Reactions of Nucleophiles with the Cationic Dicyclopentadienyl-Bridged Ditungsten Complex $[\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}W_2(CO)_6(\mu\text{-}H)]^+$

Scott G. McKinley and Robert J. Angelici*

Department of Chemistry, Iowa State University, Ames, Iowa 50011

Moon-Gun Choi

Molecular Structure Laboratory, Yonsei University, Seoul, 120-749, Korea

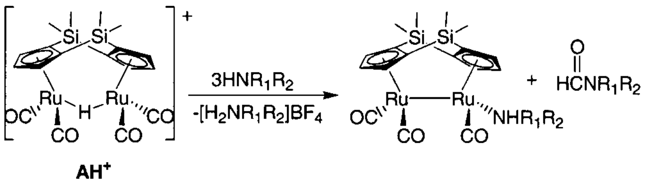
Received October 2, 2001

The dihydride $\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}W_2(CO)_6(H)_2$ (**1**), which contains a linked dicyclopentadienyl ligand, reacts with Ph_3C^+ to give $[\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}W_2(CO)_6(\mu\text{-}H)]^+$ ($\mathbf{2H^+}$). The W−H−W bond in $\mathbf{2H^+}$ is cleaved upon reaction with I^- to give $\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}W_2(CO)_6(H)(I)$ (**3**). Crystal structures of $[\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}W_2(CO)_6(\mu\text{-}H)]^+$ ($\mathbf{2H^+}$) and its unprotonated analogue $\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}W_2(CO)_6$ (**2**) are also reported and discussed.

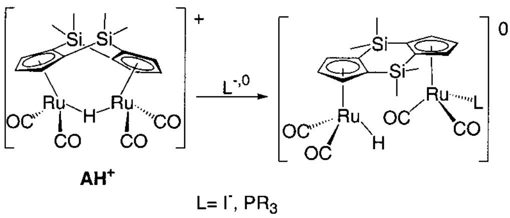
Introduction

The concept that two metals in close proximity may promote novel chemical reactivity has been investigated widely in recent years.[1] In contrast to mononuclear complexes, dinuclear species have the capacity to form an expanded range of oxidation states and μ-bridged intermediates, which may allow for unique reactions.[2] Recently this research group reported the synthesis and reactions of $[\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}Ru_2(CO)_4(\mu\text{-}H)][BF_4]$ ($\mathbf{AH^+BF_4^-}$).[3] Among cyclopentadienyl ligands in dinuclear $(Cp')_2Ru_2(CO)_4(\mu\text{-}H)^+$ complexes, $\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}$ is unique because it reduces the rate of bridging hydride deprotonation in $\mathbf{AH^+}$, which allows nucleophiles to attack at the CO ligands in the cationic complex. Reactions of $\mathbf{AH^+}$ with amines (Scheme 1) lead to products that result from amine attack on a CO ligand. Thus, despite being very acidic ($pK_a(H_2O) = 1.0$ (±0.5)),[4] $\mathbf{AH^+}$ undergoes deprotonation at a rate that is slower than nucleophilic attack on one of its CO ligands.

Scheme 1. Reactions of AH^+ with Primary and Secondary Amines



Scheme 2. Reactions of AH^+ with L = I− or PR_3



Another type of reaction that was observed with the $[\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}Ru_2(CO)_4(\mu\text{-}H)][BF_4]$ complex was that with ligands such as I^- and PR_3, which cleave the Ru−H−Ru bond (Scheme 2).[5] In the present studies, we sought to determine whether the related tungsten $[\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}W_2(CO)_6(\mu\text{-}H)][BF_4]$ complex ($\mathbf{2H^+BF_4^-}$) could be prepared and whether it would undergo reactions with nucleophiles at a CO ligand or at the W−H−W bridge, analogous to reactions of $\mathbf{AH^+}$ (Schemes 1 and 2).

Experimental Section

General Considerations. All reactions were carried out under an atmosphere of dry argon or nitrogen using standard Schlenk techniques. Tetrahydrofuran (THF), methylene chloride (CH_2Cl_2), diethyl ether (Et_2O), and hexanes were purified on alumina using a Solvo-Tech solvent purification system,

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* To whom correspondence should be addressed. E-mail: angelici@iastate.edu.

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10.1021/om010861w CCC: $22.00 © 2002 American Chemical Society
Publication on Web 02/22/2002

Table 1. Crystal and Structure Refinement Data for 2 and $2H^+$

	2	**$2H^+$**
empirical formula	$C_{20}H_{18}O_6Si_2W_2$	$H_{22}C_{21.50}Cl_3O_6F_4Si_2W_2B$
fw	779.22	993.43
temperature	293(2) K	173(2) K
wavelength	0.71073 Å	0.71073 Å
cryst syst	monoclinic	orthorhombic
space group	*C*2/*c*	*Pnnm*
unit cell dimens	$a = 25.190(4)$ Å, $\alpha = 90.000(1)°$ $b = 13.583(2)$ Å, $\beta = 125.196(2)°$ $c = 16.017(3)$ Å, $\gamma = 90.000(1)°$	$a = 16.370(2)$ Å, $\alpha = 90.000(1)°$ $b = 15.172(2)$ Å, $\beta = 90.000(1)°$ $c = 12.589(2)$ Å, $\gamma = 90.000(1)°$
volume	4478.3(13) Å^3	3126.7(5) Å^3
Z	8	4
density (calcd)	2.308 Mg/m^3	2.110 Mg/m^3
abs coeff	10.407 mm^{-1}	7.743 mm^{-1}
F(000)	2896	1868
cryst size	$0.58 \times 0.32 \times 0.28$ mm^3	$0.21 \times 0.19 \times 0.06$ mm^3
θ range for data collection	1.80 to 25.51°	1.83 to 27.54°
index ranges	$-27 \le h \le 30, -16 \le k \le 15, -17 \le l \le 19$	$21 \le h \le 21, -19 \le k \le 19, -16 \le l \le 16$
no. of reflns collected	4176 [R(int) = 0.0366]	3766 [R(int) = 0.0490]
no. of obsd reflns		3538
completeness to θ	25.51° = 99.9%	27.54° = 99.8%
abs corr	none	semiempirical from equivalents
max. and min. transmn	0.1587 and 0.0649	1.00000 and 0.42792
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	4176/0/ 268	3766/4/205
goodness-of-fit on F^2	1.180	1.152
final R indices [$I > 2\sigma(I)$]	R1 = 0.0321, wR2 = 0.0725	R1 = 0.0338, wR2 = 0.0833
R indices (all data)	R1 = 0.0383, wR2 = 0.0744	R1 = 0.0362, wR2 = 0.0845
largest diff peak and hole	0.701 and −2.169 e Å^{-3}	1.630 and −2.008 e Å^{-3}

as described by Grubbs and co-workers.[6] Nitromethane was dried over calcium chloride and distilled. All other chemicals were used without further purification as purchased from Aldrich. Neutral alumina (activity I) for chromatography was degassed under vacuum at room temperature for 4 h, then treated with 7.5% water by weight. Silica gel (J.T. Baker, 40−140 mesh) was degassed at room temperature for 4 h prior to use. Filtrations were performed with Celite on filter paper. Solution infrared spectra were recorded on a Nicolet-560 spectrometer using NaCl cells with 0.1 mm spacers. NMR spectra were obtained on either a 300 MHz Varian VXR-300 or a modified 400 MHz Varian VXR-400 spectrometer using CD_2Cl_2 or C_6D_6 as solvent, internal lock, and internal reference. Elemental analyses were performed on a Perkin-Elmer 2400 series II CHNS/O analyzer.

X-ray diffraction data for $\mathbf{2H^+BF_4^-}$ and **2** were collected using Siemens SMART and Bruker SMART CCD diffractometers, respectively. Successful solutions for both were obtained from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. The structure of $\mathbf{2H^+BF_4^-}$ was solved using SHELXS-86 and refined using SHELXL-97. The structure of **2** was solved using SHELXTL and refined using SHELXL-97. All hydrogen atoms for $\mathbf{2H^+BF_4^-}$ and **2** were placed in ideal positions and refined as riding atoms with individual (or group if appropriate) isotropic displacement parameters. The hydrogen atom between the tungsten atoms in $\mathbf{2H^+BF_4^-}$ was placed and refined to be on the crystallographic mirror at a similar distance to both metal atoms. Other relevant crystallographic data are given in Table 1.

Synthesis of *cis*-$\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}W_2(CO)_6(H)_2$ (1). This compound was prepared by a modification of the reported method.[7] To a flask containing 50 mL of THF were added $W(NCEt)_3(CO)_3$ (100 mg, 0.023 mmol)[8] and $(C_5H_4(SiMe_2))_2$ (28 mg, 0.012 mmol).[9] The solution was stirred at room temperature for 15 min. The solvent was removed under vacuum, and the tan solid was washed with 4 × 50 mL of hexanes and subsequently dried under vacuum, yielding 83% **1** as a tan powder. The compound was characterized by its IR and ^1H NMR spectra, which were reported previously.[7] IR (CH_2Cl_2): 2019 (s), 1924 (vs) cm^{-1}. ^1H NMR (300 MHz, CD_2Cl_2): δ 5.86 (t, J = 2.2 Hz, 2 H, Cp-*H*), 5.63 (d, J = 2.2 Hz, 4 H Cp-*H*), 0.61 (s, 6 H, Si(C*H*$_3$)), 0.40 (s, 6 H Si(C*H*$_3$)), −6.67 (s, J_{W-H} =18 Hz, 1 H, W-*H*).

Synthesis of $[\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}W_2(CO)_6(\mu\text{-}H)][BF_4]\cdot 1.5CH_2Cl_2$ ($2H^+BF_4^-$). Compound **1** (50 mg, 0.064 mmol) was dissolved in 15 mL of CH_2Cl_2 and treated with $[Ph_3C][BF_4]$ (21 mg, 0.064 mmol). After being stirred for 1.5 h, the solution was evaporated under vacuum to dryness, and the residue was washed with 2 × 20 mL of Et_2O followed by 15 mL of hexanes. The red powder was formed in nearly quantitative yield (95%). X-ray quality crystals were obtained by adding compound **1** (50 mg, 0.064 mmol) and $[Ph_3C][BF_4]$ (21 mg, 0.064 mmol) to 15 mL of CH_2Cl_2 and immediately filtering through Celite, then cooling to −78 °C. Anal. Calcd for $H_{22}C_{21.5}O_6F_4Cl_3Si_2W_2B$: C, 25.97; H, 2.21. Found: C, 25.58; H, 2.16. IR (CH_2Cl_2): 2066 (s), 2044 (w), 1980 (s, br) cm^{-1}. ^1H NMR (300 MHz, CD_2Cl_2): δ 6.21 (d, J_{H-H} = 1.8 Hz, 4 H, Cp-*H*), 5.96 (t, J_{H-H} = 1.8 Hz, 2 H, Cp-*H*), 0.63 (s, 6 H, Si(C*H*$_3$)), 0.56 (s, 6 H, Si(C*H*$_3$)), −25.38 (s, J_{W-H} = 18 Hz, 1 H, W-*H*-W).

Synthesis of *cis*-$\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}W_2(CO)_6$ (2). Compound $\mathbf{2H^+BF_4^-}$ (50 mg, 0.058 mmol) was dissolved in 50 mL of CH_2Cl_2. Triethylamine was added in 20 μL increments until all of **2** was consumed, as determined by IR spectra of the solution. The solution was evaporated under vacuum to dryness; then the red product was dissolved in CH_2Cl_2 and chromatographed on a 2 × 20 cm column of alumina. The column was eluted with CH_2Cl_2. The red fraction containing **2** was collected, and the solvent was removed under vacuum, to give an 81% yield of **2**. The compound was characterized by its IR and ^1H NMR spectra, which were the same as those of the same compound prepared by the reaction of *cis*-$\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}W_2(CO)_6(Cl)_2$ with MeMgBr.[7] X-ray quality crystals

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were grown by layering a CH_2Cl_2 solution of **2** with hexanes at −20 °C. IR (CH_2Cl_2): 2010 (s), 1954 (vs), 1919 (s, br) cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 4.73 (d, $J_{H-H} = 2.3$, 4 H, Cp-*H*), 4.69 (t, $J_{H-H} = 2.3$, 2 H, Cp-*H*), 0.28 (s, 6 H, Si(CH_3)), 0.10 (s, 6 H, Si(CH_3)).

Synthesis of *cis*-$\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}W_2(CO)_6(H)(I)$ (3). Compound $\mathbf{2H^+BF_4^-}$ (50 mg, 0.057 mmol) in 50 mL of CH_2Cl_2 was treated with tetra(*n*-butyl)ammonium iodide (21 mg, 0.057 mmol), and the solution was stirred for 15 min. The solution was filtered, and the solvent was removed under vacuum. The residue was dissolved in a 3:1 mixture of hexanes/CH_2Cl_2 and chromatographed on silica gel. The same hexanes/CH_2Cl_2 solvent was used to elute an orange fraction. The solvent was removed under vacuum, yielding an orange solid in 78% yield. Anal. Calcd for $C_{20}H_{19}O_6Si_2W_2I$: C, 26.49, H, 2.10. Found: C, 26.77, H, 2.14. IR (CH_2Cl_2): 2034 (m), 2019 (m), 1954 (s, br), 1921 (s, br) cm^{-1}. ^1H NMR (300 MHz, CD_2Cl_2): δ 6.21 (t, $J_{H-H} = 2.3$ Hz, 1 H, Cp-*H*), 5.86 (t, $J_{H-H} = 2.8$ Hz, 1 H, Cp-*H*), 5.80 (d, $J_{H-H} = 2.3$ Hz, 2 H, Cp-*H*), 5.68 (d, $J_{H-H} = 2.8$ Hz, 2 H, Cp-*H*), 0.70 (s, 6 H, Si(CH_3)), 0.45 (s, 6 H, Si(CH_3)), −7.01 (s, $J_{W-H} = 18$ Hz, 1 H, W-*H*).

Synthesis of *cis*-$\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}W_2(CO)_6(I)_2$ (4). A flask containing **1**, $\mathbf{2H^+BF_4^-}$, **2**, or **3** (50 mg) was dissolved in 20 mL of CH_2Cl_2. After adding I_2 (20 mg, 0.078 mmol), the solution was stirred for 30 min. The solvent was removed under vacuum, and the resulting solid was dissolved in 2:1 hexanes/CH_2Cl_2. This solution was chromatographed on silica gel using the same hexanes/CH_2Cl_2 solution as eluent. The dark red fraction was removed to give a red solid in 60−72% yield. Anal. Calcd for $C_{20}H_{18}O_6Si_2W_2I_2$: C, 23.26; H, 1.74. Found: C, 23.13; H, 1.70. IR (CH_2Cl_2): 2034 (s), 1948 (vs) cm^{-1}. ^1H NMR (300 MHz, CD_2Cl_2): δ 6.15 (t, 2 H, $J_{H-H} = 2.7$ Hz, Cp-*H*), 5.74 (d, $J_{H-H} = 2.7$ Hz, 4 H, Cp-*H*), 0.90 (s, 6 H, Si(CH_3)), 0.51 (s, 6 H, Si(CH_3)).

pK_a Determination for $[\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}W_2(CO)_6(\mu\text{-}H)][BF_4]\cdot 1.5CH_2Cl_2$ ($2H^+BF_4^-$). We applied the method of Morris[10] to the determination of the pK_a of $\mathbf{2H^+BF_4^-}$ by measuring K_1 for the reaction (eq 1)

$$\mathbf{2} + \text{DMSOH}^+ \underset{}{\overset{K_1}{\rightleftharpoons}} \mathbf{2H^+} + \text{DMSO} \tag{1}$$

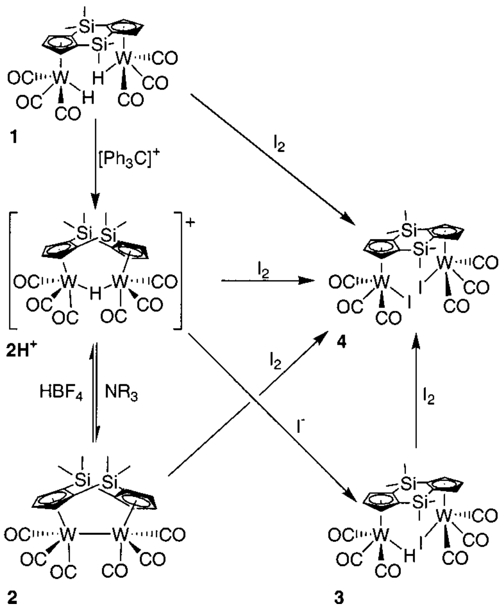
$$pK_a^{\,\mathbf{2H+}} = pK_a^{\,\text{DMSOH+}} - pK_1 \tag{2}$$

of reference acid ($DMSOH^+$) with **2** to give $\mathbf{2H^+}$ and DMSO. This was done by adding equimolar amounts of $\mathbf{2H^+BF_4^-}$ (25 mg, 0.032 mmol) and DMSO (dimethyl sulfoxide) (2.3 μL, 0.032 mmol) to 10 mL of CD_2Cl_2 that was rigorously dried over CaH_2 and freshly distilled. The K_1 value was calculated from the ratio of integrations of the ^1H NMR resonances for $\mathbf{2/2H^+}$ (0.51 and 0.63 ppm, respectively). Then the $pK_a^{\mathbf{2H+}}$ of $\mathbf{2H^+}$ was calculated using eq 2, where the $pK_a^{\text{DMSOH+}}$ of $DMSOH^+$ in H_2O is −1.8.[11] This gave a $pK_a^{\mathbf{2H+}}$ value for $\mathbf{2H^+}$ of −1.6 (± 0.3).

Results and Discussion

Syntheses and Structures of $[\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}W_2(CO)_6(\mu\text{-}H)][BF_4]$ ($2H^+BF_4^-$) and $[\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}W_2(CO)_6$ (2). The syntheses of *cis*-$\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}W_2(CO)_6(H)_2$ (**1**) and $\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}W_2(CO)_6$ (**2**) were first reported by Royo and co-workers.[7] By replacing $W(CO)_3(NCMe)_3$ used by these authors, with the more easily prepared $W(CO)_3(NCEt)_3$,[8] product **1** was obtained in minutes rather than hours and without heating. This synthesis gives the desired cis-isomer in 83% yield, versus 66% previously reported.

Scheme 3. Summary of Reactions of $2H^+$



The reported synthesis[7] of **2** involves treatment of dihydride **1** with CCl_4 to give *cis*-$\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}W_2(CO)_6(Cl)_2$, which is reduced to **2** by addition of MeMgBr in THF at −78 °C. We were unable to achieve the reported yield (56%) but have found that a hydride ligand can be removed from **1** by reaction (Scheme 3) with $[Ph_3C][BF_4]$ to give $\mathbf{2H^+}$ in 95% yield. Deprotonation of $\mathbf{2H^+}$ with triethylamine gives **2** in 81% yield. Complex $\mathbf{2H^+}$ is air sensitive because it is deprotonated by water. While **1** and **2** are very soluble in CH_2Cl_2, $\mathbf{2H^+}$ is much less soluble (1 mg per mL). In other polar solvents such as THF, MeOH, and EtOH, $\mathbf{2H^+}$ is even less soluble than in CH_2Cl_2.

The major structural differences between $\mathbf{2H^+}$ (Figure 1) and **2** (Figure 2) are (a) the longer W−W distance in $\mathbf{2H^+}$ (3.657(6) Å) than in **2** (3.260(5) Å), (b) the larger ∠Cp−Cp fold angle (defined as the angle between the two Cp planes) in $\mathbf{2H^+}$ (149.7°) than in **2** (135.67°), as expected for the longer W−W distance in $\mathbf{2H^+}$, and (c) the staggered CO groups (∠C(1)−W(1)−W(2)−C(4), 36.4(4)°) in **2**, but nearly eclipsed CO groups in $\mathbf{2H^+}$ (∠C(8)−W(1)−W(2)−C(9), 1.9(4)°). The average W−CO bond distances in the unprotonated complex **2** (1.95 Å) are slightly shorter than those in $\mathbf{2H^+}$ (2.00 Å), due to enhanced π-back-bonding in the neutral complex.

The structure of unprotonated $\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}W_2(CO)_6$ (**2**) exhibits a Cp(centroid 1)−W(1)−W(2)−Cp(centroid 2) dihedral angle of 28.7°. The 28.7° twist in **2** is much smaller than that measured for the singly bridged complexes $\{(C_5H_4)_2CH_2\}\{W(CO)_3\}_2$[12a] and $\{(C_5H_4)_2SiMe_2\}\{W(CO)_3\}_2$,[12b] both having Cp(centroid 1)−W(1)−W(2)−Cp(centroid 2) angles close to 47.8(6)°. The W−W distances are 3.166(1) and 3.196(1) Å for the CH_2 and $SiMe_2$ complexes, respectively, both shorter than that (3.260(5) Å) in **2** (Figure 2). In these bridged complexes, a relationship appears to exist between the degree of twist in a molecule and its W−W distance (Table 2). The flexibility of the $(C_5H_4)_2CH_2$ ligand in $\{(C_5H_4)_2CH_2\}\{W(CO)_3\}_2$ allows the CO groups to reduce

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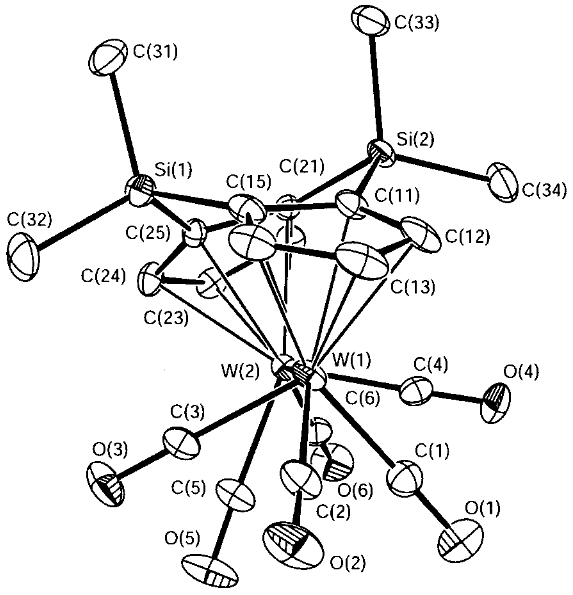

Figure 1. Thermal ellipsoid drawing at the 30% probability level of $\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}W_2(CO)_6$ (**2**) showing the labeling scheme. Selected bond distances (Å) and angles (deg) are as follows: W(1)−W(2), 3.260(5); W(1)−C(1), 1.972(7); W(1)−C(2), 1.954(7); W(1)−C(3), 1.954(7); W(2)−C(4), 1.949(7); W(2)−C(5), 1.999(7); W(2)−C(6), 1.960(7); W(1)−Cp(centroid), 2.012(7); W(2)−Cp(centroid), 2.015(7); ∠C(1)−W(1)−C(3), 100.6(3); ∠C(4)−W(2)−C(5), 99.1(3); ∠W(1)−W(2)−C(4), 77.62(6); ∠C(3)−W(1)−W(2)−C(5), 38.8(8); ∠C(1)−W(1)−W(2)−C(4), 36.4(4); ∠Cp(centroid)−W(1)−W(2)−Cp(centroid) 28.7(4); ∠Cp−Cp fold angle, 135.6(7).

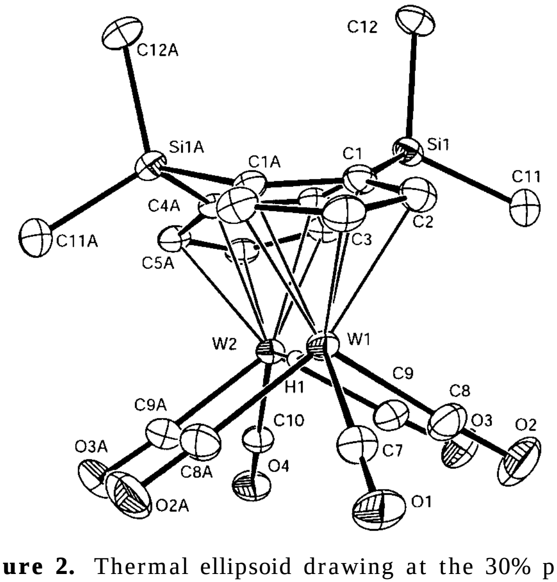

Figure 2. Thermal ellipsoid drawing at the 30% probability level of $[\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}W_2(CO)_6(\mu\text{-}H)]^+$ ($\mathbf{2H}^+$) showing the labeling scheme. Selected bond distances (Å) and angles (deg) are as follows: W(1)−W(2), 3.657(6); W(1)−C(7), 2.000(10); W(1)−C(8), 2.010(7); W(2)−C(9), 2.007(7); W(2)−C(10), 2.028(9); W(1)−Cp(centroid), 1.996(7); W(2)−Cp(centroid), 1.992(8); ∠C(8)−W(1)−C(8A), 110.1(4); ∠C(9)−W(2)−C(9A), 113.7(4); ∠C(9)−W(2)−W(1), 83.1(3); ∠C(8)−W(1)−W(2), 83.3(4); ∠C(8)−W(1)−W(2)−C(9), 1.9(4); ∠Cp−Cp fold angle, 149.7(2).

Table 2. Twist Angle and W−W Bond Distance in $[Cp'W(CO)_3]_2$ Compounds

compound	twist angle (deg)[a]	bond length (Å)
$[CH_2\{CpW(CO)_3\}_2]$[b]	47.8(6)	3.166(1)
$[CH_2\{(Cp)(C_5H_3COCH_3)W_2(CO)_3\}_2]$[b]	47.1(4)	3.175(1)
$[SiMe_2\{CpW(CO)_3\}_2]$[c]	~47[e]	3.196(1)
[**2**]	28.7(4)	3.260(5)
$[FvW_2(CO)_6]$[d]	5.0(2)	3.347(7)

[a] Twist angle is defined as ∠Cp(centroid 1)−W(1)−W(2)-Cp-(centroid 2). [b] Reference 12a. [c] Reference 12b. [d] Reference 13. [e] Approximate value.

steric repulsions which force the W atoms away from each other; this contrasts with the inflexibility of the bridging ligand in **2** which forces the CO groups on the different W atoms to repel each other and thereby increases the length of the W−W bond. Another illustration of this point is the small twist angle (5.0(2)°) in $FvW_2(CO)_6$ (Fv = fulvalene), which forces the W−W distance to be one of the longest reported W−W single bonds (3.347 Å); the inflexibility of the Fv backbone may also contribute to the long W−W bond.[13] It is interesting that $\{(C_5H_4)_2CH_2\}\{W(CO)_3\}_2$ has a slightly shorter W−W distance than $Cp_2W_2(CO)_6$ (3.222(1) Å),[14] as noted previously.[12a]

Although the bridging hydride was not located in the structure of $\mathbf{2H}^+$, it is undoubtedly located on the crystallographically defined mirror plane that includes the two tungsten atoms and the Cp centroids. If the hydride were off of the mirror plane, the CO positions on opposite sides of this plane would be different, as observed in $\mathbf{AH}^+$, whose structure was established by both neutron and X-ray studies.[4] As in $\mathbf{AH}^+$, the CO groups on the different tungsten atoms in $\mathbf{2H}^+$ are also essentially eclipsed (C(8)−W(1)−W(2)−C(9) = 1.9(4)°). The related structure and reactions of the $Cp_2Mo_2(CO)_4(dppm)(\mu\text{-}H)^+$ have been previously reported.[15]

Acidity of $[\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}W_2(CO)_6(\mu\text{-}H)][BF_4]$ ($\mathbf{2H}^+$). The protonated complex $\mathbf{2H}^+$ has a pK_a of −1.6 (± 0.3) on the water scale but measured in CD_2Cl_2 solvent. This pK_a value makes it the least acidic of related complexes whose acidities increase in the order: $\mathbf{2H}^+$ [pK_a= −1.6(3)] < $(Fv)W_2(CO)_6H^+$ [pK_a = −2.05 to −3.8] < $Cp_2W_2(CO)_6H^+$ [pK_a< −3.8].[1b] The pK_a values for $(Fv)W_2(CO)_6H^+$ and $Cp_2W_2(CO)_6H^+$ are ranges based on the observations that $(Fv)W_2(CO)_6$ is protonated by Et_2OH^+ (pK_a = −3.8) but not $THFH^+$ (pK_a = −2.05), and $Cp_2W_2(CO)_6$ is not protonated by either. If the acidities of these compounds were controlled by the W−W bond length in the unprotonated form, one would expect the acidities of the protonated complexes to increase in the following order: $(Fv)W_2(CO)_6$ (3.347(7) Å) < **2** (3.260(5) Å) < $Cp_2W_2(CO)_6$ (3.222(1) Å). That this is not the case means that other factors are involved.

Reactions of Nucleophiles with $[\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}W_2(CO)_6(\mu\text{-}H)][BF_4]$ ($\mathbf{2H}^+$). One of the goals of this project was to determine whether amines would react at the CO ligands in $\mathbf{2H}^+$, as occurs with $\mathbf{AH}^+$ (Scheme 1). When $\mathbf{2H}^+\mathbf{BF_4}^-$ in CH_2Cl_2 or THF was treated with amines (methylamine, ethylamine, pyrrolidine, and pyridine), an immediate reaction occurred that gave complete conversion of $\mathbf{2H}^+$ to **2** (Scheme 3). Thus, the $(C_5H_3(SiMe_2))_2$ ligand is ineffective in making $\mathbf{2H}^+$ reactive in a way that leads to nucleophilic attack

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at a CO ligand rather than deprotonation. The reason for preferential deprotonation in **2H**$^+$ but not in **AH**$^+$ may be related to the fact that the W−H−W distance is longer than the Ru−H−Ru distance, which makes the bridging hydride in **2H**$^+$ more accessible to deprotonation by nucleophiles. Another reason for the rapid deprotonation of **2H**$^+$may be the more exposed location of the bridging hydride on the plane of symmetry, which is not shielded by the CO ligands as it is in **AH**$^+$.[4] In addition, the higher kinetic acidity of **2H**$^+$ may be related to its higher thermodynamic acidity (p$K_a^{\mathbf{2H}^+} = -1.6$) compared to that (p$K_a^{\mathbf{AH}^+} = 1.0$) for **AH**$^+$; similar trends in kinetic and thermodynamic acidities have been previously reported.[16]

Other nucleophiles react (Scheme 3) with **2H**$^+$ to form compounds containing a terminal W−hydride and a new W−ligand bond. However competing with this reaction is simple deprotonation of the bridging ligand to give **2**. In each of these reactions, equimolar amounts of the desired nucleophile and **2H**$^+$**BF$_4$**$^-$ were added to CH_2Cl_2. The I$^-$ ion cleaves the W−H−W unit in **2H**$^+$ to yield the iodide−hydride complex **3** (78% isolated yield) along with minor amounts of deprotonated product **2**. Compound **3** is unstable with respect to **2** and presumably HI; at room temperature in CD_2Cl_2, **3** gives **2** as the only metal complex product with an approximate half-life of 10 h. The IR spectrum of **3** in CH_2Cl_2 solution shows the expected four ν_{CO} absorptions corresponding to the (η^5-C_5H_3)W(CO)$_3$H (2019 (m), 1921 (s, br) cm^{-1}) and (η^5-C_5H_3)W(CO)$_3$I (2034 (m), 1954 (s, br) cm^{-1}) portions of the molecule; these assignments are based on a comparison with ν_{CO} bands for (η^5-C_5H_3)$_2$(SiMe$_2$)$_2$}-W$_2$(CO)$_6$(H)$_2$ (**1**) (2019 (s), 1924 (vs) cm^{-1}) and (η^5-C_5H_3)$_2$-(SiMe$_2$)$_2$}W$_2$(CO)$_6$(I)$_2$ (**4**) (2034 (s), 1948 (vs) cm^{-1}). A related cleavage reaction is that of (Fv)W$_2$(CO)$_6$(μ-H)$^+$ with MeCN to give (Fv)W$_2$(CO)$_6$(H)(NCMe)$^+$.[1b] Reaction of Br$^-$ with **2H**$^+$ gives a small amount of the analogous bromide−hydride complex, as indicated by the ^{1}H NMR spectrum, but the major product from this reaction is **2**. Salts of Cl$^-$ and F$^-$ attack the Si−C bonds in the SiMe$_2$ bridging groups of the ligand, which leads to the decomposition of **2H**$^+$.

A variety of other nucleophiles either did not react or gave products that could not be characterized or purified. Reactants that gave unpurifiable products include NaSEt, [Na][V(CO)$_6$], [(*n*-Bu)$_4$N][CN], tolylisocyanide, trimethylphosphine, and triphenylphosphine. The following reactants primarily deprotonated **2H**$^+$: trimethylamine *N*-oxide, [Na][Mn(CO)$_5$], [Na][Re(CO)$_5$], [Na][Co(CO)$_4$], ethylamine, triethylamine, pyridine, and water. Reactants that decomposed **2H**$^+$ include [Na]-[OEt], [(*n*-Bu)$_4$N][Cl], and [(*n*-Bu)$_4$N][F]. Finally reactants that did not react with **2H**$^+$ are CS$_2$, thiophenol, *p*-tolyl disulfide, benzylethyl sulfide, Mn$_2$(CO)$_{10}$, *N*-bromosuccinimide, phenylacetylene, diphenylacetylene, dimethyl acetylenedicarboxylate, and styrene.

Treatment of **1**, **2H**$^+$, **2**, and **3** with I$_2$ leads to the diiodide complex *cis*-{(η^5-C_5H_3)$_2$(SiMe$_2$)$_2$}W$_2$(CO)$_6$(I)$_2$ (**4**) within minutes. The reactions of **1** and **3** with I$_2$ to give **4** are similar to the analogous reaction of I$_2$ with CpW-(CO)$_3$H.[17] The reaction of **2** with I$_2$ to give **4** is analogous to the reaction of I$_2$ with Cp$_2$W$_2$(CO)$_6$.[18] To our knowledge, there are no other I$_2$ reactions of protonated M−M bonds as occurs in the reaction of **2H**$^+$ with I$_2$ to give **4**.

Conclusions

Although the (η^5-C_5H_3)$_2$(SiMe$_2$)$_2$ ligand is essential to the observed attack of amine on a CO ligand in {(η^5-C_5H_3)$_2$(SiMe$_2$)$_2$}Ru$_2$(CO)$_4$(H)$^+$ (**AH**$^+$) (Scheme 1), the same ligand in {(η^5-C_5H_3)$_2$(SiMe$_2$)$_2$}W$_2$(CO)$_6$(H)$^+$ (**2H**$^+$) does not produce the same effect because primary, secondary, and tertiary amines simply deprotonate **2H**$^+$. However, **2H**$^+$ does react with I$^-$ (Scheme 3) to give *cis*-{(η^5-C_5H_3)$_2$(SiMe$_2$)$_2$}W$_2$(CO)$_6$(H)(I), analogous to the reaction of **AH**$^+$ with I$^-$ (Scheme 2).[5] Other similarities between the diruthenium and ditungsten systems are the structures of the unprotonated **2** and **A**, which both have staggered CO groups across the metal−metal bonds; on the other hand, these CO groups in the protonated **2H**$^+$ and **AH**$^+$ complexes are eclipsed.

Acknowledgment. We thank Maren Pink, Victor G. Young, Jr., and the X-ray crystallographic laboratory of the University of Minnesota. This work was supported by the National Science Foundation through Grant No. CHE-9816342.

Supporting Information Available: Tables giving crystallographic data for **2** and **2H**$^+$ including atomic coordinates, bond lengths and angles, and anisotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010861W

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