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# Carbide Formation via Carbon Monoxide Dissociation Across a W≡W Bond

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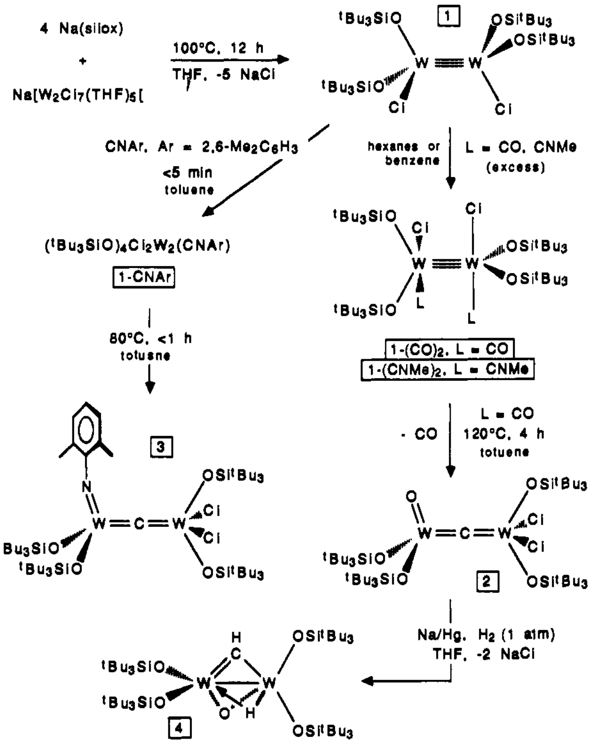
The dissociative adsorption of carbon monoxide[1] is the putative initial step in the heterogeneous Fischer–Tropsch (F-T) process, the catalytic conversion of synthesis gas ($CO/H_2$) to hydrocarbons[2] and oxygenates.[3] Few homogeneous analogues of CO dissociation exist, and these reactions often follow somewhat convoluted pathways[4–6] or rely on CO disproportionation to provide carbide and $CO_2$.[7,8] In attempting to prepare monomeric W(III) derivatives coordinated by silox ($^tBu_3SiO^-$),[5,9,10] dinuclear complexes containing the inherently stable $(W{\equiv}W)^{6+}$ unit were instead formed.[11] Fortunately, the steric and electronic properties of silox permitted observation of intriguing C≡O and C≡NAr bond cleavages by the $W_2$ triple bond, transformations that differ significantly from the reactivity of related group 6 species studied by Chisholm *et al.*[4,11]

## Scheme I



As Scheme I indicates, thermolysis (12 h, 100 °C) in THF of 4.0 equiv of Na(silox) and $NaW_2Cl_7(THF)_5$,[12] typically generated *in situ* from $WCl_4$ and Na/Hg,[13] provided brown, crystalline $[(silox)_2ClW]_2$ (**1**) in 75% yield. Inequivalent $^tBu_3Si$ resonances were observed in $^1H$ and $^{13}C\{^1H\}$ NMR spectra, indicative of $C_2$ symmetry and slow rotation about the W≡W unit ($\Delta G^\ddagger > 21$ kcal/mol).[14] Addition of excess CO (2.0 equiv uptake) or MeNC to **1** in hexanes afforded purple, sparingly soluble, crystalline $[(silox)_2Cl(L)W]_2$ (**1**-$L_2$, L = CO (95%), CNMe (79%)). Terminal $\nu$(CO) bands (IR (Nujol) 2055, 2035 $cm^{-1}$), inequivalent $^tBu_3Si$ signals ($^1H$ and $^{13}C\{^1H\}$ NMR), and steric factors implicated a $C_2$ structure of interlocked trigonal bipyramids for **1**-$(CO)_2$; similar evidence points to the same geometry for **1**-$(CNMe)_2$.[15] A mixed valence, $C_{2v}$ $(silox)_2Cl_2W{=}WL_2(silox)_2$ alternative was tentatively ruled out when exposure of **1** to CO (1 atm) and CNMe (~17 equiv) yielded a ~1:1:2 mixture of **1**-$(CO)_2$, **1**-$(CNMe)_2$, and $(silox)_2Cl(CO)W{\equiv}W(CNMe)Cl(silox)_2$ (**1**-CO,CNMe). The ~1:1:1:1 ratio of $^tBu_3Si$ resonances ($^1H$ NMR) attributed to **1**-CO,CNMe contradicted the 2:1:1 ratio expected for the mixed-valence structure.[15]

Thermolysis of $[(silox)_2Cl(CO)W]_2$ (**1**-$(CO)_2$) in toluene (4 h, 120 °C) produced 0.87 equiv of CO and green, crystalline $(silox)_2(O)W{=}C{=}WCl_2(silox)_2$ (**2**) in 70% yield.[16] The dinuclear oxo-$\mu$-carbido formulation was based on molecular weight measurements ($M_r$ found 1281, calcd 1328), a $^{13}C$ NMR resonance at $\delta$ 379.14 ($J_{CW}$ = 200, 187 Hz), $CH_4$ formation from an $H_2O$ quench, and a crude X-ray crystal structure that corroborated the tetrahedral/square-pyramidal structure but failed to detail it.[17] An IR absorption (Nujol) attributed to a $\nu(W_2C)$ at 1155 $cm^{-1}$ shifted to 1120 $cm^{-1}$ when $^{13}CO$ was used but was unchanged when $C^{18}O$ was the source, implicating CO bond scission. Two of the silox resonances (2:1:1) in the $^1H$

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(14) **1**: $^1H$ NMR ($C_6D_6$) $\delta$ 1.28, 1.25; $^{13}C$ NMR $\delta$ 31.00, 30.89 ($CH_3$), 24.53, 24.16 (SiC). Anal. Calcd for $W_2Cl_2Si_4O_4C_{48}H_{108}$: C, 44.34; H, 8.37. Found: C, 44.21; H, 8.38.

(15) **1**-$(CO)_2$: $^1H$ NMR ($C_6D_6$) $\delta$ 1.33, 1.25 (s, 54 H, silox); $^{13}C$ NMR $\delta$ 233.39 ($J_{CW}$ = 142 Hz, CO, $^{183}W$ satellites observed at 13% intensity), 31.39, 31.36 ($CH_3$), 24.74, 24.57 (SiC); IR (Nujol) $\nu(^{13}CO/C^{18}O)$ = 2010/1983, 1985/1965. Anal. Calcd for $W_2Cl_2Si_4O_6C_{50}H_{108}$: C, 44.28; H, 8.03. Found: C, 43.96; H, 7.87. **1**-$(CNMe)_2$: $^1H$ NMR ($C_6D_6$) $\delta$ 3.22 (s, 6 H, $Me_2$), 1.42, 1.25 (s, 54 H, silox); IR (Nujol) $\nu$(CN) = 2180 (br). Anal. Calcd for $W_2Cl_2Si_4O_4N_2C_{52}H_{114}$: C, 45.18; H, 8.31; N, 2.03. Found: C, 45.06; H, 8.34; N, 2.01. **1**-CO,CNMe: $^1H$ NMR ($C_6D_6$) $\delta$ 3.10 (s, 3 H, CNMe), 1.40, 1.34, 1.28, 1.23 (s, 27 H, silox).

(16) **2**: $^1H$ NMR ($C_6D_6$) $\delta$ 1.49, 1.45 (s, 27 H, silox), 1.20 (s, 54 H, silox); $^{13}C$ NMR $\delta$ 30.93, 30.68, 29.73 (2) ($CH_3$), 24.77, 24.74, 23.81 (2) (SiC). Anal. Calcd for $W_2Cl_2Si_4O_5C_{49}H_{108}$: C, 44.31; H, 8.20. Found: C, 44.26; H, 8.23.

(17) Disorder in the tetrahedral half of **2** has hindered analysis: monoclinic, $P2_1$ (disordered as $P2_1/m$), $a$ = 12.726(5), $b$ = 22.963(11), and $c$ = 13.144(3) Å, $\beta$ = 112.35(2)°, $V$ = 3552.2 Å$^3$, $T$ = 235 K, 6436 independent reflections (Mo K$\alpha$), 3255 observed ($3\sigma F_o$), $R \sim 18\%$.

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NMR spectrum coalesced (1:1) at 48 °C, consistent with a 16.9(2) kcal/mol barrier to rotation about the WCW vector.

Related CO cleavage reactions of $(RO)_3W{\equiv}W(OR)_3$ result in carbides supported by tetranuclear tungsten frameworks,[4] thus the molecularity of this reaction was examined. In THF, carbide **2** formation was first-order in [**1**-$(CO)_2$] ($k \sim 1.1(2) \times 10^{-4}$ s$^{-1}$, 80.0 °C), and inhibition by added CO was noted.[18] A reasonable pathway includes a preequilibrium involving CO dissociation from **1**-$(CO)_2$ to give **1**-CO, followed by CO addition across the $W{\equiv}W$ bond in a manner similar to the breakdown of ketones and aldehydes by $W_2(OCH_2{}^tBu)_6(py)_2$[19] and $WCl_2(PMePh_2)_4$.[20]

Since $(silox)_2Cl(CO)W{\equiv}WCl(silox)_2$ (**1**-CO) was implicated as a plausible intermediate, 1.0 equiv of sterically bulky 2,6-$Me_2C_6H_3NC$ (ArNC) was added to **1** in an attempt to form a stable monoadduct. In toluene, a brown complex formulated as $(silox)_4Cl_2W_2(CNAr)$ (**1**-CNAr, IR (Nujol) $\nu$(CN) = 2020 cm$^{-1}$)[21] rapidly formed but degraded ($C_7D_8$, 80 °C, $k = 9(1) \times 10^{-4}$ s$^{-1}$) to afford dark yellow $(silox)_2(ArN)W{=}C{=}WCl_2(silox)_2$ (**3**) in 58% yield.[22] Imido-$\mu$-carbide **3** was characterized by a carbide resonance at $\delta$ 406.25 in the $^{13}C$ NMR spectrum, a $\nu$-$(W_2C)$ IR band at 1120 cm$^{-1}$ (Nujol), and an HCl quench that produced $CH_4$, $ArNH_2$, and (silox)H. Coalescence of two silox resonances at −40 °C ($^1H$ NMR, $\Delta G^\ddagger$ = 11(1) kcal/mol) again manifested rotation about the WCW linkage.

An X-ray structural study of **3**[23] revealed a tetrahedral tungsten (W1) core (Figure 1) displaying a normal imido distance (1.753(14) Å),[24] somewhat short W1–O bond lengths (1.847(13)$_{av}$ Å), and an elongated W1–C bond (1.994(17) Å). An arylimide $CH_3$-group is oriented between a silox and chloride of the adjacent, distorted square-pyramidal tungsten (W2) that is the other terminus of the nearly linear $W_2C$ unit (176.0(12)°).[25] Its silox oxygens are bent at 108.4(7)° and 109.0(7)° from the carbide, as compared to 97.4(7)° and 97.8(7)° for the chlorides. The W2–O (1.879(13)$_{av}$ Å) and W2–Cl (2.361(6)$_{av}$ Å) distances are somewhat long, while the short W2–C bond length of 1.769(17) Å lends credence to $(silox)_2(ArN)W^{\delta+}{-}C{\equiv}W^{\delta-}Cl_2(silox)_2$ or $(silox)_2(ArN^{\delta+}{\equiv})W{-}C{\equiv}W^{\delta-}Cl_2(silox)_2$ resonance depictions[25] similar to asymmetric $\mu$-nitrides.[26]

Upon reduction of the oxo-$\mu$-carbido complex **2** with Na/Hg in the presence of 1 atm of $H_2$, partial hydrogenation of the carbide was observed. The green color of **2** dissipated to give tan $[(silox)_2W]_2(\mu\text{-}CH)(\mu\text{-}O)(\mu\text{-}H)$ (**4**) in 44% yield (~90% by $^1H$ NMR).[27] The 25 °C $^1H$ NMR spectrum of **4** exhibited resonances assigned to four inequivalent $^tBu_3Si$ groups (25 °C), a $\mu$-methylidyne at $\delta$ 19.62 ($J_{WH} \sim J_{W'H}$ = 20 Hz, satellite intensities ~20–25%), and an asymmetric $\mu$-hydride at $\delta$ 11.77 ($J_{WH}$ = 188 (14%), 20 Hz (14%)). The four silox signals merged at 80 °C, as symmetrization of the complex was effected ($\Delta G^\ddagger \sim 17(1)$ kcal/mol), presumably via hydride hopping ($J_{WH}$ = 105 Hz, ~25%) with concomitant rotation of the $(silox)_2W$ fragments. The $\mu$-methylidyne was found at $\delta$ 319.51 in the 25 °C $^{13}C$ NMR spectrum, and it also displayed disparate couplings to tungsten ($J_{WC}$ = 178, 150 Hz; $J_{CH}$ = 168 Hz).

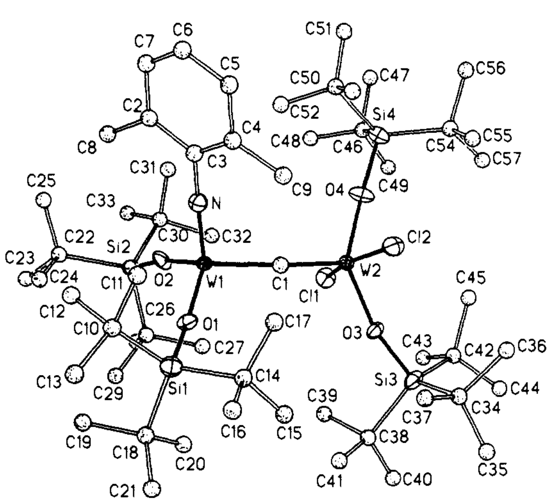

**Figure 1.** Molecular structure of $(silox)_2(2,6\text{-}Me_2C_6H_3N)W{=}C{=}WCl_2(silox)_2$ (**3**), drawn with 35% thermal ellipsoids. Selected bond distances (Å): W1–O1, 1.845(13); W1–O2, 1.848(13); C3–N, 1.404(24); W2–O3, 1.886(11); W2–O4, 1.872(13); W2–Cl1, 2.357(6); W2–Cl2, 2.365(5). Selected bond angles (deg): C1–W1–N, 104.2(7); C1–W1–O1, 110.2(7); C1–W1–O2, 110.8(8); N–W1–O1, 108.6(7); N–W1–O2, 109.9(6); O1–W1–O2, 112.8(6); Cl1–W2–Cl2, 164.8(2); Cl1–W2–O3, 87.5(4); Cl1–W2–O4, 88.1(5); Cl2–W2–O3, 86.9(4); Cl2–W2–O4, 87.8(5); O3–W2–O4, 142.6(3); W1–N–C3, 177.2(13).

The reductive cleavage of CO requires 6 e$^-$, exactly the number provided by the $(W{\equiv}W)^{6+}$ core; therefore, the scission of CO by putative **1**-CO represents a discrete homogeneous analogue to the dissociative adsorption of CO on heterogeneous surfaces, modeling this critical, initial step of the F-T process. Strong W=C and W=O bonds in **2** are necessary to rationalize the loss of the ~257 kcal/mol CO bond and that of the $W{\equiv}W$ unit, typically estimated at ~85 kcal/mol.[12] Once again, the bond strengths of the early metal oxo and alkylidene-like carbide ligands[5] enable the observation of transformations common to highly reactive catalyst surfaces.

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**Supplementary Material Available:** X-ray structural data pertaining to $(silox)_2(2,6\text{-}Me_2C_6H_3N)W{=}C{=}WCl_2(silox)_2$ (**3**), including a summary of crystallographic parameters, atomic coordinates, bond distances and angles, and anisotropic thermal parameters (13 pages); listing of observed and calculated structure factors (28 pages). Ordering information is given on any current masthead page.

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(21) **1**-CNAr: $^1H$ NMR ($C_7D_8$) $\delta$ 7.03 (d, 2 H, *m*-CH, *J* = 7.6 Hz), 6.38 (t, 1 H, *p*-CH, *J* = 7.6 Hz), 3.12 (s, 6 H, $Me_2$), 1.32, 1.24 (s, 27 H, silox), 1.16 (s, 54 H, silox). Color changes and related adducts implicated a $(silox)_2ClW{\equiv}W(silox)_2Cl(CNAr)$ structure, but two silox groups must be accidentally degenerate; $(silox)_2Cl_2W{=}W(silox)_2(CNAr)$ is a compelling alternative from the standpoint of the subsequent product **3**.

(22) **3**: $^1H$ NMR ($C_6D_6$) $\delta$ 6.99 (d, 2 H, *m*-CH, *J* = 7.6 Hz), 6.54 (t, 1 H, *p*-CH, *J* = 7.6 Hz), 2.94 (s, 6 H, Me), 1.39, 1.23 (s, 54 H, silox); $^{13}C$ NMR $\delta$ 406.26 ($J_{WC}$ = 194 Hz; S/N difficulties, only one $J_{WC}$ observed), 154.61 ($J_{WC}$ = 33 Hz), 137.21, 128.61, 126.89 (Ar), 31.12, 30.27 ($C(CH_3)_3$), 25.17, 23.38 (SiC), 20.49 (ArMe). Anal. Calcd for $W_2Cl_2Si_4O_4NC_{57}H_{117}$: C, 47.83; H, 8.24; N, 0.98. Found: C, 47.74; H, 8.34; N, 0.96.

(23) **3**: $C_{57}H_{117}Cl_2NO_4Si_4W_2$, monoclinic, $P2_1/n$, $a$ = 20.867(7), $b$ = 13.275(4), and $c$ = 27.152(8) Å, $\beta$ = 111.78(3)°, $V$ = 6984(3) Å$^3$, $Z$ = 4, $D_x$ = 1.361 g/cm$^3$, $T$ = 230 K, $T_{min}/T_{max}$ = 0.66. Of 12 540 data collected (Siemens P4, $2\theta_{max}$ = 50°), 12 264 were independent and 6682 were observed ($5\sigma F_o$). All atoms with $Z \geq 7$ were anisotropically refined; H-atoms were treated as idealized contributions. $R(F)$ = 6.40%, $R(wF)$ = 8.45%.

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(27) **4**: $^1H$ NMR ($C_6D_6$) $\delta$ 1.38, 1.25, 1.21, 1.12 (s, 27 H, silox); $^{13}C$ NMR $\delta$ 31.27, 30.72, 30.60, 30.25 (Me), 24.07, 23.61, 23.52 (2) (SiC). Anal. Calcd for $W_2Si_4O_5C_{49}H_{110}$: C, 46.73; H, 8.80. Found: C, 46.80; H, 8.89.