# A tungsten-mediated closed cycle of reactivity for the reduction of $CO_2$ to $CO^{\, \dagger}_{\, \uparrow}$

Upul Jayarathne, Perumalreddy Chandrasekaran, Heiko Jacobsen, Joel T. Mague and James P. Donahue\*

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The recycling of  $CO_2$  by reduction to CO is an important objective in the context of renewable carbon feedstock chemicals. A tungsten-mediated reduction of  $CO_2$  to CO reported by Mayer and coworkers has been re-examined, and it is shown that a series of four well-defined stoichiometric steps can be executed which form a closed cycle and sum as  $CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$ . Energetic parameters of this system are probed by cyclic voltammetry, by calculations of gas-phase reaction enthalpies for each of the four steps, and by calculation of the W=O bond dissociation energy for the tungsten species that results from oxidation addition of  $CO_2$ .

# Introduction

Concerns about the nonrenewable nature of fossil fuel reserves have stimulated broad ranging efforts aimed at the recycling of  $CO_2$ . Established uses for  $CO_2$  include its incorporation into organic polymers, particularly polycarbonates,<sup>1-2</sup> its niche use in certain small molecule syntheses, such as salicylic acid and urea production,<sup>3-4</sup> and its application as a supercritical fluid in extractions<sup>5-7</sup> and coatings<sup>8-9</sup> and as a medium for chemical reactions.<sup>10-12</sup> Reduction of  $CO_2$  to the valuable lower oxide CO is, however, a much greater challenge owing to the thermodynamic stability of  $CO_2$  and the appreciable kinetic barrier to its activation. Thus, a successful practical system for reduction of  $CO_2$  must implement some form of catalyst.

Metal-mediated catalytic schemes for the reduction of  $CO_2$  to lower carbon oxides that are chemically driven,<sup>13-15</sup> electrolyticallydriven,<sup>16-19</sup> or photolytically driven<sup>20</sup> have been described, each with distinctive advantages and shortcomings. Of these systems, the electrolytic and photolytic are more desirable because of their ability to more directly use energy from a renewable source. Among the many issues demanding consideration with any such catalyst are catalyst lifetime and cost, catalyst rate, efficiency of energy usage, and product selectivity.

Compared to complexes of the late and middle-late transition metals, notably Ni, Pd, Co, Fe, Ru, and Re, complexes of the early and early-middle transition metals and of the f-block metals have been subject to considerably less scrutiny for their ability to reduce  $CO_2$ . The reduction of  $CO_2$  to CO and oxo-bridged di- and trimetallic products was reported by Floriani with titanocene and zirconocene compounds (eqn (1)),<sup>21</sup> while Mayer and coworkers described the reaction of chlorophosphine complexes of W(II) to

form the corresponding *cis* oxo-carbonyl tungsten(IV) complexes (eqn (2)).<sup>22</sup> More recently, the formation of CO and an oxo-bridged diuranium(IV) species arising from the reaction of CO<sub>2</sub> with a U(III) triazacyclononane compound was reported by Meyer and Castro-Rodriguez (eqn (3)).<sup>23</sup> However, further studies of these Group 4, Group 6 and actinide systems were not undertaken, possibly being dissuaded by a belief that the resulting metal oxides are thermodynamic dead-ends.

$$3[Cp_2Zr^{II}(CO)_2] + 3CO_2 \rightarrow [Cp_2Zr]_3(\mu-O)_3 + 9CO^{21}$$
(1)

$$[W^{II}Cl_2(PMePh_2)_4] + CO_2 \rightarrow [W^{IV}O(CO)Cl_2(PMePh_2)_2] + 2PMePh_2^{22}$$
(2)

$$2LU + CO_2 \rightleftharpoons LU - (CO_2) - UL \rightarrow LU - O - UL + CO^{23}$$
(3)

L = 1,4,7-tris(3,5-di-*tert*-butyl-2-hydroxybenzylate)-1,4,7-triazacyclonone.

Motivated by (i) the high specificity of the tungsten chlorophosphine complexes for CO formation from CO<sub>2</sub> (ii) the greater exposure, and hence greater opportunity for further reactivity, of a terminal oxo versus a bridging oxo ligand and (iii) the relatively affordability of tungsten metal, we initiated an investigation of the possibility for turnover of the [W<sup>IV</sup>(=O)(CO)Cl<sub>2</sub>(PMePh<sub>2</sub>)<sub>2</sub>] product that results in the Mayer system. The rationale underpinning this effort was that successful reduction of [W<sup>IV</sup>(=O)(CO)Cl<sub>2</sub>(PMePh<sub>2</sub>)<sub>2</sub>] back to non-oxo tungsten(II) species would at least demonstrate stoichiometric catalysis, which is a requisite first step if this system could hope, with appropriate modifications, to operate *electro*catalytically in the reduction of CO<sub>2</sub> to CO. Described here are experimental results that extend Mayer's observations into a closed cycle of four stoichiometric steps that provide for the reduction of CO<sub>2</sub> to CO and H<sub>2</sub>O. These reactivity studies are augmented with electrochemical data and computational work that bring additional clarification to the energetic parameters within which this closed cycle is constrained. While this work was in the course of preparation for publication, a conceptually similar cycle mediated with a niobium tris(amido) platform was reported by the Cummins Group.24

Department of Chemistry, Tulane University, 6400 Freret Street, New Orleans LA 70118-5698

<sup>†</sup> Electronic supplementary information (ESI) available: X-ray diffraction data collection procedures, complete crystallographic data in CIF format, thermal ellipsoid plots for all compounds with complete atom labeling, and computational details (optimized geometries, convergence criteria, final energies, thermodynamic data, Table S6). CCDC reference numbers 769389–769400. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00489h

Current address: Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853-1301.

# Experimental

#### Syntheses

A literature procedure was employed for the generation of gaseous HCl.25 This procedure was modified by passing the HCl(g) through a trap of concentrated  $H_2SO_4$  immediately before use in order to scavenge traces of moisture. All other reagents were purchased from commercial sources and used as received (PMe<sub>3</sub> (1.0 M in toluene), PMe<sub>2</sub>Ph, PMePh<sub>2</sub>, PPh<sub>3</sub>, dppe  $(dppe = 1,2-bis(diphenylphosphino)ethane), P(NMe_2)_3, Cp*_2Co,$  $WCl_4$ ,  $WCl_6$ ). Solvents either were dried with a system of drying columns from the Glass Contour Company (CH<sub>2</sub>Cl<sub>2</sub>, n-pentane, hexanes, Et<sub>2</sub>O, THF, C<sub>6</sub>H<sub>6</sub>, toluene) or distilled according to standard procedures (1.2-dichloroethane).<sup>26</sup> A numbering system for compound identification is defined in Chart 1. Compounds 1 and 2 were prepared by literature methods (by Na/Hg reduction of 4c in the presence of additional PMePh<sub>2</sub><sup>27</sup> and by oxidative addition of  $CO_2$  to  $1,^{22}$  respectively.). Compounds **4b,c,d,e** were synthesized by published procedures from WCl<sub>6</sub> and the corresponding phosphine.<sup>27b,28-29</sup> All reactions and manipulations were conducted under an atmosphere of Ar or N<sub>2</sub> unless indicated otherwise.

$[W^{II}Cl_2(PMePh_2)_4]$	1
[W <sup>IV</sup> O(CO)Cl <sub>2</sub> (PMePh <sub>2</sub> ) <sub>2</sub> ]	2
[W <sup>IV</sup> OCl <sub>2</sub> (PMePh <sub>2</sub> ) <sub>3</sub> ]	3c
[W <sup>IV</sup> OCl <sub>2</sub> (PMePh <sub>2</sub> )(dppe)]	3e
$[W^{IV}Cl_4(PMe_3)_2]$	4a
$[W^{IV}Cl_4(PMe_2Ph)_2]$	4b
$[W^{IV}Cl_4(PMePh_2)_2]$	4c
$[W^{IV}Cl_4(PPh_3)_2]$	4d
[W <sup>IV</sup> Cl <sub>4</sub> (dppe)]	<b>4e</b>
$[W^{III}Cl_4(PMePh_2)_2]^{1-}$	[4c] <sup>1-</sup>
$[W^{IV}Cl_5(PMePh_2)]^{1-}$	[5] <sup>1-</sup>
$[W^{IV}Cl_3(NMe_2)(PMePh_2)_2]$	6

Chart 1 Numbering system for compound identification.

[WOCl<sub>2</sub>(PMePh<sub>2</sub>)<sub>3</sub>], **3c.** Preparations of 3c from  $WCl_6/PMePh_2$  in  $EtOH^{28}$  and from  $[WCl_4(PMePh_2)]$  in wet acetone or THF<sup>30</sup> have been described earlier. A solution of [W<sup>IV</sup>O(CO)Cl<sub>2</sub>(PMePh<sub>2</sub>)<sub>2</sub>] (0.201 g, 0.287 mmol) and PMePh<sub>2</sub> (0.258 mL, 0.278 g, 1.39 mmol) in toluene (40 mL) under Ar was heated to 55 °C and bubbled continuously with a slow stream of Ar over an 8 h period. During this time, the initial reddish-purple color of the solution gradually changed to a mauve color. The toluene solution was cooled to room temperature and evaporated to dryness under reduced pressure, and the resulting solid residue was washed with  $Et_2O$  (5 × 10 mL). Recrystallization from benzene-hexane produced block-shaped crystals with a blue-red dichroic aspect. Yield: 0.192 g, 0.220 mmol, 77%. <sup>31</sup>P NMR ( $\delta$ , ppm in C<sub>6</sub>D<sub>6</sub>): 1.05 (s,  $J_{PW} = 336$  Hz), -15.75 (s,  $J_{PW} = 415$  Hz).

UV/vis (THF),  $\lambda_{max}$  ( $\epsilon_M$ ): 342 nm (5500), 548 nm (230). Anal. Calcd for  $C_{39}H_{39}Cl_2OP_3W$ : C, 53.75; H, 4.51; P, 10.66. Found: C, 53.48; H, 4.53; P, 10.58.

[WOCl<sub>2</sub>(dppe)(PMePh<sub>2</sub>)], 3e. A 50 mL Schlenk flask with magnetic bar was charged with [W(O)(CO)Cl<sub>2</sub>(PMePh<sub>2</sub>)<sub>2</sub>](0.208 g, 0.297 mmol) and dppe (0.118 g, 0.296 mmol) under an Ar atmosphere. Freshly distilled toluene (15 mL) was added, and the resulting reaction mixture was heated to 70 °C for 4 h with constant stirring. After being cooled to room temperature, the solution was reduced to dryness under reduced pressure. The residual solid was washed with pentane and dried under vacuum. Redissolution of this crude product in CH<sub>2</sub>Cl<sub>2</sub> (10 mL), followed by addition of hexanes (30 mL) led to formation of a microcrystalline precipitate, which was isolated by cannula filtration and dried under vacuum for 24 h. Yield: 0.210 g, 0.242 mmol, 81%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.97–7.92 (m, 2H, Ph), 7.86 (t,  $J_{\rm HH}$  = 8.4 Hz, 2H, Ph), 7.66–7.61 (m, 2H, Ph), 7.55 (t,  $J_{\rm HH}$  = 8.8 Hz, 2H, Ph), 7.41–7.28  $(m, 12H, Ph), 7.20 (t, J_{HH} = 7.6 Hz, 4H, Ph), 7.11-7.03 (m, 4H, Ph),$ 6.84 (t,  $J_{\rm HH}$  = 8.8 Hz, 2H, Ph), 3.20–2.91 (m, 2H, PCH<sub>2</sub>CH<sub>2</sub>P), 2.77-2.62 (m, 1H, PCH2CH2P), 2.11-1.99 (m, 1H, PCH2CH2P), 1.84 (d,  $J_{PH} = 8.4$  Hz, 3H, PMePh<sub>2</sub>). <sup>31</sup>P NMR ( $\delta$ , ppm in CDCl<sub>3</sub>): 32.01 (d of d,  ${}^{2}J_{PP}$  = 4.3 Hz, 17.8 Hz;  ${}^{1}J_{PW}$  = 391 Hz, *P*CH<sub>2</sub>CH<sub>2</sub>P *cis* to PMePh<sub>2</sub>), 25.91 (d of d,  ${}^{2}J_{PP} = 17.8$  Hz, 211.8 Hz;  ${}^{1}J_{PW} =$ 327.84 Hz,  $PCH_2CH_2P$  trans to  $PMePh_2$ ), 0.50 (d of d,  ${}^2J_{PP}$  = 4.5 Hz, 211.8 Hz,  ${}^{1}J_{PW}$  = 346.6 Hz, *P*MePh<sub>2</sub>). IR (KBr, cm<sup>-1</sup>): 3050 (w), 1481 (m), 1435 (s), 1092 (m), 940 (m), 742 (m), 742 (s), 690 (vs), 525 (m).

trans-[WCl<sub>4</sub>(PMe<sub>3</sub>)<sub>2</sub>], 4a. The following is a simplified alternative to a literature preparation for 4a.<sup>30</sup> A 100 mL Schlenk flask with stir bar was charged with [WCl<sub>4</sub>]<sub>∞</sub> (1.00 g, 3.07 mmol) and 30 mL of CH<sub>2</sub>Cl<sub>2</sub> under an Ar atmosphere. To this mixture was slowly added a solution of PMe<sub>3</sub> in toluene (6.2 mL, 6.2 mmol) via syringe at ambient temperature. The resulting dark red reaction mixture was stirred for 4 h at ambient temperature. The solvent was removed under reduced pressure to afford a brownish red solid. The formation of a mixture of  $[WCl_4(PMe_3)_2]$  and  $[WCl_4(PMe_3)_3]$ was indicated by <sup>1</sup>H NMR spectroscopy. The flask containing the brownish red solid was heated with an oil bath to 120 °C under vacuum for 24 h. During this period, an orange solid progressively deposited on the sides of the flask. After being cooled to room temperature, the flask was taken inside a N2 box. The dark orange solid was collected from the walls of the flask, dissolved in 50 mL of CH<sub>2</sub>Cl<sub>2</sub> and filtered through a Celite pad on a medium porosity frit. The dark orange filtrate was reduced to a volume of 20 mL and cooled to -30 °C for 24 h to afford square-shaped red crystals, which were collected by filtration, washed with  $2 \times$ 10 mL of hexanes and dried under vacuum for 24 h. Yield: 0.645 g, 1.35 mmol, 44%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  –26.67 (s). Anal. Calcd for C<sub>6</sub>H<sub>18</sub>P<sub>2</sub>Cl<sub>4</sub>W: C, 15.08; H, 3.80; P, 12.96. Found: C, 15.16; H, 3.64; P, 13.01.

**Conversion of [WOCl<sub>2</sub>(PMePh<sub>2</sub>)<sub>3</sub>] (3c) to [WCl<sub>4</sub>(PMePh<sub>2</sub>)<sub>2</sub>] (4c).** A 200 mL three-neck flask with a stir bar was charged with [WOCl<sub>2</sub>(PMePh<sub>2</sub>)<sub>3</sub>] (0.330 g, 0.38 mmol) and connected to a Schlenk line. The middle neck was fitted to a special glass tube for the delivery of gaseous HCl, and the remaining neck was closed by a septum. The system was placed under Ar, and 50 mL of dry toluene were added to the flask *via* syringe. A mauve color solution resulted, and the mixture was stirred for several minutes until the solid completely dissolved. Gaseous HCl was bubbled through the solution and vented through the Schlenk line for 1 h, during which time the solution assumed a bright yellow color. The solvent was removed under reduced pressure. The resulting wet solid was washed with dry pentane ( $3 \times 10$  mL) and dried *in vacuo* overnight. Diffusion of hexanes vapor into a THF solution of the product produced single crystals with unit cell parameters that matched those obtained in an earlier structural characterization of [WCl<sub>4</sub>(PMePh<sub>2</sub>)<sub>2</sub>]. Yield: 0.240 g, 0.33 mmol, 87%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  11.26 (d, 8H, Ph), 8.35 (t, 8H, Ph), 8.02 (t, 4H, Ph), -27.42 (s, 6H, PMePh<sub>2</sub>); UV/vis (THF),  $\lambda_{max}$  ( $\varepsilon_{M}$ ): 306 nm (5383), 410 nm (1449). Anal. Calcd for C<sub>26</sub>H<sub>26</sub>P<sub>2</sub>Cl<sub>4</sub>W: C, 43.01; H, 3.61; P, 8.53. Found: C, 42.81; H, 3.52; P, 8.78.

 $[Cp*_2Co][WCl_4(PMePh_2)_2],$ [Cp\*<sub>2</sub>Co][4c] and [Cp\*<sub>2</sub>Co]-[WCl<sub>5</sub>(PMePh<sub>2</sub>)], [Cp\*<sub>2</sub>Co][5]. A 200 mL Schlenk flask with a stir bar was charged with [WCl<sub>4</sub>(PMePh<sub>2</sub>)<sub>2</sub>] (0.200 g, 0.28 mmol) and 40 mL of dry toluene. A solution of Cp<sup>\*</sup><sub>2</sub>Co (0.090 g, 0.27 mmol) in 30 mL dry toluene was transferred via cannula to the [WCl<sub>4</sub>(PMePh<sub>2</sub>)<sub>2</sub>] solution. Formation of a light brown precipitate was observed. This mixture was stirred for 2 h, and the solvent was reduced to ~10 mL under reduced pressure. The precipitate was collected on a frit under Ar and dried overnight (0.230 g). Diffusion of diethyl ether vapor into a 1,2-dichloroethane solution produced a mixture of orange prism and pale yellow plate crystals, which were identified by X-ray crystallography as  $[Cp_{2}^{*}Co][WCl_{4}(PMePh_{2})_{2}]$  and [Cp<sup>\*</sup><sub>2</sub>Co][WCl<sub>5</sub>(PMePh<sub>2</sub>)], respectively. A manual separation of crystals produced 3.0 mg of [Cp\*<sub>2</sub>Co][4c], 0.9% yield, and 3.3 mg [Cp\*<sub>2</sub>Co][5], 1.1% yield (based on tungsten). Approximately 0.025 g of mixed crystals remained, which were not separable by hand. [Cp\*<sub>2</sub>Co][**4**c]: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 11.26 (d,  $J_{\rm HH} = 7.2$  Hz, 8H, Ph), 8.36 (t,  $J_{\rm HH} = 7.4$  Hz, 8H, Ph), 8.03 (t,  $J_{\rm HH} = 7.4$  Hz, 4H, Ph), 1.75 (s, 30H,  $[(C_5(CH_3)_5)_2Co]^+)$ , -27.40 (s, 6H, PMePh<sub>2</sub>). UV/vis (1,2-dichloroethane),  $\lambda_{max}$  ( $\varepsilon_{M}$ ): 416 nm (1450), ~470 nm (sh, 460). MS (MALDI-TOF): 726.0 (M<sup>-</sup>, mode)), 329.2  $[(C_5(CH_3)_5)_2Co]^+$  (+ mode). HRMS (MALDI-TOF) monoisotopic m/z: 723.9785 (Calcd for C<sub>26</sub>H<sub>26</sub>Cl<sub>4</sub>P<sub>2</sub>W (M<sup>-</sup>) 723.9773). [Cp\*<sub>2</sub>Co][**5**]: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 12.09 (d,  $J_{\rm HH}$  = 7.2 Hz, 4H, Ph), 8.59 (t,  $J_{\rm HH}$  = 7.2 Hz, 4H, Ph), 8.02 (d,  $J_{\rm HH}$  = 7.2 Hz, 2H, Ph), 1.70 (s, 30H, [(C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>)<sub>2</sub>Co]<sup>+</sup>), -19.21 (s, 3H, PMePh<sub>2</sub>). UV/vis (1,2-dichloroethane),  $\lambda_{max}$  ( $\varepsilon_{M}$ ): ~344 nm (sh, 3800), ~388 nm (sh, 1400). MS (MALDI-TOF): 555.2 (M<sup>-</sup>). HRMS (MALDI-TOF) monoisotopic m/z: 558.8701 (Calcd for C<sub>13</sub>H<sub>13</sub>Cl<sub>5</sub>PW (M<sup>-</sup>) 558.8707). Electrochemistry:  $[WCl_5(PMePh_2)] + e^- \rightarrow [WCl_5(PMePh_2)]^{1-}$  (quasireversible,  $E_{\perp} =$ +0.69 V vs. Ag/AgCl, +0.15 V vs. [Cp<sub>2</sub>Fe]<sup>+</sup>/Cp<sub>2</sub>Fe).

**[WCl<sub>3</sub>(NMe<sub>2</sub>)(PMePh<sub>2</sub>)<sub>2</sub>], 6.** A solution of **4c** (0.976 g, 1.3 mmol) in toluene (70 mL) was treated with neat  $P(NMe_2)_3$  *via* syringe (0.51 mL, 0.45 g, 2.8 mmol). The resulting mixture was allowed to stir 12 h at ambient temperature, during which time a white precipitate and orange-yellow supernatant formed. The white precipitate was removed by filtration, and the filtrate was concentrated to a volume of 15 mL under reduced pressure. Diethyl ether (50 mL) was layered on top of the toluene concentrate. Small yellow prism-shaped crystals deposited over a period of 24–48 h, which were isolated by filtration, washed

with Et<sub>2</sub>O (4 × 10 mL), and dried *in vacuo*. Yield: 0.152 g, 0.21 mmol, 15%. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  8.76 (d,  $J_{\rm HH}$  = 7.6 Hz, 8H, Ph), 8.51 (t,  $J_{\rm HH}$  = 7.4 Hz, 8H, Ph), 7.54 (t,  $J_{\rm HH}$  = 7.6 Hz, 4H, Ph), -18.00 (s, 6H PMePh<sub>2</sub>). NMe<sub>2</sub> peaks were not visible. <sup>31</sup>P NMR ( $\delta$ , ppm in C<sub>6</sub>D<sub>6</sub>): 0.52 (s,  $J_{\rm PW}$  = 337 Hz, PMePh<sub>2</sub>), -16.34 (s,  $J_{\rm PW}$  = 416 Hz, signal tentatively attributed to a ditungsten impurity). UV/vis (C<sub>6</sub>H<sub>6</sub>),  $\lambda_{\rm max}$  ( $\varepsilon_{\rm M}$ ): ~308 nm (sh, 7000), ~362 nm (sh, 2600). MS (ESI, + mode): 699.3 (M<sup>+</sup> - Cl). Electrochemistry: [WCl<sub>3</sub>(NMe<sub>2</sub>)(PMePh<sub>2</sub>)<sub>2</sub>]<sup>1+</sup> + e<sup>-</sup>  $\rightarrow$  [WCl<sub>3</sub>(NMe<sub>2</sub>)(PMePh<sub>2</sub>)<sub>2</sub>], (reversible,  $E_{\perp}$  = +0.52 V vs. Ag/AgCl, -0.02 V vs. [Cp<sub>2</sub>Fe]<sup>+</sup>/Cp<sub>2</sub>Fe,  $\Delta E_{\rm p}$  = 0.101 V). Anal. Calcd for C<sub>28</sub>H<sub>32</sub>Cl<sub>3</sub>NP<sub>2</sub>W: C, 45.77; H, 4.39; N, 1.91. Found: C, 42.47: H, 4.28; N, 1.27.

## **Physical methods**

UV-vis spectra (molar absorptivities reported in  $M^{-1}$  cm<sup>-1</sup>) were obtained at ambient temperature with a Hewlett-Packard 8452A diode array spectrometer, while IR spectra were taken as pressed KBr pellets with a Thermo Nicolet Nexus 670 FTIR instrument in absorption mode. All NMR spectra were recorded at 25 °C with a Varian Unity Inova spectrometer operating at 400 and 161.8 MHz for <sup>1</sup>H and <sup>31</sup>P, respectively. Spectra were referenced to the solvent residual for <sup>1</sup>H and to external 85% H<sub>3</sub>PO<sub>4</sub> for <sup>31</sup>P. Electrochemical measurements were made with a CHI620C electroanalyzer workstation using a Ag/AgCl reference electrode, a platinum disk working electrode, Pt wire as auxiliary electrode, and  $[Bu_4N][PF_6]$  as the supporting electrolyte. The  $[Cp_2Fe]^+/Cp_2Fe$  couple occurred at +0.54 mV (by CV) in 0.10 M [Bu<sub>4</sub>N][PF<sub>6</sub>] in CH<sub>2</sub>Cl<sub>2</sub>. Elemental analyses were performed by Midwest Microlab, LLC of Indianapolis, IN. Details regarding methods of crystallization, X-ray diffraction data collection, and structure solution and refinement are deferred to the ESI.†

### **Computational methods**

Geometries have been optimized and final energies have been evaluated in DFT calculations, using the PBE exchange-correlation functional as prescribed by Perdew, Burke and Ernzerhof.<sup>31</sup> For all calculations, tungsten was modeled by a small-core, quasirelativistic effective core potential with an associated (8s7p6d)/[6s5p3d] valence basis set contracted according to a (311111/22111/411) scheme.32 All main group elements except for those that are part of a phenyl group have been described by contracted Gaussian basis sets of triple zeta valence quality augmented by polarization functions (TZVP).<sup>33</sup> For phenyl groups, the C atom bonded to phosphorus has been described by a TZVP basis, whereas the remaining atoms were described by contracted Gaussian splitvalence basis sets (SV).34 The nature of stationary points located on the potential energy surface has been checked by harmonic frequency calculations, and all molecules considered in this work possess a harmonic spectrum without any imaginary frequencies. Enthalpies H have been evaluated at zero K from total energies E and zero-point energy correction terms (ZPE). The calculated frequency data provide thermodynamic corrections to calculate free energies G at 298 K. The Gaussian 03 suite of programs constitutes the underlying computational engine of the present work.35

### **Results and discussion**

The [WCl<sub>2</sub>(PMePh<sub>2</sub>)<sub>4</sub>] system, which was studied in some detail by Mayer in oxidative addition reactions with various heterocumulenes, is to the best of our knowledge, the only instance in which a terminal oxo ligand results from the reduction of  $CO_2$ to CO by a metal complex. Other outcomes for this reaction type are the formation of sterically protected oxo-bridged di- or trimetallic species<sup>21,23</sup> or products in which oxygen atom is inserted into another metal–ligand bond.<sup>36</sup> Despite the formidable strength of the W=O bond in [W<sup>IV</sup>O(CO)Cl<sub>2</sub>(PMePh<sub>2</sub>)<sub>2</sub>], we believed that the terminal oxo-ligand resulting from oxidative addition of  $CO_2$ in this system could be amenable to some form of electrophilic attack, ligand exchange, or other pathway leading back to reduced [W<sup>II</sup>Cl<sub>2</sub>(PMePh<sub>2</sub>)<sub>4</sub>].

Beginning with air- and moisture-sensitive  $[W^{II}Cl_2(PMePh_2)_4]$ , we re-examined the CO<sub>2</sub> reactions described by Mayer and, as reported, found the oxidative addition reaction with CO<sub>2</sub> to occur in a timescale of approximately ten minutes under the mild conditions of 1 atm pressure CO<sub>2</sub> and ambient temperature  $(1 \rightarrow 2, \text{Scheme 1})$ . The preparation, isolation, and handling of  $[W^{II}Cl_2(PMePh_2)_4]$  was most effectively accomplished under an Ar atmosphere up to the moment of CO<sub>2</sub> introduction. The oxo carbonyl species (2 in Scheme 1) that is the immediate product of oxidative addition of CO<sub>2</sub> is relatively robust and isolable in spectroscopically pure form. Displacement of CO by PMePh<sub>2</sub> liberated in the initial oxidative addition reaction creates

$$M = O + H_2 S \rightarrow M = S + H_2 O^{51}$$

$$(4)$$

$$\mathbf{M} = \mathbf{O} + \mathbf{RNH}_2 \rightarrow \mathbf{M} = \mathbf{NR} + \mathbf{H}_2 \mathbf{O}^{52} \tag{5}$$

$$M = O + 2HCl \rightarrow MCl_2 + H_2O^{53}$$
(6)

an equilibrium that was reported by Mayer as being a 9:1 mixture favoring the oxo-carbonyl species,  $2^{.22c}$  Complete formation of [W<sup>IV</sup>OCl<sub>2</sub>(PMePh<sub>2</sub>)<sub>3</sub>] (**3c** in Scheme 1) is readily accomplished by mild heating of [W<sup>IV</sup>O(CO)Cl<sub>2</sub>(PMePh<sub>2</sub>)<sub>2</sub>] in the presence of excess PMePh<sub>2</sub> under a slow purge of Ar gas that sweeps away substituted CO(g). With the chelating effect enjoyed by dppe, the displacement of CO from isolated **2** is accomplished without the additional drive afforded by excess phosphine and Ar purge to quantitatively afford [W<sup>IV</sup>OCl<sub>2</sub>(dppe)(PMePh<sub>2</sub>)], **3e**. While structural determinations for **1**<sup>22b</sup> and **2**<sup>22a</sup> have been previously reported, atomic coordinates useful for DFT calculations are unavailable. Thus, new, higher resolution structural determinations were undertaken (Scheme 1, Table 1); unit cells obtained for **1** and **2** are different than those reported by Mayer owing to differences with co-crystallized solvent molecules.

The reduction of  $[W^{IV}OCl_2(PMePh_2)_3]$  back down to  $[W^{II}Cl_2(PMePh_2)_4]$  is a challenge that may be addressed in several distinctly different ways. One approach is *via* successive coupled proton–electron transfer reactions that, by analogy to the mechanism by which molybdenum and tungsten oxotransferase and hydroxylase enzymes<sup>37-38</sup> are known to function, ultimately remove the oxo ligand as H<sub>2</sub>O. Another approach is by direct oxygen atom acceptor more oxophilic even than W(II). Although phosphines are common oxygen atom acceptors from transition metal complexes,<sup>39</sup> a report



Scheme 1 A W-mediated cycle for  $CO_2$ -to-CO reduction by direct O atom excision. The oxo-for-chloride ligand exchange and the two electron reduction that regenerates active W(II) are accomplished as separate steps. All compounds are isolable and have been characterized by X-ray crystallography. Thermal ellipsoid plots are drawn at the 50% probability level. H atoms are omitted for clarity.

oxygen atom abstraction from Ph<sub>2</sub>P(O)CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub> of  $[W^{II}Cl_2(Ph_2P(O)CH_2CH_2PPh_2)(PMePh_2)_2]$ to in afford  $[W^{IV}OCl_2(Ph_2PCH_2CH_2PPh_2)(PMePh_2)]$  indicates that the thermodynamics are unfavorable for this process for phosphines with basicity comparable to PMePh2.40 Available thermodynamic data<sup>41</sup> suggest that silanes such as Me<sub>3</sub>SiSiMe<sub>3</sub> may have the thermodynamic strength to compete with low valent tungsten for an oxygen atom. Furthermore, direct silvlation of a terminal metal-oxo ligand by an electrophilic silane reagent, with a concomitant lowering of the metal-oxo bond order, is amply precedented.42-49 However, efforts to apply this reaction to [W<sup>IV</sup>OCl<sub>2</sub>(PMePh<sub>2</sub>)<sub>3</sub>] using Me<sub>3</sub>SiI or Me<sub>3</sub>SiOTf resulted in facile Table 1 Crystal and refinement data for compounds 1, 2, 3c,e, 4a,b,c,d,e, [4c]<sup>1-</sup>, [5]<sup>1-</sup>, and 6

Compound	$1 \cdot C_6 H_5 C H_3$	$2.0.5C_6H_6$	3c	<b>3e</b> ·CH <sub>2</sub> Cl <sub>2</sub>
Formula	$C_{59}H_{60}Cl_2P_4W$	$C_{30}H_{29}Cl_2O_2P_2W$	$C_{39}H_{39}Cl_2OP_3W$	$C_{40}H_{39}Cl_4OP_3W$
FW Createl avatem	114/./0 Trialinia	/ 38.22 Manaalinia	8/1.30 Trialinia	954.27 Manaalinia
Space group	P1 Oranga blaak	$P_{2_1}/n$	P1 Durmla aclumn	C2/C Plue plate
$\alpha/\Lambda$	11 4060(8)	p urple column		22,522(2)
u/A	11.4009(8)	9.3417(0)	9.0030(0)	25.352(2)
0/A	14.3408(9)	14.0420(9)	10.5088(9)	14.205(1)
C/A	76 522(1)	20.405(1)	16.707(2) 78.520(1)	23.020(2)
$\mathcal{L}(\mathcal{L})$	70.323(1)	90	76.330(1) 82.485(1)	90
$\mu()$	71.990(1) 84.221(1)	90.775(1)	72 102(1)	105.890(1)
$V(\lambda^3)$	2585 0(3)	2858 8(3)	1780 5(3)	8271(1)
T/K	100	100	100	100
7	2	4	2	8
$R_{a} W R \gamma^{b}$	$\frac{2}{0.0194}$ 0.0466	0.0233 0.0456	0.0217 0.0493	0.0265.0.0618
GoF	1 048	1 066	1 046	1 050
001	1.040	1.000	1.040	1.050
Compound	<b>4</b> a	4b	4c	<b>4</b> e
Formula	$C_6H_{18}Cl_4P_2W$	$C_{16}H_{22}Cl_4P_2W$	$C_{26}H_{26}Cl_4P_2W$	$C_{26}H_{24}Cl_4P_2W$
FW	477.79	601.93	726.06	724.04
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_{1}/c$	$P2_1/c$	$P\bar{1}$	$P2_{1}/c$
Color, habit	Orange block	Orange block	Orange block	Orange plate
a/Å	6.5351(6)	9.644(1)	8.860(3)	11.300(4)
b/Å	8.4615(8)	13.781(2)	9.491(3)	21.711(9)
c/Å	13.326(1)	8.203(1)	9.765(3)	13.943(5)
α (°)	90	90	66.983(4)	90
$\beta$ (°)	99.717(1)	106.744(2)	89.510(4)	109.633(4)
γ (°)	90	90	63.041(4)	90
$V/A^3$	726.3(1)	1044.0(2)	659.3(3)	3222(2)
T/K	100	100	100	100
Z	2	2	1	4
$R_1,^a \le R2^b$	0.0208, 0.0605	0.0146, 0.0336	0.0152, 0.0388	0.0548, 0.1278
GoF	1.144	1.032	1.048	1.065
Compound	[Cp* <sub>2</sub> Co][ <b>4c</b> ]	[Cp* <sub>2</sub> Co][ <b>4c</b> ]	[Cp* <sub>2</sub> Co][ <b>5</b> ]	6
Formula	C <sub>46</sub> H <sub>56</sub> Cl <sub>4</sub> CoP <sub>2</sub> W	C <sub>46</sub> H <sub>56</sub> Cl <sub>4</sub> CoP <sub>2</sub> W	C <sub>22</sub> H <sub>42</sub> Cl <sub>5</sub> CoPW	C <sub>20</sub> H <sub>22</sub> Cl <sub>2</sub> NP <sub>2</sub> W
FW	1055.43	1055.43	890.67	734.69
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	C2/c	$P2_1/n$	$P\bar{1}$	C2/c
Color, habit	Orange block	Orange column	Yellow plate	Yellow column
a/Å	27.23(1)	9.600(2)	9.654(1)	13.8088(8)
b/Å	11.087(4)	11.047(2)	10.162(1)	13.2473(8)
c/Å	17.943(6)	21.228(3)	17.949(2)	16.0074(9)
α (°)	90	90	80.677(2)	90
$\beta$ (°)	125.829(4)	93.333(2)	80.642(2)	93.997(1)
γ (°)	90	90	89.713(2)	90
$V/\text{\AA}^3$	4392(3)	2247.3(6)	1714.2(3)	2921.1(3)
T/K	100	100	100	100
Ζ	4	2	2	4
$R_1$ , <sup><i>a</i></sup> wR2 <sup><i>b</i></sup>	0.0414, 0.1039	0.0196, 0.0442	0.0385, 0.0967	0.0161, 0.0339
GoF	1.340	1.033	1.030	1.065

chloride abstraction to afford Me<sub>3</sub>SiCl instead of addition of the Me<sub>3</sub>Si<sup>+</sup> electrophile to the W<sup>IV</sup> $\equiv$ O ligand. Although an undesired outcome here, chloride abstraction by electrophilic silylium cations has been described by Heinekey and coworkers as useful for the preparation of otherwise inaccessible iridium and rhodium hydrido complexes.<sup>50</sup>

Another reaction type to which metal oxo ligands are subject is ligand exchange without reduction of the metal. Because these reactions are not attended by a change in oxidation state at the metal, they are often, if not generally, easier to accomplish than direct atom abstractions. The reaction of  $H_2S$  or a primary amine (RNH<sub>2</sub>) upon a terminal metal oxo ligand, M=O, is widely applicable for the synthesis of corresponding terminal sulfido (M=S)<sup>51</sup> and imido (M=NR) compounds<sup>52</sup> (eqn (4)–(5)). Analogous to the foregoing reaction types, but less extensively developed, are halide-for-oxo exchange reactions (eqn (6)).<sup>53</sup>

Treatment of [W<sup>IV</sup>OCl<sub>2</sub>(PMePh<sub>2</sub>)<sub>3</sub>] with anhydrous HCl(g) does indeed effect chloride-for-oxo exchange (Scheme 1) and remove the oxo ligand as H<sub>2</sub>O to produce the known compound *trans*-[WCl<sub>4</sub>(PMePh<sub>2</sub>)<sub>2</sub>], a species that is easily identified by its distinctive NMR spectrum.<sup>27b,28</sup> We have also identified *trans*-[WCl<sub>4</sub>(PMePh<sub>2</sub>)<sub>2</sub>] by X-ray crystallography since its structure has

W(1)-Cl(1)	2.4270(4)	Cl(1)-W(1)-Cl(2)	178.78(2)	Cl(2)-W(1)-P(4)	84.12(2)
W(1) - Cl(2)	2.4289(4)	Cl(1)-W(1)-P(1)	83.14(2)	P(1)-W(1)-P(2)	90.09(2)
W(1) - P(1)	2.5282(5)	Cl(1) - W(1) - P(2)	96.21(2)	P(1) - W(1) - P(3)	167.26(2)
W(1) - P(2)	2.5199(5)	Cl(1) - W(1) - P(3)	84.12(2)	P(1) - W(1) - P(4)	90.85(2)
W(1) - P(3)	2.5191(5)	Cl(1) - W(1) - P(4)	95.58(2)	P(2) - W(1) - P(3)	91.04(2)
W(1) - P(4)	2.5214(5)	Cl(2)-W(1)-P(1)	98.05(2)	P(2)-W(1)-P(4)	168.20(2)
		Cl(2)-W(1)-P(2)	84.11(2)	P(3) - W(1) - P(4)	90.63(2)
		Cl(2)–W(1)–P(3)	94.70(2)		
Table 3   Selected	bond lengths (Å), angles	(deg.) for [W <sup>IV</sup> O(CO)Cl <sub>2</sub> (PMePh	$)_2$ ], compound <b>2</b>		
W(1)–O(1)	1.713(2)	O(1)-W(1)-C(27)	88.3(1)	C(27)-W(1)-P(1)	92.28(8)
W(1) - C(27)	2.043(2)	O(1)-W(1)-Cl(1)	100.83(7)	C(27)-W(1)-P(2)	91.62(8)
W(1) - Cl(1)	2.4326(7)	O(1)-W(1)-Cl(2)	166.33(7)	Cl(1)-W(1)-Cl(2)	92.75(2)
W(1)-Cl(2)	2.4964(7)	O(1)-W(1)-P(1)	98.88(7)	Cl(1)-W(1)-P(1)	87.37(2)
W(1) - P(1)	2.5284(7)	O(1) - W(1) - P(2)	101.43(7)	Cl(1) - W(1) - P(2)	85.61(2)
W(1) - P(2)	2.5429(7)	W(1) - C(27) - O(2)	178.6(3)	Cl(2) - W(1) - P(1)	80.04(2)
C(27) - O(2)	1.135(3)	C(27) - W(1) - Cl(1)	170.83(8)	Cl(2) - W(1) - P(2)	81.01(2)
		C(27)–W(1)–Cl(2)	78.18(8)	P(1)-W(1)-P(2)	159.42(2)
Table 4   Selected	bond lengths (Å), angles	(deg.) for $[W^{IV}OCl_2(PMePh_2)_3]$ , c	ompound <b>3c</b>		
W(1)–O(1)	1.716(2)	O(1)–W(1)–Cl(1)	97.99(6)	Cl(1)-W(1)-P(3)	86.63(2)
W(1) = Cl(1)	2.4668(6)	O(1)-W(1)-Cl(2)	172.19(6)	Cl(2)-W(1)-P(1)	84.24(2)
	2.4915(6)	O(1)-W(1)-P(1)	99.25(6)	Cl(2)-W(1)-P(2)	84.63(2)
W(1)-Cl(2)	=, == (=)		88 03(6)	$C_{1}(2)-W(1)-P(3)$	82.77(2)
W(1)-Cl(2) W(1)-P(1)	2.5530(6)	O(1)-W(1)-P(2)	00.05(0)		~=···(=)
W(1) - Cl(2) W(1) - P(1) W(1) - P(2)	2.5530(6) 2.5172(6)	O(1)–W(1)–P(2) O(1)–W(1)–P(3)	95.26(6)	P(1)-W(1)-P(2)	96.24(2)
$ \begin{array}{l} W(1) - Cl(2) \\ W(1) - P(1) \\ W(1) - P(2) \\ W(1) - P(3) \end{array} $	2.5530(6) 2.5172(6) 2.5463(6)	O(1)–W(1)–P(2) O(1)–W(1)–P(3) Cl(1)–W(1)–Cl(2)	95.26(6) 89.46(2)	P(1)–W(1)–P(2) P(1)–W(1)–P(3)	96.24(2) 161.80(2)
W(1)-Cl(2) W(1)-P(1) W(1)-P(2) W(1)-P(3)	2.5530(6) 2.5172(6) 2.5463(6)	O(1)-W(1)-P(2) O(1)-W(1)-P(3) Cl(1)-W(1)-Cl(2) Cl(1)-W(1)-P(1)	95.26(6) 89.46(2) 80.54(2)	P(1)–W(1)–P(2) P(1)–W(1)–P(3) P(2)–W(1)–P(3)	96.24(2) 161.80(2) 95.18(2)

 $\textbf{Table 5} \quad \text{Selected bond lengths (Å), angles (deg.) for [W^{IV}Cl_4(PMePh_2)_2], \textbf{4c}, and [Cp*_2Co][W^{IV}Cl_4(PMePh_2)_2], [\textbf{4c}]^{1-\alpha} = 0$ 

4c	[ <b>4</b> c] <sup>1-</sup>		4c	<b>[4c]</b> <sup>1–</sup>
2.3379(7) 2.3466(6) 2.5672(7) 1.821[1] 1.817(2)	2.4355(6) 2.4092(6) 2.5303(6) 1.829[1] 1.820(2)	Cl(1)-W(1)-Cl(1A) Cl(1)-W(1)-Cl(2) Cl(1)-W(1)-Cl(2A) Cl(1)-W(1)-Cl(2A) Cl(1)-W(1)-P(1) Cl(1)-W(1)-P(1A) Cl(2)-W(1)-Cl(2A)	180 89.84(3) 90.16(3) 92.10(2) 87.90(2)	180 89.41(2) 90.59(2) 88.71(2) 91.29(2)
		Cl(2)-W(1)-Cl(2A) Cl(2)-W(1)-P(1) Cl(2)-W(1)-P(1A) P(1)-W(1)-P(1A)	90.34(3) 89.66(3) 180	93.93(2) 86.07(2) 180

not been previously reported. This transformation of  $3c \rightarrow 4c$ (Scheme 1) has been performed on a scale of 0.20 g with an isolated yield of 87%, product identity and purity being confirmed spectroscopically and analytically. A particularly fortunate aspect of this reaction is that [WCl<sub>4</sub>(PMePh<sub>2</sub>)<sub>2</sub>], which is an easily handled airstable molecule, is the immediate precursor to [WCl<sub>2</sub>(PMePh<sub>2</sub>)<sub>4</sub>] and is transformed to it by Na/Hg reduction in the presence of PMePh<sub>2</sub>.<sup>27</sup> Thus, a tungsten-mediated reactivity cycle for CO<sub>2</sub>to-CO reduction, with an oxygen atom removed as H<sub>2</sub>O, is formed in a series of stoichiometric steps that are well-defined and unambiguous. The tungsten species involved at each point along the way is definitively established by X-ray crystallography. Crystal and refinement data for 1, 2, 3c and 4c, are presented in Table 1, while selected metrical parameters are collected in Tables 2–5, respectively.

The overall balanced equation obtained from adding the individual steps of Scheme 1 is  $CO_2 + 2e^- + 2HCl \rightarrow CO +$ 

 $H_2O + 2CI^-$ . The essential reducing equivalents for  $CO_2$ -to-CO reduction are provided, at present, by sodium metal. However, the reduction of 4c to 1 in Scheme 1 should be feasible with reducing agents less potent than Na<sup>0</sup> metal or, in principle, via bulk electrolytic means at an electrode surface that is poised at the minimal potential necessary. Redox potentials for simple chlorophosphine complexes of the type  $[WCl_4(PMe_{3-x}Ph_x)_2]$  (x = 0-3) appear not to have been previously reported. With the aim of disclosing the minimal energetic parameters within which the closed cycle for CO<sub>2</sub>-to-CO reduction that is defined by Scheme 1 might be made to operate, a cyclic voltammetry study of the series  $[WCl_4(PMe_{3-x}Ph_x)_2]$  (x = 0-3) was undertaken. This electrochemical study establishes specific  $W(IV) \rightarrow W(III)$  and  $W(III) \rightarrow W(II)$  reduction potentials and clarifies the extent to which the window of redox potentials may be manipulated in these simple chlorophosphine complexes by variation of the phosphine substituents.

W(1)-Cl(1)	2.3953(4)	Cl(1)-W(1)-Cl(1A)	176.58(2)	Cl(2)-W(1)-N(1)	180
W(1)-Cl(2)	2.4500(6)	Cl(1)-W(1)-Cl(2)	88.29(1)	P(1)-W(1)-P(1A)	168.76(2)
W(1) - P(1)	2.5638(5)	Cl(1)-W(1)-P(1)	92.67(2)	P(1)-W(1)-N(1)	95.62(1)
W(1) - N(1)	1.928(2)	Cl(1) - W(1) - P(1A)	86.99(2)	W(1) - N(1) - C(14)	125.6(1)
N(1) - C(14)	1.470(2)	Cl(1) - W(1) - N(1)	91.71(1)	C(14) - N(1) - C(14A)	108.9(2)
		Cl(2) - W(1) - P(1)	84.38(1)	$\Phi^a$	138.9

The chlorophosphine complexes *trans*-[WCl<sub>4</sub>(PMe<sub>3-x</sub>Ph<sub>x</sub>)<sub>2</sub>] (x = 0-3, compounds **4a–4d**, respectively) and [WCl<sub>4</sub>(dppe)] (**4e**), were prepared by literature methods either from WCl<sub>4</sub> or from WCl<sub>6</sub> with excess phosphine or Zn metal as reductant.<sup>27b,28–29</sup> Synthesis of *trans*-[WCl<sub>4</sub>(PMe<sub>3</sub>)<sub>2</sub>] is invariably attended by formation of the related seven-coordinate species [WCl<sub>4</sub>(PMe<sub>3</sub>)<sub>3</sub>].<sup>30,54</sup> As its preparation in pure form has only been *via* a sealed tube reaction,<sup>30</sup> a more convenient, simplified, synthesis procedure is described here in some detail. The identity of these compounds has been established by X-ray crystallography (Fig. S1†). Crystallographic data are deferred to ESI.† Only *trans*-[WCl<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] has been previously identified by X-ray diffraction.<sup>55</sup>

In the continuum of available phosphine ligands, those of the type  $P(Me_{3-x}Ph_x)_3$  (x = 0-3) exert appreciably less  $\pi$ -acidity than phosphines of the type  $P(OR)_3$  (R = alkyl, aryl),  $P(NR_2)_3$ , and  $PX_3$  (X = halide).<sup>56</sup> The new tungsten chlorophosphine complex [WCl<sub>4</sub>( $P(NMe_2)_3)_2$ ] was thus anticipated as a complex that would reveal less negative  $W(IV) \rightarrow W(III)$  and  $W(III) \rightarrow$ W(II) couples because of the electron-withdrawing character of the supporting phosphine. Efforts to prepare [WCl<sub>4</sub>( $P(NMe_2)_3)_2$ ] from [WCl<sub>4</sub>( $PMePh_2)_2$ ] *via* simple ligand displacement instead resulted in facile chloride-for-amido ligand exchange to produce [WCl<sub>3</sub>( $NMe_2$ )( $PMePh_2)_2$ ], **6**, and, possibly,  $PCl(NMe_2)_2$ . Multiple chloride-for-amido ligand exchanges were observed in reactions of WCl<sub>6</sub> with  $P(NMe_2)_3$ . A similar chloride-for-dimethylamido ligand exchange at tungsten has been described using  $Me_2N-$ SiMe<sub>3</sub>.<sup>57</sup>

Compound **6** has been identified structurally (Tables 1 and 6, Fig. 1), and its structure reveals the NMe<sub>2</sub> plane to be oriented at a ~139° angle with respect to the WCl<sub>3</sub>N mean plane, presumably a balance between the conflicting demands for optimal  $\pi$ -donation into the tungsten  $t_{2g}$  orbitals and minimization of steric crowding with the phosphine ligands. The appreciably greater  $\pi$ -donor ability of the NMe<sub>2</sub> ligand is underscored by the absence of any reversible reduction for **6**, as was seen for **4c**, but instead the occurrence of a reversible oxidation corresponding to formation of [W<sup>v</sup>Cl<sub>3</sub>(NMe<sub>2</sub>)(PMePh<sub>2</sub>)<sub>2</sub>]<sup>1+</sup> (0.51 V, Fig. S2†).

Although highly crystalline, samples of **6** appeared, on the combined evidence of elemental analysis, NMR spectroscopy, and mass spectrometry to be adulterated both with small amounts of an unidentified organophosphine species and with a ditungsten species of color similar to **6**, which is tentatively formulated as the edge-sharing bioctahedron  $[(Ph_2MeP)WCl_3(\mu-NMe_2)(\mu-Cl)WCl_3(PMePh_2)]$ . Recrystallization was ineffective in removing these minor species, nor was an exhaustive screening of crystals by X-ray diffraction successful in identifying anything different from **6**.

Table 7 summarizes the reduction potentials measured for *trans*- $[WCl_4(PMe_{3-x}Ph_x)_2]$  (x = 0-3, compounds **4a–4d**, respectively) and



Fig. 1 Thermal ellipsoid plots at the 50% probability level for (a)  $[WCl_3(NMe_2)(PMePh_2)_2]$ , 6, and (b)  $P2_1/n$  polymorph of  $[Cp*_2Co][WCl_4(PMePh_2)_2]$ . H atoms are omitted for clarity.

[WCl<sub>4</sub>(dppe)] (4e) in THF. Little effect is seen upon the potentials for the W(IV)  $\rightarrow$  W(III) reduction for the *trans*-[WCl<sub>4</sub>(PMe<sub>3-x</sub>Ph<sub>x</sub>)<sub>2</sub>] (x = 0-3) series, consistent with the orbital into which the electron is added being a tungsten  $d_{xz}, d_{yz}$  orbital. The W(IV)  $\rightarrow$  W(III) reduction generally occurs at quite mild potentials and reveals reversible behavior (Fig. 2); the mildest reduction potential is observed for [WCl<sub>4</sub>(dppe)]. The observed  $\Delta E_p$  of 0.10 V and  $i_a/i_c$ of 1.1 for 4c + e<sup>-</sup>  $\rightarrow$  [4c]<sup>1-</sup> (Fig. 2), while greater than the theoretical values of 0.059 V and 1.0, respectively, for a fully reversible process, are typically observed for [Cp<sub>2</sub>Fe]<sup>+</sup> + e<sup>-</sup>  $\rightarrow$  Cp<sub>2</sub>Fe under these same conditions with our system. For this reason, and because [4c]<sup>1-</sup> can be chemically prepared and isolated (*vide infra*), we attribute the departure of  $\Delta E_p$  from its ideal value to uncompensated solution resistance effects rather than to chemical instability. Further, a

**Table 7** Reduction potentials,  $E_{\frac{1}{2}}$  (V vs. Ag/AgCl), for [W<sup>IV</sup>Cl<sub>4</sub>(PRR'<sub>2</sub>)<sub>2</sub>] complexes.<sup>*a*</sup>

	$W(IV) \rightarrow W(III)^b$	$W(IV) \rightarrow W(III)^c$	$W(III) \rightarrow W(II)$
$[WCl_4(PMe_3)_2]$	-0.40	-0.39	-1.69 cd
$[WCl_4(PMe_2Ph)_2]$	-0.35	-0.37	-1.70 cd
$[WCl_4(PMePh_2)_2]$	-0.36	-0.37	-1.60 de
$[WCl_4(PPh_3)_2]$	-0.44	-0.45	-1.43 <sup>cd</sup>
[WCl <sub>4</sub> (dppe)]	-0.21	-0.22	-1.43 <sup>cd</sup>

<sup>*a*</sup> Solvent and supporting electrolyte were THF and  $[Bu_4N][PF_6]$ . All data were obtained under a blanketing atmosphere of Ar. Under the conditions employed, the  $[Cp_2Fe]^{I+} + e^- \rightarrow Cp_2Fe$  coupled occurred at +0.54 V. <sup>*b*</sup> Data obtained by cyclic voltammetry (CV) by the relationship  $E_{\frac{1}{2}} = (E_a + E_c)/2$ . <sup>*c*</sup> Data obtained by differential pulse voltammetry by the relationship  $E_{\frac{1}{2}} = E_{max} + \Delta E/2$ , where  $\Delta E$  is the pulse amplitude. <sup>*d*</sup> All W(III)  $\rightarrow$  W(II) couples were irreversible. <sup>*c*</sup> Estimated from CV.



**Fig. 2** Cyclic voltammogram of  $[WCl_4(PMePh_2)_2]$  in  $CH_2Cl_2$  with  $[Bu_4N][PF_6]$  supporting electrolyte and scan rate of 100 mV s<sup>-1</sup>. Under these conditions, the  $[Cp_2Fe]^+ + e^- \rightarrow Cp_2Fe$  coupled occurred at +0.54 V.

plot of a  $i_c/v^{1/2}$  ( $i_c$  = current in the forward (reducing) direction; v = scan speed) is linear in the range 20–500 mV s<sup>-1</sup> (Fig. S3†). For [WCl<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] and [WCl<sub>4</sub>(PMePh<sub>2</sub>)<sub>2</sub>], voltammetric data had to be obtained quickly owing to facile sample degradation. The remaining compounds were stable toward repeated scanning because the more basic (or chelating) nature of the phosphine ligand diminishes the rate of phosphine dissociation.

The mild potentials and reversible nature found for the  $W(IV) \rightarrow W(III)$  couples suggested the feasibility of isolating a [W<sup>III</sup>Cl<sub>4</sub>(PMePh<sub>2</sub>)<sub>2</sub>]<sup>1-</sup> anion, a species which has not been previously isolated. Introduction of a toluene solution of Cp<sub>2</sub>\*Co to a solution of [WCl<sub>4</sub>(PMePh<sub>2</sub>)<sub>2</sub>] induces immediate formation of a light brown precipitate. Isolation and crystallization of this solid from 1,2-dichloroethane/ether produced a mixture of orange columnar and pale yellow plate crystals, both of which were interrogated by X-ray diffraction. The former proved to be the intended [Cp\*<sub>2</sub>Co][W<sup>III</sup>Cl<sub>4</sub>(PMePh<sub>2</sub>)<sub>2</sub>], which was found to occur in both primitive  $(P2_1/n)$  and C-centered (C2/c) polymorphs. An ellipsoid plot of  $[Cp_{2}^{*}Co][4c]$  in the  $P2_{1}/n$  polymorph is presented in Fig. 1. The average W-Cl bond distance in this anion is 2.4195[7] Å, in contrast to the value of 2.3423[5] Å for the corresponding charge neutral compound 4c. This change is consistent with a diminution of chloride  $\pi$ -bonding into the  $t_{2r}$ -type orbitals due to the presence of an additional tungsten d electron. Further, the W-P and P-C bond distances slightly decrease and increase, respectively, changes consistent with  $\pi$ -acid character of the phosphine ligand.58 The pale yellow species was determined to be [Cp\*2Co][W<sup>IV</sup>Cl<sub>5</sub>(PMePh<sub>2</sub>)], [Cp\*2Co][5], also a new chlorophosphine complex of tungsten (See ESI<sup>†</sup>).

An important aspect of the closed reaction cycle illustrated in Scheme 1 is a quantification of the thermodynamics for each step. The reaction enthalpies for each step were evaluated computationally in the gas phase for tungsten complexes bearing the PH3 and PMe3 supporting ligands as well as the PMePh2 ligand that is used for the reactions of Scheme 1. The first reaction, labeled as (Rxn 1) on the x axis in Fig. 3, is the oxidative addition reaction  $[W^{II}Cl_2(phosphine)_4] + CO_2 \rightarrow [W^{IV}O(CO)Cl_2(phosphine)_2] +$ 2(phosphine). For convenience, since it is reaction enthalpies that are of immediate interest, the enthalpy of  $[W^{II}Cl_2(phosphine)_4] +$ CO<sub>2</sub> is assigned a relative value of zero. Reaction 1 is exothermic for all three systems (Fig. 3), but the calculated exothermicity increases by ~50 kJ mol-1 in going from [WIICl2(PH3)4] to [W<sup>II</sup>Cl<sub>2</sub>(PMePh<sub>2</sub>)<sub>4</sub>]. A possible reason for the greater exothermicity for the latter is suggested in the thermal ellipsoid plot of 1 in Scheme 1 by its appreciable distortions from an idealized octahedral coordination geometry. The high degree of steric crowding in [W<sup>II</sup>Cl<sub>2</sub>(PMePh<sub>2</sub>)<sub>4</sub>] appears to diminish each PMePh<sub>2</sub> ligand's ability to form a good dative bond to tungsten and thus



**Fig. 3** Calculated enthalpy profile  $(kJ \text{ mol}^{-1})$  for reactions that are part of the cycle of Scheme 1. Reactions 1, 2 and 3 along the x axis in the plot are as defined in the line equations at the right, where reactions with differing phosphine supporting ligands tungsten are distinguished by use of different colors (red for PH<sub>3</sub>, blue for PMe<sub>3</sub>, green for PMeP<sub>2</sub>). All calculations are for species in the gas phase.

Table 8 Calculated bond dissociation energies, kJ mol<sup>-1</sup>

$C=0.CO_{2}$	543
W=O, [WOCl <sub>2</sub> (PH <sub>3</sub> ) <sub>3</sub> ]	610
W=O, [WOCl <sub>2</sub> (PMePh <sub>2</sub> ) <sub>3</sub> ]	617
$W \equiv O, [WOCl_2(PMe_3)_3]$	624

primes the complex for ligand dissociation and oxidative addition of CO<sub>2</sub>. Reaction 2,  $[W^{IV}O(CO)Cl_2(phosphine)_2] + phosphine \rightarrow$  $[W^{IV}OCl_2(phosphine)_3] + CO$ , is essentially isoenergetic for all three systems. The surprisingly large endotherm calculated for reaction 2 reflects a special stability arising from a synergistic "push-pull" effect of the *cis*-oriented  $\pi$ -donating oxo and  $\pi$ -acidic carbonyl ligands interacting through the same d orbital(s) of tungsten.<sup>22,52</sup>

Movement from the third to fourth position along the x axis in Fig. 3 corresponds to the enthalpy of the gas phase reaction  $[WOCl_2(phosphine)_3] + 2HCl \rightarrow [WCl_4(phosphine)_2] + H_2O +$ phosphine (**Rxn 3**). Despite the formidable strength of the W=O bond, substitution of the multiply-bonded oxo ligand for two chloride ligands is calculated to be slightly exothermic or, at worst, near thermoneutral (Fig. 3). While solvation effects are certainly important to these reactions, the stabilizing solvation effects enjoyed by reactants and products are likely to be largely offsetting. Thus, the general trend that reaction 3 is slightly exothermic is a plausible one. Although the two additional W-Cl single bonds in [WCl<sub>4</sub>(phosphine)<sub>2</sub>] may not, at first thought, appear to be enough to compensate for a W=O bond and a  $W \leftarrow$  (phosphine) dative bond, it is probably the case that the degree of  $\pi$ -bonding with tungsten enjoyed by each of the four chloride ligands in [WCl<sub>4</sub>(phosphine)<sub>2</sub>] is significant enough that these W-Cl bonds are worth appreciably more than bona fide single bonds. The substantial W-Cl bond lengthening in reducing 4c to  $[4c]^{1-}$  is consistent with a disruption of this  $\pi$ -bonding (Table 5). The significance of this computational result is first that it corroborates the immediate experimental observation that the oxo-for-chloride ligand exchange does occur and is relatively facile. More generally, the result suggests that metal oxo multiple bonds may be transformable via nonredox ligand exchange into intermediates that offer greater tractability for designed turnover.

Considering the perception that metal—oxo multiple bonds in early and middle transition metal complexes are an obstacle against turnover in a cycle for small molecule reduction, it would be useful to have an experimentally determined W $\equiv$ O bond dissociation energy. The W $\equiv$ O bond strength has been estimated by Mayer to be at least 577 kJ mol<sup>-1</sup>,<sup>22c,59</sup> moderately greater than the 531 kJ mol<sup>-1</sup> determined for the C $\equiv$ O bond of CO<sub>2</sub>.<sup>60-61</sup> We have computationally assessed the W $\equiv$ O bond dissociation energies in [WOCl<sub>2</sub>(PH<sub>3</sub>)<sub>3</sub>], [WOCl<sub>2</sub>(PMePh<sub>2</sub>)<sub>3</sub>] and [WOCl<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>] in the gas phase (Table 8) and found them to agree reasonably well with Mayer's estimate. These W $\equiv$ O bond strengths appear to correlate in a plausible way with phosphine ligand basicity.

#### Summary and conclusions

In the face of accumulating atmospheric  $CO_2$  levels and diminishing carbon feedstocks, systems that catalytically activate  $CO_2$ are highly desirable. The tungsten-mediated  $CO_2$ -to-CO reduction

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first described by Mayer and elaborated upon here has some attraction in this context because of the mild conditions under which it functions and because of its high specificity for CO formation. A series of four well-defined stoichiometric steps have been demonstrated that collectively form a closed cycle. Significantly, the tungsten-oxygen multiple bond that results from oxidative addition of CO<sub>2</sub> has been shown both experimentally and computationally to be amenable to ligand exchange. These data indicate that, if removed in the form of H<sub>2</sub>O and substituted with two chloride ligands, the multiply bonded terminal oxo ligand is not at all a thermodynamic dead-end that obviates turnover. By effecting the removal of the oxygen atom in a nonredox ligand exchange reaction, as opposed to a redox atom abstraction reaction, we have an insight via the electrochemistry into the approximate overpotential diminution offered by this tungsten system over the noncatalyzed reduction of CO<sub>2</sub>. Compared to a potential of ~-2.6 V (vs [Cp<sub>2</sub>Fe]<sup>+</sup>/Cp<sub>2</sub>Fe) for the direct, uncatalyzed reduction of  $CO_2$  to  $CO_2^{1-,19}$  the W(II) oxidation state that is competent for oxidative addition of CO<sub>2</sub> is accessible from W(IV) at ~-2.1 V (vs [Cp<sub>2</sub>Fe]<sup>+</sup>/Cp<sub>2</sub>Fe).<sup>62</sup> Thus, the lowering of the overpotential barrier to CO<sub>2</sub> reduction that is offered by this tungsten system is ~0.5 V.

Although each of the reactions in Scheme 1 has some degree of precedent, taken together they make the point that early and middle transition metal systems such as this deserve some renewed consideration as potential catalysts for reduction of  $CO_2$ . The perceived disadvantage of metal–ligand multiple bond formation is, we submit, more than compensated for by the metal's ability to activate a thermodynamically and kinetically stable small molecule and to effect a multi-electron reduction under mild conditions. Among our continuing interests with the Mayer system are efforts to perform clean, bulk electrolytic reduction of  $[WCl_4(PMePh_2)_2]$ , or a suitable variant thereof, to W(II), an exploration of other spectator ligand types that can support the oxidative addition of  $CO_2$  to W(II), and a temperature-dependent spectrophotometric study of the oxidative addition of  $CO_2$  to  $[WCl_2(PMePh_2)_4]$  such that an experimental  $E_a$  may be determined.

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