; H, 6.65; N, 0.00%. Calcd. for $C_{39}H_{62}O_2P_2TeW$: C, 50.03; H, 6.67; N, 0.00%. Crystals suitable for crystallographic analysis were obtained *via* slow evaporation of a solution of the complex in benzene at room temperature.

Crystal Data for $C_{39}H_{62}O_2P_2TeW$: M_w = 936.27, monoclinic, space group $P2_1/n$ (no. 14), a = 10.62715(11) Å, b = 15.6401(2) Å, c = 24.3392(3) Å, β = 100.1600(11)°, V = 3981.98(9) Å^3, Z = 4, T = 150(2) K, μ(CuKα) = 12.026 mm^{-1}, ρ_{calc} = 1.562 Mgm^{-3}, 41443 reflections measured (6.75° ≤ 2Θ ≤ 147.97°), 8049 unique (R_{int} = 0.0428) which were used in all calculations. The final R_1 was 0.0356 ($I > 2\sigma(I)$) and wR_2 was 0.0975 (all data). CCDC 1515558.

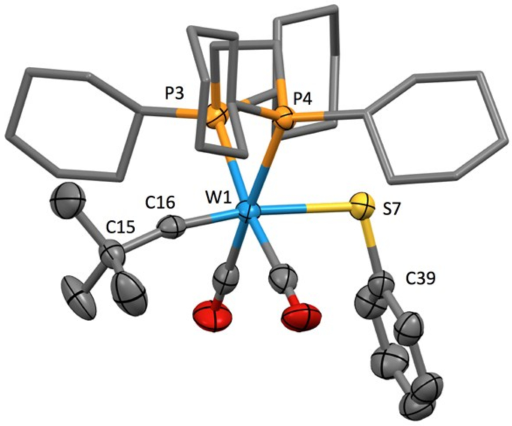

Figure S1. Molecular Structure of $[W(\equiv C^tBu)(SPh)(CO)_2(dcpe)]$ (Hydrogen atoms omitted, cyclohexyl groups simplified, 60% displacement ellipsoids). One of two independent molecules shown. Selected bond lengths (Å) and angles (deg.): W1–P3 2.5622(13), W1–P4 2.5515(12), W1–S7 2.6008(12), W1–C16 1.821(5), W1–C7 2.003(6), W2–P5 2.5498(12), S7–C39 1.777(5), C15–C16 1.502(7), P3–W1–S7 88.96(4), P4–W1–P3 78.70(4), P4–W1–S7 85.90(4), C15–C16–W1 168.2(4), C39–S7–W1 107.36(17).

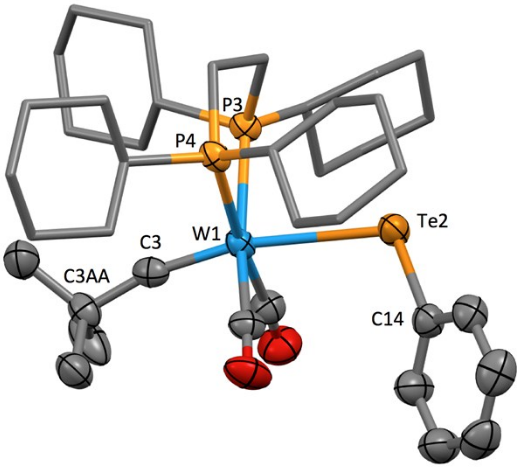

Figure S2. Molecular Structure of $[W(\equiv C^tBu)(TePh)(CO)_2(dcpe)]$ (Hydrogen atoms omitted, cyclohexyl groups simplified, 60% displacement ellipsoids). Selected bond lengths (Å) and angles (deg.): W1–Te2 2.9393(3), W1–P3 2.5464(10), W1–P4 2.5730(11), W1–C3 1.823(5), Te2–C14 2.131(4), C3–C3AA 1.496(6), P3–W1–Te2 84.71(2), P3–W1–P4 78.33(3), P4–W1–Te2 95.46(2), C3–W1–Te2 165.47(14), C3–W1–P3 101.78(13), C3–W1–P4 98.58(14), C14–Te2–W1 104.84(12), C3AA–C3–W1 167.5(4).

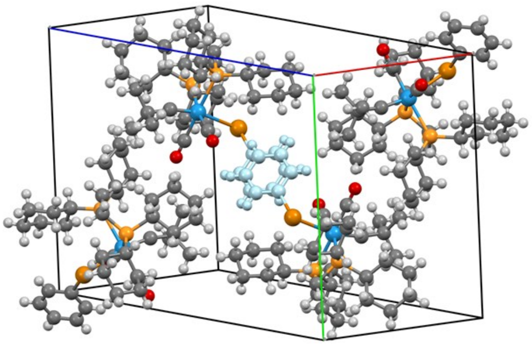

Figure S3. Crystal packing for $[W(\equiv C^tBu)(TePh)(CO)_2(dcpe)]$ (**3c**) showing incipient π-stacking between adjacent molecules (pale blue).

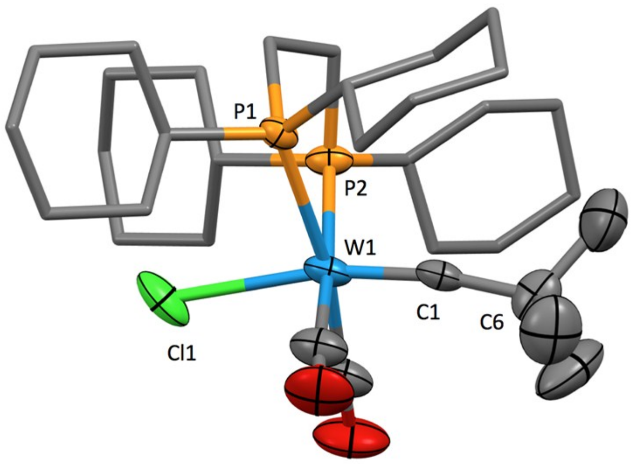

Figure S4. Molecular Structure of $[W(\equiv C^tBu)(Cl)(CO)_2(dcpe)]$ (Hydrogen atoms omitted, cyclohexyl groups simplified, 60% displacement ellipsoids). Selected bond lengths (Å) and angles (deg.): W1–Cl1 2.582(2), W1–P1 2.557(2), W1–P2 2.5429(19), W1–C1 1.734(9), C1–C6 1.527(12), P1–W1–Cl1 85.39(8), P2–W1–Cl1 90.54(7), P2–W1–P1 79.79(6), C1–W1–Cl1 168.2(3), C1–W1–P1 104.6(3), C1–W1–P2 97.3(2), C6–C1–W1 170.2(7).

Figure S5. HOMO for the anionic model complex $[W(\equiv CMe)(CO)_2(dmpe)]^-$ (DFT: B3LYP-LACVP) indicating likely site of orbital controlled electrophilic attack *trans* to carbyne ligand. Views (a) Along $P\cdots W$ vector; (b) Normal to the $P\cdots W$ vector.

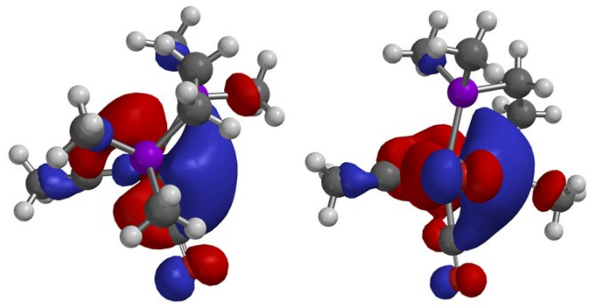
(a) (b)

Figure S6. Atom labelling for Computational Results.

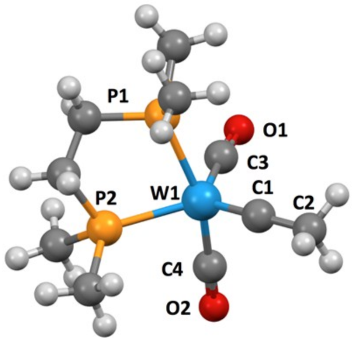

Table S1. Calculated Atomic Cartesian Coordinates (Å) for the model anionic Complex $[W(\equiv CMe)(CO)_2(dmpe)]^-$

Atom	X	Y	Z
W1	-0.6667451	0.2676392	-0.0016996
C1	-1.4172092	1.1726645	-1.4303085
C2	-2.2028512	1.9507866	-2.4311130
H1	-1.9602192	1.6950072	-3.4761016
H6	-2.0579121	3.0381777	-2.3149794
H7	-3.2800630	1.7591669	-2.2938187
C3	-0.8473371	1.2078019	1.7236614
O1	-1.0243562	1.8992105	2.7034380
C4	-2.2981001	-0.7763166	0.4225128
O2	-3.2748884	-1.4310856	0.6794109
P1	1.7483234	1.0560140	-0.0342062
P2	0.5748178	-1.9400371	-0.1002710
C5	2.5205690	1.7540379	-1.6396885
H4	1.9552090	2.6454509	-1.9249782
H10	2.4001813	1.0052832	-2.4268145
H11	3.5812641	2.0051999	-1.5126256
C6	2.4171394	2.3507100	1.1932581
H3	2.0494854	2.0977121	2.1895629
H12	2.0179608	3.3301995	0.9162686
H13	3.5129114	2.3851972	1.1846736
C7	2.9636971	-0.4077071	0.3235686
H5	2.9817145	-0.5135927	1.4141641
H14	3.9721256	-0.1300605	-0.0150239
C8	2.4823838	-1.7014630	-0.3395680
H16	2.6532380	-1.6665956	-1.4226700
H17	3.0071262	-2.5810837	0.0565313
C9	0.2166492	-3.1279347	-1.5568058
H8	0.2884847	-2.5518248	-2.4821893
H18	-0.8098977	-3.4914226	-1.4539279
H19	0.9092146	-3.9795202	-1.5780337
C10	0.5263577	-3.2426733	1.3104491
H9	-0.5241703	-3.4821431	1.4984627
H20	0.9402307	-2.7798313	2.2096432
H21	1.0813012	-4.1547110	1.0561959

Table S2. Calculated Atomic Charges for Inner Coordination Sphere of $[W(\equiv CMe)(CO)_2(dmpe)]^-$

Atom	Electrostatic	Mulliken	Natural
W1	+0.423	-0.162	+0.410
C1	-0.781	-0.154	-0.507
C2	+0.123	-0.532	-0.778
C3	-0.317	+0.143	+0.090
O1	-0.259	-0.481	-0.572
C4	+0.193	+0.140	+0.187
O2	-0.396	-0.465	-0.551
P1	+0.482	+0.645	+0.822
P2	-0.004	+0.629	+0.779

Figure S7. Local Ionisation Potential Surface for $[W(\equiv CMe)(CO)_2(dmpe)]^-$, two views indicating likely sites of attack in charge-controlled electrophilic attack trans to carbyne. NB: Although there is considerable negative charge in the vicinity of the W≡C bond, in the real complex $[W(\equiv C^tBu)(CO)_2(dcpe)]^-$ this region is sterically protected from direct attack by larger electrophiles.

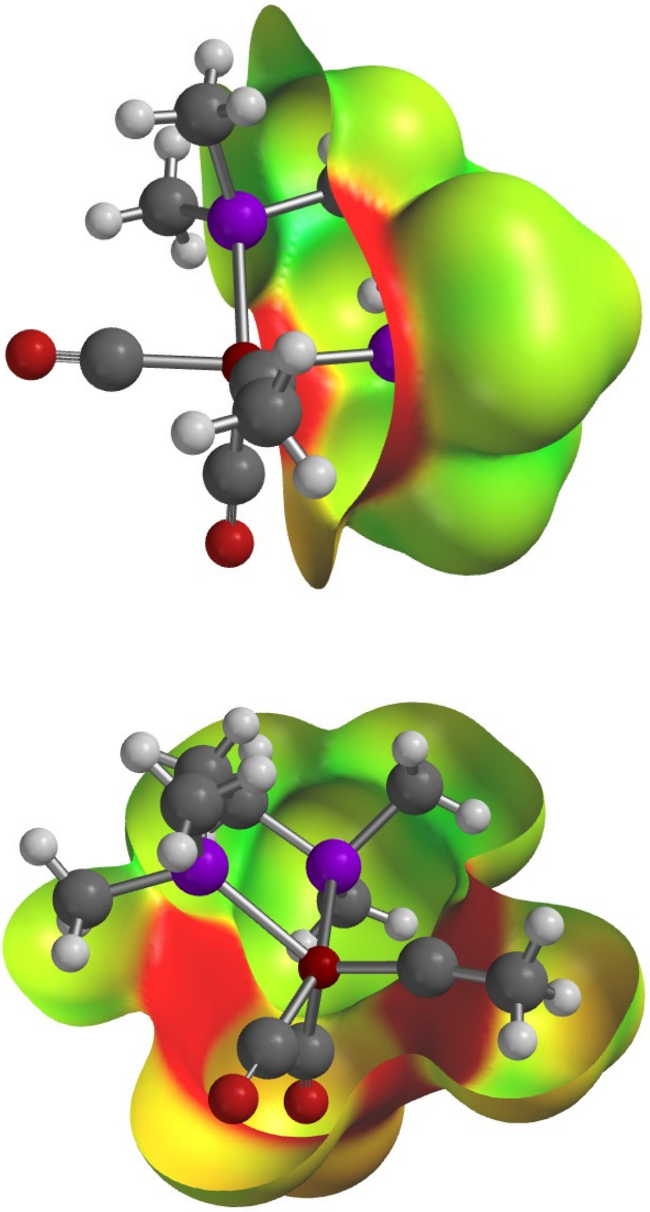

Figure S8. ^1H-^{13}C HMBC NMR Spectrum of the intermediate **B** showing correlation of $\delta_H(CH_3)$ with $\delta_C(W{\equiv}C)$.