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Synthesis and Reactivity of Tungsten Pentacarbonyl Hydroxo and Bicarbonato Complexes. Molecular Structure of [PPN][$W(CO)_5HCO_3$], an Organometallic Analog for Carbonic Anhydrase

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Carbonic anhydrase catalyzes the hydration of carbon dioxide to bicarbonate, and structural studies have shown the active site to consist of a zinc ion coordinated to three histidine residues and either a water molecule[1] or a hydroxide anion, depending on pH.[2] Experimental[3] and theoretical[4] investigations of the enzyme's activity have led to the proposal that the key intermediate is a monodentate zinc bicarbonate complex, and other researchers have prepared monodentate zinc bicarbonate complexes which are models for carbonic anhydrase.[5] We have for some time been interested in studying the reactivity of metal alkoxide complexes with carbon dioxide in an effort to understand the fundamental organometallic chemistry of carbon dioxide.[6] Furthermore, this process is pivotal in the catalytic copolymerization of carbon dioxide and epoxides to afford polycarbonates.[7] In order to extend these investigations to an organometallic analog of the carbonic anhydrase reaction (eq 1), an examination of tungsten pentacarbonyl hydroxo and bicarbonato complexes has been initiated. Herein are presented the synthesis and characterization of [Et_4N][$W(CO)_5OH$] and [PPN][$W(CO)_5HCO_3$], their reactivity with carbon dioxide, and the molecular structure of the bicarbonato complex.

$$[W(CO)_5OH]^- + CO_2 \rightleftharpoons [W(CO)_5O_2COH]^- \qquad (1)$$

In solution, $[W(CO)_5OR]^-$ (R = H, alkyl, aryl) complexes are extremely unstable to decarbonylation, forming $[W(CO)_3(\mu_3\text{-}OR)]_4^{4-}$ aggregates.[8,9] Hydrogen-bonding solvents have been shown to retard the CO dissociation process considerably;[6c] hence, [Et_4N][$W(CO)_5OH$] was prepared in methanol from photogenerated $W(CO)_5(MeOH)$ and Et_4NOH[10] and characterized by IR and NMR spectroscopies.[11,12] Due to its high solubility in methanol and susceptibility to form clusters upon solvent removal under vacuum, this complex was not isolated. The preparation of [dibenzo-18-crown-6-K][$W(CO)_5OH$] has previously been published,[13] but the infrared spectrum provided is significantly different from that observed for the complex reported upon herein as well as for the closely related alkoxide derivatives[6] such as to raise doubt about its authenticity.

The addition of CO_2, COS, or CS_2 to methanol solutions of [Et_4N][$W(CO)_5OH$] results in an instantaneous reaction as indicated by an increase in the υ(CO) modes of the $-W(CO)_5$ moiety.[14] This is consistent with insertion of the three cumulenes into the W–OH bond. The insertion reaction occurs with equal facility in a carbon monoxide atmosphere with *no* formation of $W(CO)_6$, hence ruling out hydroxide ion dissociation prior to its reaction with CO_2. The asymmetric and symmetric $\upsilon(^{12}CO_2)$ frequencies for the CO_2 insertion product were observed in methanol at 1647 and 1312 cm^{-1}, respectively, and were *unambiguously* confirmed by $^{13}CO_2$ substitution, which provided corresponding $\upsilon(^{13}CO_2)$ vibrations at 1602 and 1285 cm^{-1}. The difference between the asymmetric and symmetric $\upsilon(^{12}CO_2)$ ($\Delta = 335$ cm^{-1}) supports a unidentate mode of coordination for the bicarbonate to the tungsten center. The CO_2 insertion product was characterized further by ^{13}C NMR spectroscopy. That is, using ^{13}CO-enriched [Et_4N][$W(CO)_5OH$] and $^{13}CO_2$, a ^{13}C NMR spectrum with carbonyl resonances at 198 ppm (*cis*) and 203 ppm (*trans*) along with a singlet at 159 ppm assigned to the bound bicarbonate ligand was observed. This latter signal splits into a doublet with a carbon–hydrogen coupling constant of 15 Hz when the proton decoupler is turned off.[15] In the case of CO_2, the insertion is reversible, with the removal of the CO_2 atmosphere rapidly leading to decarboxylation. For COS and CS_2, the insertion is irreversible due to the stronger W–S bond formation.

In order to facilitate isolation of the bicarbonato complex, [PPN][$W(CO)_5HCO_3$] was prepared from $W(CO)_5$(acetone)

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(10) The complex was prepared by photolyzing 0.20 g of $W(CO)_6$ (0.57 mmol) and 80 mL of dry methanol for 2 h (IR of $W(CO)_5MeOH$ in methanol: 2069 (w), 1927 (s), and 1888 (m) cm^{-1}). This solution was then added to 0.48 g (0.81 mmol) of 25% Et_4NOH in methanol at 0°C. The solution was immediately placed under an atmosphere of CO to prevent aggregation.

(11) Infrared in υ(CO) region in methanol: 2061 (w), 1917 (s), and 1864 (m). ^{13}C NMR in methanol: 200 ppm (4 CO's), 204 ppm (1 CO). The complex was identified by enriching it in ^{13}CO by stirring a solution of [Et_4N][$W(CO)_5OH$] in methanol in the presence of an atmosphere of ^{13}CO for 2.5 h at ambient temperature.

(12) Although the υ(CO) and ^{13}C NMR spectra of the $[W(CO)_5OMe]^-$ anion are expected to be quite similar to those of the $[W(CO)_5OH]^-$ species, the complex we report herein is clearly the latter derivative on the basis of its *quantitative* reaction with CO_2 to afford the bicarbonate complex. Nevertheless, it is anticipated that upon *prolonged* dissolution of $[W(CO)_5OH]^-$ in methanol the methoxide derivative is likely formed: Bates, A.; Muraoka, M. T.; Trautman, R. J. *Inorg. Chem.* **1993**, *32*, 2651.

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(14) Infrared in the υ(CO) region in methanol: CO_2, 2067 (w), 1927 (s), 1866 (m) cm^{-1}; COS, 2064 (w), 1924 (s), 1873 (m) cm^{-1}; CS_2, 2063 (w), 1926 (s), 1880 (m) cm^{-1}.

(15) The ^1H NMR spectra show resonances for the O*H* group of the $HOCO_2^-$ and $HOCS_2^-$ ligands at 11.9 ppm. The ^{13}C resonance for the carbonate carbon in $W(CO)_4CO_3^{2-}$ was observed at 161 ppm in acetonitrile.[6a]

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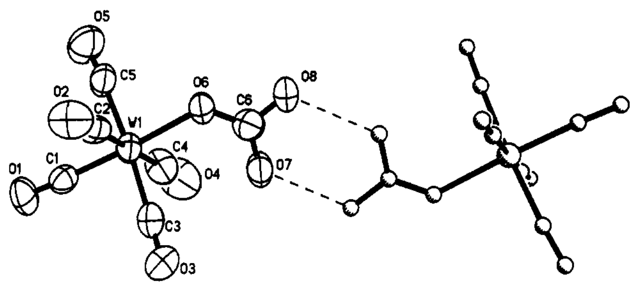

Figure 1. Drawing of the two $[W(CO)_5HCO_3]^-$ anions in each unit cell showing the hydrogen bonding between them.

and PPN(HCO_3) and characterized by IR and ^{13}C NMR spectroscopies.[16] An infrared spectrum of the complex in methanol confirmed it to be the same as the complex resulting from the insertion of carbon dioxide into the hydroxo complex. This complex decarboxylates readily in the absence of carbon dioxide, and consequently undergoes a very facile CO_2 exchange reaction (eq 2).

$$[W(CO)_5O_2COH]^- + {}^{13}CO_2 \rightleftharpoons [W(CO)_5O_2{}^{13}COH]^- + CO_2 \quad (2)$$

Slow diffusion of hexane into a concentrated acetone solution of [PPN][$W(CO)_5HCO_3$] under CO_2 at −10 °C produced X-ray-quality crystals. The complex exists as a slightly distorted octahedron with five CO ligands and a monodentate bicarbonate group. The bicarbonate ligand is positioned 2.19 Å away from the tungsten atom diagonally in the plane of the *cis* carbonyl ligands so that the distal oxygen atom (3.4 Å away from the tungsten center) lies directly between two carbonyl carbon atoms. Although the bicarbonate hydrogen atom was not specifically located, its presence is confirmed by both the single counterion and the hydrogen bonding between the two anions in the unit cell as illustrated in Figure 1.[17] In addition, it was located in solution by ^1H and $^{13}C\{^1H\}$ NMR spectroscopic measurements. It is worth noting that there are few unidentate bicarbonate metal complexes structurally characterized by X-ray diffraction due to their tendency to afford more stable carbonate derivatives[18,19] Furthermore, there is a scarcity of definitive infrared data on structurally characterized bicarbonate complexes. The hydrogen bonding between the two bicarbonate anions is quite strong, with the O···O distance being 2.57(1) Å. In the structure of $[Et_4N]_2[W(CO)_4(CO_3)]\cdot H_2O$, the hydrogen bonding between the complex and the water molecule was considerably weaker with an O···O distance of 2.834 Å.[6a]

The fact that the bicarbonate ligand is monodentate in this instance is consistent with previous findings on related carboxylate complexes, $[W(CO)_5O_2CR]^-$.[20] The first-order rate constant for *cis* CO loss via a dissociative mechanism in $[W(CO)_5O_2CR]^-$ derivatives displays a linear free energy relationship when plotted against Taft's polar substituent constants (σ^*), with CO dissociation being facilitated by electron-releasing groups. Furthermore, electron-releasing R substituents lead to bidentate carboxylate binding, whereas electron-withdrawing R substituents afford only unidentate binding. In this regard the predicted rate constant for CO dissociation in $[W(CO)_5HCO_3]^-$ ($\sigma^* = 1.34$ for R = OH) is $7.9 \times 10^{-4}\ s^{-1}$ at 40 °C with no chelation anticipated, whereas the deprotonated complex $[W(CO)_5CO_3]^{2-}$ ($\sigma^* = -2.78$ for R = O^-) is expected to have a k_1 value of $4.2 \times 10^{-1}\ s^{-1}$ at 40 °C with chelation occurring. The observations reported upon herein and elsewhere are completely in accord with these predictions.

Forthcoming studies are aimed at understanding the mechanistic aspects of the decarboxylation process involving the $[W(CO)_5HCO_3]^-$ anion in aprotic solvents in the presence and absence of hydrogen-bonding reagents such as water.

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Supplementary Material Available: Tables describing details of the structure analysis, an ORTEP drawing of [PPN][$W(CO)_5HCO_3$], and tables giving a summary of the crystal structure determination data, atomic coordinates and equivalent isotopic displacement coefficients, bond lengths and angles, and anisotropic thermal parameters for [PPN][$W(CO)_5HCO_3$] (13 pages). Ordering information is given on any current masthead page.

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(16) In a typical synthesis, 0.20 g of $W(CO)_6$ (0.57 mmol) and 75 mL of dry acetone were photolyzed for 45 min to give $W(CO)_5$(acetone) and a small amount of $W(CO)_4(acetone)_2$. This solution was then added to 0.30 g of PPN(HCO_3) (0.50 mmol) under a CO_2 atmosphere *via* cannula. The product was precipitated using a mixture of hexane and ether to give a yellow-orange powder. Yield: 0.145 g, 31%. IR (acetone): 2063 (w), 1914 (s), 1848 (m) cm^{-1}. Anal. Calcd for [PPN][$W(CO)_5HCO_3$]·H_2O: C, 53.58; H, 4.53. Found: C, 53.19; H, 4.45.

(17) The details of the structure analysis may be found in the supplementary material.

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