



## Chemical Communications

### Supporting Information

## High Oxidation State Bromocarbyne Complexes

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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 (<sup>1</sup>H at 400.1 MHz, <sup>13</sup>C at 100.5 MHz, <sup>31</sup>P at 162.0 MHz), Bruker Avance 700 (<sup>1</sup>H at 700.1 MHz, <sup>13</sup>C at 176.1 MHz, <sup>31</sup>P at 283.5 MHz), or Bruker Avance 800 with cryoprobe (<sup>1</sup>H at 800.1 MHz, <sup>13</sup>C at 200.2 MHz) spectrometer. Chemical shifts ( $\delta$ ) are reported in ppm and referenced to the solvent peak (<sup>1</sup>H, <sup>13</sup>C) or external 85% H<sub>3</sub>PO<sub>4</sub>. 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 <sup>n</sup>J<sub>ab</sub> reported in Hz. Assignments of phenyl ring resonances are denoted C<sub>i</sub> for *ipso*, C<sub>o</sub> for *ortho*, C<sub>m</sub> for *meta* and C<sub>p</sub> for *para* carbon environments. Whilst <sup>13</sup>C{<sup>1</sup>H} for carbon nuclei of the (C<sub>6</sub>H<sub>11</sub>)<sub>2</sub>P(CH<sub>2</sub>CH<sub>2</sub>)P(C<sub>6</sub>H<sub>11</sub>)<sub>2</sub> 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(≡CPh)Br(CO)<sub>2</sub>(dcpe)

**To a** To a suspension of W(CO)<sub>6</sub> (1.76 g, 5.00 mmol) in THF (50 mL), 2.6 mL of PhLi (1.9M in *n*-butyl ether, 5.0 mmol) was

added. The resultant dark brown solution was stirred at room temperature for 30 minutes before being cooled to -78°C. 2.5 mL of oxalyl bromide (2.0M in DCM, 5.0 mmol) was added *via* syringe and the resultant solution allowed to stir for 1 hour at -78°C before the addition of 2.0 mL of 4-picoline (1.9 g, 20 mmol). The reaction was allowed to warm to room temperature and the THF was removed *in vacuo*. The product was redissolved in DCM and filtered through celite to filter the LiCl, before the addition of dcpe (2.11 g, 5.00 mmol) and the resultant mixture left to stir overnight. Subjection of the crude mixture to a hexanes packed column, eluting with DCM afforded the product as a bright yellow powder. Yield: 1.02 g (25%). IR (CH<sub>2</sub>Cl<sub>2</sub>) v/cm<sup>-1</sup>: 1997 (CO), 1924 (CO). IR (nujol) v/cm<sup>-1</sup>: 1993 (CO), 1928 (CO). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25°C): 7.25-7.23 (dd, 1 H, C<sub>p</sub>H in W≡CPh), 7.20-7.15 (m, 4 H, 2x C<sub>o</sub>H and 2x C<sub>m</sub>H in W≡CPh), 2.29-2.23 (m, 2 H, dcpe), 2.19-2.14 (m, 2 H, dcpe), 2.05-0.92 (m, 40 H, dcpe). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25°C):  $\delta_c$  263.7 (t, <sup>2</sup>J<sub>CP</sub> = 9.3, W≡C), 213.4 (dd, <sup>cis</sup>J<sub>CP</sub> = 6.29 <sup>trans</sup>J<sub>CP</sub> = 40.7, W(CO)<sub>2</sub>), 194.8 (C<sub>i</sub> in Ph), 129.1 (C<sub>m</sub> in Ph), 127.9 (C<sub>o</sub> in Ph), 127.0 (C<sub>p</sub> in Ph), 39.1 (d, <sup>1</sup>J<sub>CP</sub> = 20.9, CH[C<sub>6</sub>H<sub>11</sub>]), 34.7 (d, <sup>1</sup>J<sub>CP</sub> = 18.7, CH[C<sub>6</sub>H<sub>11</sub>]), 30.4 (CH<sub>2</sub>[C<sub>6</sub>H<sub>11</sub>]), 30.3 (CH<sub>2</sub>[C<sub>6</sub>H<sub>11</sub>]), 29.4 (CH<sub>2</sub>[C<sub>6</sub>H<sub>11</sub>]), 30.0 (CH<sub>2</sub>[C<sub>6</sub>H<sub>11</sub>]), 27.62 (d, J<sub>CP</sub> = 12.4, CH<sub>2</sub>[C<sub>6</sub>H<sub>11</sub>]), 27.35 (CH<sub>2</sub>[C<sub>6</sub>H<sub>11</sub>]), 27.29 (CH<sub>2</sub>[C<sub>6</sub>H<sub>11</sub>]), 27.18 (d, J<sub>CP</sub> = 9.75, CH<sub>2</sub>[C<sub>6</sub>H<sub>11</sub>]), 26.25 (CH<sub>2</sub>[C<sub>6</sub>H<sub>11</sub>]), 25.87 (CH<sub>2</sub>[C<sub>6</sub>H<sub>11</sub>]), 22.83 (dd, <sup>1</sup>J<sub>CP</sub> = 22.7, <sup>2</sup>J<sub>CP</sub> = 11.4, P(CH<sub>2</sub>)<sub>2</sub>P). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 25°C):  $\delta_p$  43.97 (<sup>1</sup>J<sub>PW</sub> = 225 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 25°C):  $\delta_p$  43.97 (<sup>1</sup>J<sub>PW</sub> = 225 Hz). MS-ESI(+): 791.3331 [M]<sup>+</sup>. Accurate mass: found 831.2293 [M]<sup>+</sup>. Calcd for C<sub>35</sub>H<sub>54</sub>O<sub>2</sub>P<sub>2</sub><sup>79</sup>Br<sup>184</sup>W 831.2292. Anal. found: C, 50.48; H, 6.59; N, 0.00%. Calcd. for C<sub>35</sub>H<sub>53</sub>BrO<sub>2</sub>P<sub>2</sub>W: C, 50.56; H, 6.43; N, 0.00%. Crystals suitable for crystallographic analysis were obtained *via* diffusion of pentane into a solution of **2** in DCM at room temperature.

*Crystal Data for C<sub>35</sub>H<sub>53</sub>BrO<sub>2</sub>P<sub>2</sub>W (M = 831.47 g/mol):* monoclinic, space group P2<sub>1</sub>/n (no. 14), *a* = 11.41025(11) Å, *b* = 13.66762(12) Å, *c* = 23.3661(3) Å,  $\beta$  = 100.0542(10)°, *V* = 3588.01(6) Å<sup>3</sup>, *Z* = 4, *T* = 150.01(10) K,  $\mu$ (CuK $\alpha$ ) = 8.322 mm<sup>-1</sup>,  $\rho_{calc}$  = 1.539 g/cm<sup>3</sup>, 55340 reflections measured (7.524° ≤ 2 $\theta$  ≤ 148.702°), 7242 unique (*R*<sub>int</sub> = 0.0486, *R*<sub>sigma</sub> = 0.0212) which

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were used in all calculations. The final  $R_1$  was 0.0339 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.0914 (all data). CCDC 1515752

### Synthesis of $W(\equiv CPh)(Br)_3(dcpe)$

To a yellow solution of  $W(CPh)(Br)(dcpe)(CO)_2$  (166 mg, 0.200 mmol) in DCM (10 mL) at  $-78^\circ C$  (dry ice/acetone), 0.20 mL of a 1.0 M solution of  $Br_2$  in DCM was added *via* syringe. The resultant dark brown solution was allowed to stir for 30 minutes at  $-78^\circ C$  before being allowed to room temperature, upon which the solution turns dark green. The DCM was removed *in vacuo* to afford a crude green solid. Washing with 1x10 mL of benzene and 1x10 mL of  $Et_2O$  afforded the product as a light green powder. Yield: 184 mg, 98%.  $^1H$  NMR ( $CDCl_3$ ,  $25^\circ C$ ): 7.53-7.50 (dd, 2H,  $C_mH$  in  $W\equiv CPh$ ), 7.04-7.02 (d, 4H,  $2x C_oH$  and  $2x C_mH$  in  $W\equiv CPh$ ), 2.29-2.23 (m, 2 H, dcpe), 2.19-2.14 (m, 2 H, dcpe), 3.06-3.00 (2 H, dcpe), 2.48-2.35 (6 H, dcpe), 2.27-2.22 (4 H, dcpe), 2.20-2.14 (2 H, dcpe), 1.89-1.79 (4 H, dcpe), 1.72-1.68 (4 H, dcpe), 1.65-1.60 (2 H, dcpe), 1.59-1.43 (7 H, dcpe), 1.38-1.28 (7 H, dcpe), 1.26-1.18 (4 H, dcpe), 1.13-1.07 (2 H, dcpe), 1.05-0.98 (2 H, dcpe), 0.86-0.80 (2 H, dcpe).  $^{13}C$  NMR ( $CDCl_3$ ,  $25^\circ C$ ):  $\delta_c$  309.74 (t,  $^2J_{CP} = 13.4$ ,  $W\equiv C$ ), 140.16 ( $C_i(Ph)$ ), 136.72 ( $C_o(Ph)$ ), 131.03 ( $C_m(Ph)$ ), 126.33 ( $C_p(Ph)$ ), 40.80 (d,  $^1J_{CP} = 24.5$ ,  $CH[C_6H_{11}]$ ), 37.41 (d,  $^1J_{CP} = 18.15$ ,  $CH[C_6H_{11}]$ ), 30.69 ( $CH_2[C_6H_{11}]$ ), 30.02 ( $CH_2[C_6H_{11}]$ ), 29.27 ( $CH_2[C_6H_{11}]$ ), 28.00 ( $CH_2[C_6H_{11}]$ ), 27.73 (d,  $J_{CP} = 12.4$ ), 27.46 ( $CH_2[C_6H_{11}]$ ), 26.99 ( $CH_2[C_6H_{11}]$ ), 26.95 (d,  $J_{CP} = 9.75$ ,  $CH_2[C_6H_{11}]$ ), 26.15 ( $CH_2[C_6H_{11}]$ ), 25.89 ( $CH_2[C_6H_{11}]$ ), 21.14 (dd,  $^1J_{CP} = 22.0$ ,  $^2J_{CP} = 14.6$ ,  $P(CH_2)_2P$ ).  $^{31}P\{^1H\}$  NMR ( $CDCl_3$ ,  $25^\circ C$ ):  $\delta_p$  53.10 ( $^1J_{PW} = 212$  Hz). MS-ESI: 873.1588 [ $M-Br+OH_2$ ] $^+$ . Accurate mass: found 871.1603 [ $M-Br+OH_2$ ] $^+$ . Calcd for  $C_{33}H_{55}OP_2^{79}Br_2^{184}W$  861.1604. Anal. found: C, 42.32; H, 5.76; N, 0.00%. Calcd. for  $C_{33}H_{53}BrP_2W$ : C, 42.38; H, 5.71; N, 0.00%. Crystals suitable for crystallographic analysis were obtained *via* diffusion of pentane into a solution of **2** in DCM at  $-20^\circ C$ .

*Crystal Data for  $C_{66}H_{105}Br_6P_4W_2$  ( $M=1869.53$  g/mol):* triclinic, space group P-1 (no. 2),  $a = 11.7140(4)$  Å,  $b = 15.8440(3)$  Å,  $c = 20.4006(4)$  Å,  $\alpha = 81.8120(17)^\circ$ ,  $\beta = 88.384(2)^\circ$ ,  $\gamma = 84.131(2)^\circ$ ,  $V = 3727.67(17)$  Å $^3$ ,  $Z = 2$ ,  $T = 150.01(10)$  K,  $\mu(CuK\alpha) = 10.458$  mm $^{-1}$ ,  $\rho_{calc} = 1.666$  g/cm $^3$ , 61566 reflections measured ( $4.376^\circ \leq 2\theta \leq 148.164^\circ$ ), 15029 unique ( $R_{int} = 0.0491$ ,  $R_{\sigma} = 0.0423$ ) which were used in all calculations. The final  $R_1$  was 0.0379 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.1021 (all data). CCDC 1515753

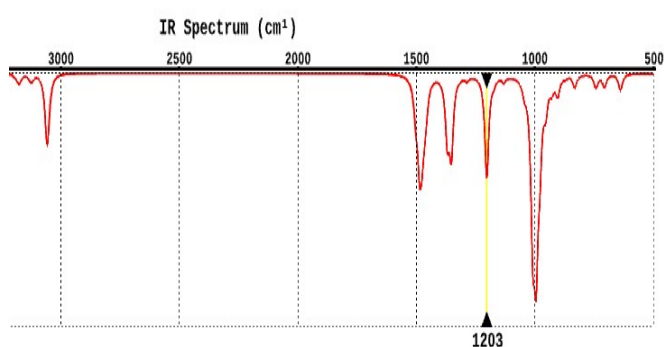
### Synthesis of $W(\equiv CBr)(Br)_3(dcpe)$

To a yellow solution of  $W(CSiPh_3)(Br)(dcpe)(CO)_2$  (101 mg, 0.100 mmol) in DCM (5 mL) at  $-78^\circ C$  (dry ice/acetone), 0.200 mL of a 1.0 M solution of  $Br_2$  in DCM (0.20 mmol) was added *via* syringe. The resultant dark brown solution was allowed to stir for 30 minutes at  $-78^\circ C$  before being allowed to warm to room temperature. To the dark brown solution, 50 mL of hexane was added, precipitating our product as a dark brown solid. The supernatant was filtered off and the product washed once with toluene (1x10 mL) to afford the product as a brown powder. Yield: 58 mg, 62%. IR (Nujol)  $\nu/cm^{-1}$ : 1260 (C-Br).  $^1H$  NMR ( $C_6D_6$ ,  $25^\circ C$ ):

$\delta_H$  3.02-2.91 (m, 2 H, dcpe), 2.42-2.15 (m, dcpe), 2.98-1.14 (m, 46 H, dcpe).  $^{13}C$  NMR ( $C_6D_6$ ,  $25^\circ C$ ):  $\delta_c$  229.0 ( $^2J_{CP} = 16.4$ ,  $W\equiv C$ ), 39.96 (d,  $^1J_{CP} = 24.3$ ,  $CH[C_6H_{11}]$ ), 37.36 (d,  $^1J_{CP} = 18.3$ ,  $CH[C_6H_{11}]$ ), 30.44 ( $CH_2[C_6H_{11}]$ ), 30.08 ( $CH_2[C_6H_{11}]$ ), 29.34 ( $CH_2[C_6H_{11}]$ ), 28.17 ( $CH_2[C_6H_{11}]$ ), 27.69 (d,  $J_{CP} = 5.7$ ,  $CH_2[C_6H_{11}]$ ), 27.55 (d,  $J_{CP} = 5.7$ ,  $CH_2[C_6H_{11}]$ ), 27.36 (d,  $J_{CP} = 10.2$ ,  $CH_2[C_6H_{11}]$ ), 27.00 (d,  $J_{CP} = 12.4$ ,  $CH_2[C_6H_{11}]$ ), 26.12 ( $CH_2[C_6H_{11}]$ ), 26.00 ( $CH_2[C_6H_{11}]$ ), 26.06 ( $CH_2[C_6H_{11}]$ ), 20.79 (dd,  $^1J_{CP} = 22.4$ ,  $^2J_{CP} = 12.9$ ,  $(Cy)_2P(CH_2)_2P(Cy)_2$ ).  $^{31}P\{^1H\}$  NMR ( $CDCl_3$ ,  $25^\circ C$ ):  $\delta_p$  50.8 ( $^1J_{PW} = 206$  Hz). Anal. found: C, 33.19; H, 5.23; N, 0.00%. Calcd for  $C_{27}H_{48}Br_4P_2W \cdot 0.5CH_2Cl_2$ : C, 33.69; H, 5.04; N, 0.00%. In the absence of in-house microanalytical facilities, the hydrolytic sensitivity of the complex has so far precluded the acquisition of satisfactory microanalytical data from the London Metropolitan University. Crystals suitable for crystallographic analysis were obtained *via* cooling a saturated solution of **2d** in  $CDCl_3$  to  $-20^\circ C$  overnight as well as *via* vapour diffusion of pentane into a solution of **2d** in DCM at  $-20^\circ C$ .

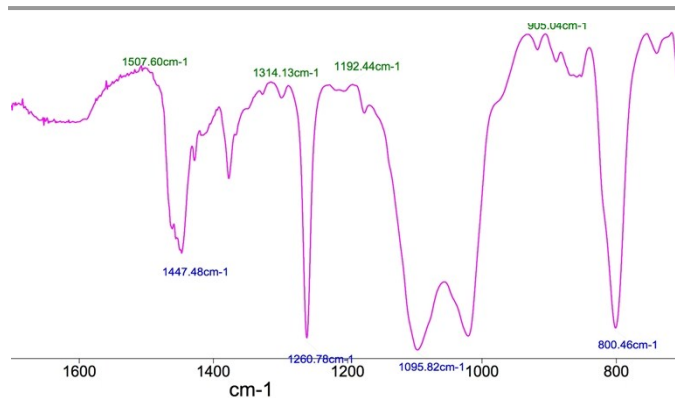
*Crystal Data for  $C_{27}H_{48}Br_4P_2W \cdot 3CDCl_3$  ( $M=1296.18$  g/mol):* orthorhombic, space group  $Pna2_1$  (no. 33),  $a = 12.26967(13)$  Å,  $b = 17.8133(2)$  Å,  $c = 20.5242(3)$  Å,  $V = 4485.82(9)$  Å $^3$ ,  $Z = 4$ ,  $T = 150.00(10)$  K,  $\mu(CuK\alpha) = 14.726$  mm $^{-1}$ ,  $\rho_{calc} = 1.919$  g/cm $^3$ , 90176 reflections measured ( $6.57^\circ \leq 2\theta \leq 148.152^\circ$ ), 9044 unique ( $R_{int} = 0.0399$ ,  $R_{\sigma} = 0.0185$ ) which were used in all calculations. The final  $R_1$  was 0.0522 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.1219 (all data)

*Crystal Data for  $C_{27}H_{48}Br_4P_2W \cdot CH_2Cl_2$  ( $M=1296.18$  g/mol):* orthorhombic, space group  $Pna2_1$  (no. 33),  $a = 12.26967(13)$  Å,  $b = 17.8133(2)$  Å,  $c = 20.5242(3)$  Å,  $V = 4485.82(9)$  Å $^3$ ,  $Z = 4$ ,  $T = 150.00(10)$  K,  $\mu(CuK\alpha) = 14.726$  mm $^{-1}$ ,  $\rho_{calc} = 1.919$  g/cm $^3$ , 90176 reflections measured ( $6.57^\circ \leq 2\theta \leq 148.152^\circ$ ), 9044 unique ( $R_{int} = 0.0399$ ,  $R_{\sigma} = 0.0185$ ) which were used in all calculations. The final  $R_1$  was 0.0522 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.1219 (all data). CCDC 1515754.



**Figure S1.** Calculated IR spectrum (DFT: MO6-LACVP) of the model complex  $[W(\equiv CBr)Br_3(dmpe)]$  with  $\nu_{WC} = 1203$  cm $^{-1}$  indicated.

NB: The calculated spectrum for  $[W(\equiv CPh)Br_3(dmpe)]$  had no significant absorptions that could be assigned primarily to  $\nu_{WC}$  however a number of rather weak absorptions involving Ph ring deformation modes showed modest  $\nu_{WC}$  character (1557, 1455, 1041, 1073 cm $^{-1}$ ).



**Figure S2.** Experimental IR spectrum (Nujol) for the complex  $[W(\equiv CBr)Br_3(dcpe)]$  with  $\nu_{WC} = 1261 \text{ cm}^{-1}$ .

### Calculated Atomic Charges

**Table S1.** Calculated Charges<sup>a</sup> for the Complexes  $[W(\equiv CR)Br_3(dmpe)]$  (R = Ph, Br)

	Electrostatic		Mulliken		Natural	
	Ph	Br	Ph	Br	Ph	Br
C	-1.08	-0.70	-0.05	-0.31	-0.29	-0.51
W	1.47	1.31	-0.46	-0.20	+0.75	+0.78
<i>trans</i> -Br	-0.66	-0.58	-0.33	-0.32	-0.59	-0.67
<i>cis</i> -Br	-0.37	-0.35	-0.10	-0.12	-0.28	-0.30

<sup>a</sup>DFT: MO6-LACVP

#### Observations

- (i) For the Mulliken and Natural charge calculations, the *trans* bromide bears more negative charge for the bromocarbyne complex than the benzylidyne suggesting a stronger *trans* influence by CBr than CPh.
- (ii) In all cases, the *trans* bromide bears a greater negative charge than do the *ci*-bromides, again reflecting the strong *trans* influence of carbyne ligands.
- (iii) Natural charges for the W–C linkage suggest little change in the charge at tungsten but an increase in charge for the carbyne carbon of the CBr complex.