Communications

α-CH Bond Activation of Coordinated Et_2O via Reaction of PR_3 (R = Ph, Cy) with the Cationic Complex $[C_5Me_5W(CO)_3(OEt_2)]^+$

Chae S. Yi* and Dariusz Wódka

Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53201-1881

Arnold L. Rheingold and Glenn P. A. Yap

Department of Chemistry, The University of Delaware, Newark, Delaware 19716

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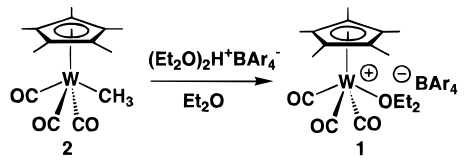
*Summary: Reaction of $C_5Me_5W(CO)_3CH_3$ (**2**) with $[Et_2O)_2H]^+BAr_4^-$ (Ar = 3,5-bis(trifluoromethyl)phenyl) produced the new cationic complex $[C_5Me_5W(CO)_3(OEt_2)]^+BAr_4^-$ (**1**) in 82% isolated yield. The complex **1** readily undergoes ligand substitution reactions with neutral donor ligands to give the complexes $[C_5Me_5W(CO)_3(L)]^+BAr_4^-$ (L = CH_3CN (**3**), MeOH (**4**), H_2O (**5**)). In contrast, reaction of **1** with tertiary phosphines PR_3 (R = Ph, Cy) produced $C_5Me_5W(CO)_3H$ (**6**) and the new phosphonium salts $EtOCH(Me)PR_3^+BAr_4^-$ (R = Ph (**7**), Cy (**8**)), where the α-CH of Et_2O has been selectively displaced by phosphines.*

Direct stereoselective C−H bond activation of organic ethers using transition-metal complexes is a potentially useful method in organic synthesis.[1] Although selective oxidation of α-CH bonds of cyclic ethers has been achieved using transition-metal-based oxidants such as Cr_2O_3 and RuO_4,[2] the selective C−H bond activation of the simple acyclic organic ethers remains as a difficult problem. Normally an extremely reactive alkali-metal species such as *n*-BuLi or KC_4H_9 is required to deprotonate Et_2O.[3] The relative ease of breaking the C−O bond compared to the C−H bond also limits the practical use of the C−H bond activation of acyclic ethers in organic synthesis. Herein we report a selective α-CH bond activation of coordinated Et_2O from the reaction of tertiary phosphines with the coordinated Et_2O complex $[C_5Me_5W(CO)_3(OEt_2)]^+BAr_4^-$ (**1**).

Acid-induced elimination of alkanes has been an effective method in preparing coordinatively unsaturated cationic organometallic complexes.[4] Following Beck's procedure,[5] we recently found that the protonation of $C_5Me_5W(CO)_3CH_3$ (**2**)[6] by strong acids HX (X = Cl, I, CO_2CF_3) produced the complexes $C_5Me_5W(CO)_3X$ and the liberation of methane.[7] One possible mechanism for this reaction involves protonation at the tungsten center to form the cationic intermediate $[C_5Me_5W(CO)_3(H)CH_3]^+$, followed by the reductive elimination of methane, and the subsequent coordination of X^- to form the complexes $C_5Me_5W(CO)_3X$.



In an attempt to directly observe the possible protonated intermediate, an acid with a noncoordinating anion, $[(Et_2O)_2H]^+BAr_4^-$ (Ar = 3,5-bis(trifluoromethyl)-phenyl),[8] was employed. An Et_2O (35 mL) solution of **2** (0.723 g, 1.72 mmol) was added dropwise to an Et_2O (25 mL) solution of $[(Et_2O)_2H]^+BAr_4^-$ (1.746 g, 1.72 mmol) at 0 °C. The initially yellow solution turned dark red, and a red crystalline solid precipitated after 15 min of additional stirring at 0 °C. The resulting precipitate was filtered and recrystallized from ether/hexanes to afford **1** as an analytically pure red crystalline solid (82% yield). The complex **1** was completely characterized by spectroscopic and analytical methods.[9] A set of downfield-shifted Et_2O peaks at δ 3.97 (q, J = 7.2 Hz, OCH_2) and 1.19 (t, J = 7.2 Hz, OCH_2CH_3) in ^{1}H NMR is consistent with a symmetric environment of the

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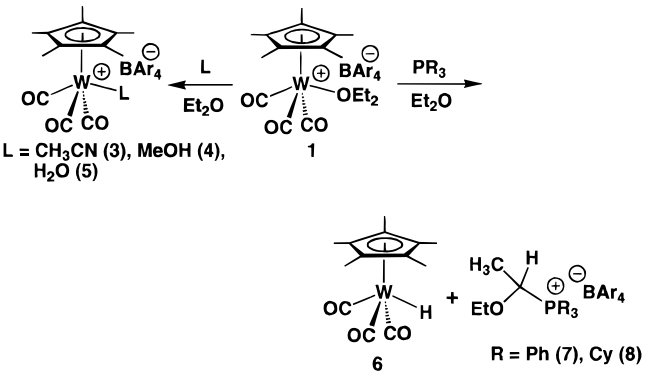
coordinated ether group. The complex **1** is remarkably stable at room temperature under a nitrogen atmosphere and can be handled briefly in air without significant decomposition. Previously, syntheses of the cycloepntadienyl analogue $[C_5H_5(CO)_3W(OEt_2)]^+X^-$ (X = PF_6, AsF_6) and related complexes $[C_5H_5(CO)_3M]^+X^-$ (M = Mo, W; X = OSO_2CF_3, OSO_2F, FBF_3) have been documented.[4a,5]

The structure of complex **1** was confirmed by X-ray crystallography. The red prismatic single crystals of **1**, grown from layering hexanes on an Et_2O solution, were suitable for the X-ray crystal structure determination (Figure 1).[10] The molecular structure of **1** showed a typical four-legged piano-stool arrangement. The bond distance between W and O(1) of 2.197(7) Å is similar to that in the previously reported cationic $[CpW(CO)_3(Pr^iOH)]^+$ complex (W−O distance 2.186(9) Å),[11] and no unusual structural features on the coordinated Et_2O was observed.

As expected, the coordinated Et_2O of **1** was readily displaced by neutral donor ligands. For example, treatment of **1** with CH_3CN, MeOH, and H_2O in Et_2O at room temperature led to the formation of the stable adducts $[C_5Me_5(CO)_3W(L)]^+BAr_4^-$ (L = CH_3CN (**3**), MeOH (**4**), H_2O (**5**)) in good to excellent yields.[12] In light of these



results, we were surprised to find that complex **1** displayed a completely different reactivity pattern with tertiary phosphines. Reaction of **1** with tertiary phosphines PR_3 (R = Ph, Cy) in Et_2O at room temperature cleanly produced a mixture of the previously known $C_5Me_5(CO)_3WH$ (**6**)[13] and the new phosphonium salts $EtOCH(Me)PR_3^+BAr_4^-$ (R = Ph (**7**), Cy (**8**)) in good to excellent yields. The complexes **6**−**8** were separated and completely characterized by spectroscopic methods.[12] Diagnostic spectroscopic features for the phosphonium salts, the diastereotopic OCH_2 groups (δ 3.87 (dq, J = 9.0, 7.0 Hz, OC*H*HCH$_3$), 3.49 (dq, J = 9.0, 7.0 Hz, OCH*H*CH$_3$) for **7**) due to the asymmetric center on the compound and the strong couplings between OCH-CH_3 hydrogens and the phosphorus atom (δ 5.01 (dq, J_{HH} = 6.8 Hz, J_{PH} = 4.9 Hz, OC*H*(Me)PPh_3) and 1.69 (dd, J_{PH} = 17.8, J_{HH} = 6.8 Hz, OCH(*Me*)PPh_3) for **7**), were seen by ^{1}H NMR.[14]

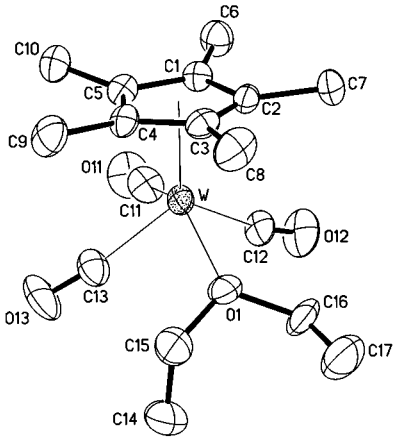


Figure 1. Crystallographic structure of the cation of $[C_5Me_5W(CO)_3(OEt_2)]^+BAr_4^-$ (**1**), drawn with 40% thermal ellipsoids. Selected bond lengths (Å) and bond angles (deg): W−cent, 1.988(8); W−O(1), 2.197(7); W−C(11), 1.978(11); W−C(12), 2.006(11); W−C(13), 2.043(11); O(1)−W−cent, 108.0(2); C(11)−W−cent, 108.5(3); C(12)−W−cent, 122.4(3); C(13)−W−cent, 124.5(3).

Instead of displacing the coordinated Et_2O, tertiary phosphines apparently prefer to react at the α-carbon of Et_2O and transfer the α-hydrogen to the tungsten center. Usually, the ligand substitution is the dominant pathway for complexes with labile ligands such as Et_2O, CH_3CN, and THF.[15] The complex **1** also preferentially undergoes ligand substitution reactions with sterically undemanding and weakly nucleophilic neutral ligands (CH_3CN, MeOH, and H_2O). When nucleophilic and sterically demanding tertiary phosphines are employed, however, an alternate pathway involving the α-CH bond activation of the Et_2O molecule was favored. The electron-withdrawing effect of the cationic tungsten center through the oxygen atom may also have facilitated the C−H bond activation. While transition-metal-mediated C−H and C−O bond activation of cyclic ethers, most notably THF, and α-CH bond activation of Et_2O

(9) Spectroscopic and analytical data for **1**: ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 7.7−7.5 (m, Ar), 3.97 (q, J = 7.2 Hz, CH_2), 2.14 (s, C_5Me_5), 1.19 (t, J = 7.2 Hz, CH_2CH_3); ^{13}C NMR (CD_2Cl_2, 75 MHz) δ 229.1 (s, J_{CW} = 80.7 Hz, 2CO's), 225.4 (s, J_{CW} = 60.1 Hz, CO), 162.3 (1:1:1:1 quartet, J_{CB} = 49.2 Hz, C_{ipso}), 135.3 (s, C_{ortho}), 129.4 (q, J_{CF} = 31.5 Hz, C_{meta}), 125.1 (q, J_{CF} = 271.8 Hz, CF_3), 118.0 (s, C_{para}), 110.0 (s, C_5Me_5), 81.9 (s, CH_2), 14.2 (s, CH_2CH_3), 11.0 (s, C_5Me_5); IR (CH_2Cl_2) ν_{CO} 2045 (s), 1968 (m), 1945 (s) cm^{-1}; FAB MS *m/e* 477 (M^+), 449 (M^+ − CO), 403 (M^+ − Et_2O). Anal. Calcd for $C_{49}H_{37}BF_{24}O_4W$: C, 43.90; H, 2.79. Found C, 43.87; H, 2.80. mp 122−124 °C.

(10) Crystallographic data for $[C_5Me_5W(CO)_3(OEt_2)]\{B[C_6H_3(CF_3)_2]_4\}$ (**1**): $C_{49}H_{37}BF_{24}O_4W$, fw 1340.4, triclinic, $P\bar{1}$, a = 13.169(7) Å, b = 13.282(5) Å, c = 15.814(8) Å, α = 72.63(4)°, β = 88.02(4)°, γ = 83.66(4)°, V = 2624(2) Å^3, Z = 2, T = 241 K. Of 9112 data collected (maximum 2θ = 49°, Mo Kα), 8759 were unique. At convergence, $R(F)$ = 5.42% and $R(wF)$ = 6.34%. Several CF_3 groups were rotationally disordered and modeled with occupancy refinement.

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(14) The J_{PH} and J_{HH} values of the phosphonium salts were unambiguously assigned from the ^{1}H{^{31}P} NMR analysis.

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in the presence of peroxides have been documented,[16] to the best of our knowledge, our finding constitutes the first example of the direct α-CH bond activation of coordinated Et_2O without any additional promoters.

We are currently investigating a detailed mechanism of the reaction. In an attempt to extend the substitution at the coordinated Et_2O, complex **1** was reacted with anionic nucleophiles. Reaction of **1** with the carbon nucleophile $KCH(CO_2Me)_2$ led to the exclusive formation of the dimeric tungsten species $[C_5Me_5W(CO)_3]_2$ (**9**)[17] and the protonated $CH_2(CO_2Me)_2$, while the reaction with $LiBEt_3D$ (99% D, 1.0 M in THF) gave predominantly the tungsten hydride **6** with <10% of deuterium on the hydride as determined by NMR.[18] The formation of dimeric **9** may have resulted from the deprotonation reaction of the initially generated tungsten hydride complex **6** to produce anionic $C_5Me_5W(CO)_3^-$, followed by its coupling reaction with the unreacted cationic **1**. The formation of hydride complex **6** (and not deuteride complex) from the reaction with $LiBEt_3D$ is also consistent with the migration of the α-hydrogen to the tungsten center. A similar reaction of **1** with the organic base Et_3N resulted in the formation of the dimer **9** and $Et_3NH^+BAr_4^-$.

In summary, selective substitution on the α-carbon of the coordinated Et_2O from the reaction with tertiary phosphines has been described. We have demonstrated that the selective α-CH bond activation of normally unreactive acyclic Et_2O can be achieved using the electrophilic organometallic complex **1**. Our method is potentially useful in the selective activation of other acyclic ethers. Studies directed on the scope and the mechanism of the reaction are currently underway.

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Supporting Information Available: Text giving spectroscopic data for complexes **3**−**5**, **7**, and **8** and tables giving the structure determination summary, positional and thermal parameters, bond distances, and bond angles for **1** (14 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet. See current masthead page for ordering information and Internet access instructions.

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(18) We also observed the formation of a small amount (∼5%) of the dimer **9** in the reaction mixture.