

The Reversible Insertion Reaction of Carbon Dioxide with the $W(CO)_5OH^-$ Anion. Isolation and Characterization of the Resulting Bicarbonate Complex $[PPN][W(CO)_5O_2COH]$

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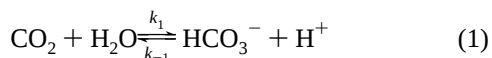
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$[Et_4N][W(CO)_5OH]$ (**1**) and $[PPN][W(CO)_5O_2COH]$ (**2**) have been synthesized and characterized by 1H and ^{13}C NMR and IR spectroscopies, and the X-ray crystal structure of **2** has been determined. Complex **2** crystallizes in the triclinic space group $P\bar{1}$ with unit cell parameters $a = 12.208(2)$ Å, $b = 13.497(2)$ Å, $c = 13.681(2)$ Å, $\alpha = 101.06(2)^\circ$, $\beta = 114.76(1)^\circ$, $\gamma = 98.45(2)^\circ$, $V = 1942.6(5)$ Å³, and $Z = 2$. The structure of the anion of complex **2** consists of a central W(0) bound to five carbonyl ligands, and the coordination around the metal is completed by a monodentate bound bicarbonate ligand located 2.19(1) Å away from the metal center. In the solid state, two anions are hydrogen bonded to one another *via* the bicarbonate ligands in the unit cell. Complex **1** inserts CO₂, COS, or CS₂ to rapidly afford the corresponding bicarbonate or thiocarbonate complexes. The lower limit for the rate constant for the carboxylation of complex **1** has been determined to be $4.2 \times 10^{-4} M^{-1} s^{-1}$ at -70.2 °C, and the lower limit for the rate constant for the decarboxylation of complex **2** has been found to be $2.5 \times 10^{-3} s^{-1}$ at 20.0 °C. In addition, the rate constant for the decarbonylation of **2** was determined to be $7.60 \times 10^{-3} s^{-1}$ at 36.0 °C, a value which is somewhat faster than anticipated on the basis of analogous data for a large variety of $W(CO)_5O_2CR^-$ derivatives. This is attributed to a diminution of the electron-withdrawing ability of the OH substituent in O_2COH as a result of hydrogen bonding to solvent. Nevertheless, it is clear that the rate of decarboxylation of the anion from complex **2** is faster than the rate of CO dissociation. Concomitantly, carboxylation of complex **1** is faster than CO dissociation, since the $W(CO)_5OH^-$ is inert toward ^{13}CO exchange on the time scale of carboxylation at -70.2 °C.

Introduction

The reversible insertion reaction of metal–hydroxide complexes with carbon dioxide remains a subject of much interest since it is a pivotal step in the carbonic anhydrase catalyzed hydration of CO₂ to HCO₃[−] (eq 1). Carbonic anhydrase (CA),



a zinc enzyme found in both plants and animals, is very efficient, with the most active form, human carbonic anhydrase II (CAII), increasing the rate constant for the forward reaction (k_1) from $3.5 \times 10^{-2} sec^{-1}$ to $1.4 \times 10^6 s^{-1}$.² The CAII isozyme has been refined at 2.2 Å resolution^{3a} (and more recently 1.54 Å),^{3b} with the active site being shown to be a zinc atom bound to three histidine residues and one water molecule.³ Experimental⁴ and theoretical⁵ investigations of the activity of the enzyme have led to the proposal that the mechanism for the enzymatic reaction involves a monodentate bicarbonate intermediate.

Several researchers have prepared zinc complexes which are models for carbonic anhydrase.⁶ One model complex which is

both a structural and a reactivity model for carbonic anhydrase, (tris(pyrazolyl)hydroborato)Zn(OH), has been fully characterized.⁷ This complex has been found to react immediately and reversibly with CO₂ to form the monodentate bicarbonate complex, which has been identified by IR spectroscopy, and to catalyze the exchange of oxygen between CO₂ and H₂¹⁷O.⁸ This exchange reaction has also been reported for carbonic anhydrase.⁹

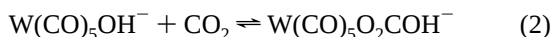
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For quite some time we have been interested in the organo-metallic chemistry of carbon dioxide. Part of these efforts has focused upon the mechanistic aspects of C–H, C–C, and C–O bond forming reactions resulting from CO₂ insertion into M–H, M–C, and M–O bonds. In this regard we are interested in examining the interactions of CO₂ with W(CO)₅OH[−]. This anionic metal carbonyl derivative provides a reactant where the coordination sphere about the metal center may be easily controlled and monitored during the CO₂ insertion reaction. However, the preparation of low-valent mononuclear group 6 carbonyl–hydroxo complexes has proven to be most difficult. This is due to the tendency of these species to aggregate. In 1959, Hieber and co-workers reported the preparation of K₃[M₂(CO)₆(OH)₃] for M = W and Mo,¹⁰ and the crystal structure of the tungsten complex was later determined.¹¹ In 1985, McNeese reported the preparation and structure of [Et₄N]₄[Cr₄(CO)₁₂(μ₃-OH)₄],¹² and the structures of the tungsten and molybdenum analogs were presented later.¹³ The formation of these clusters can be attributed to the *cis*-labilizing ability of the OH ligand.^{12,14} Similar group 6 alkoxide clusters are also known.^{15,16} The monomers are more difficult to isolate, but [PPN][W(CO)₅(OCH₃)] has been identified in solution by infrared spectroscopy.¹⁷ In addition, [Et₄N][W(CO)₅(OPh)] has been structurally characterized by X-ray crystallography.¹⁸ This complex has been found to readily insert CO₂, COS, and CS₂ and to lose CO to form the stable cubane structure [Et₄N]₄[W(CO)₃(μ-OPh)]₄ in the absence of a CO atmosphere. The reactivity patterns of the analogous hydroxide complex would be anticipated to be quite similar.

The present investigation will focus on the synthesis of the mononuclear complex [Et₄N][W(CO)₅OH] and its reaction chemistry with carbon dioxide (eq 2). Subsequent reactivity and structural studies of the thus-formed bicarbonate complex will be presented.



Experimental Section

Materials. All manipulations were carried out in an argon-filled glovebox or on a double-manifold Schlenk line. With the exception of acetone, solvents were dried by distillation from sodium–benzophenone.

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none ketyl (diethyl ether, hexane), magnesium iodide (methanol), or phosphorus pentoxide followed by calcium hydride (acetonitrile). HPLC grade acetone was dried by stirring over potassium carbonate overnight and then distilling from fresh potassium carbonate under nitrogen. Acetone and tetrahydrofuran were purchased from Fisher Scientific, and all other solvents were purchased from E.M. Science. PPN(Cl) was purchased from Aldrich. NaHCO₃ was purchased from Fisher Chemical Co. Carbon disulfide was also purchased from Fisher Chemical and was purified by shaking first with mercury, then with cold, saturated HgCl₂ solution, and finally with cold, saturated KMnO₄ solution. The carbon disulfide was then dried by distillation from P₂O₅ under nitrogen.¹⁹ W(CO)₆ was purchased from Strem. The solution of 25% Et₄N(OH) in methanol was purchased from Sigma. CO₂, COS, and CO were purchased from Matheson. ¹³CO, ¹³CO₂, ¹³CS₂, and *d*₆-acetone were purchased from Cambridge Isotopes. Infrared spectra were taken on either an IBM FTIR/32 or a Mattson Galaxy 6021 spectrometer. A standard NaCl solution cell with a 0.1 mm path length was used for all spectra. ¹H and ¹³C spectra were taken on either a Varian XL-200 or Varian XL-200e superconducting high-resolution spectrometer with an internal deuterium lock in 5 or 10 mm tubes. For variable temperature NMR experiments, the temperature was reported to ±0.1 °C by a thermocouple attached inside the magnet.

Synthesis. [PPN][HCO₃]. This salt was prepared from 30.8 g of NaHCO₃ (0.366 mol) and 5.07 g of PPN(Cl) (8.84 mmol) using the method published previously.²³ The yield was 5.32 g or 89% (based on PPN(Cl)). Anal. Found: 70.76, C; 5.50, H; 392 ppm, Cl[−]. Calcd for [PPN][HCO₃]·2H₂O: 69.92, C; 5.55, H.

[PPN][NO₃]. Similarly, this salt was prepared from 21.5 g of NaNO₃ (253 mmol) and 4.8 g of PPN(Cl) (8.4 mmol) using the method published previously.²⁰ The yield was 4.4 g or 88% (based on PPN(Cl)). Anal. Found: 70.55, C; 4.47, H; 412 ppm, Cl[−]. Calcd for [PPN][NO₃]·¹/₂(H₂O): 70.93, C; 5.13, H.

[Et₄N][W(CO)₅OH]. In a typical synthesis, this complex was prepared by photolyzing 0.20 g of W(CO)₆ (0.57 mmol) and 80 mL of dry methanol for 2 h. The solution was then added to 0.48 g (0.81 mmol) of a solution of 25% Et₄N(OH) in methanol cooled to 0 °C. The solution was immediately placed under an atmosphere of CO to prevent aggregation. IR (MeOH): 2061 (w), 1917 (s), 1864 (m) cm^{−1}. After a solution of the complex in methanol under an atmosphere of ¹³CO was stirred for 2.5 h at ambient temperature, the complex was enriched in ¹³CO. ¹³C NMR: 199.8 (*cis* CO's), 203.9 (*trans* CO) ppm.

[Et₄N][W(CO)₅S(O)COH]. The placement of a solution of the hydroxo complex prepared as described above under an atmosphere of COS gave the insertion product, as indicated by the infrared spectrum. Because the product was extremely soluble in methanol, the solvent was removed from the dark red solution *in vacuo* to give an oily brown solid. Reprecipitating the complex from acetonitrile with diethyl ether gave a yield of 0.302 g or 12.6% (based on W(CO)₆). IR (MeOH): 2064 (w), 1924 (s), 1873 (m) cm^{−1}. IR (CH₃CN): 2063 (w), 1919 (s), 1859 (m) cm^{−1}. ¹³C NMR: 197.4 (*cis* CO's), 201.5 (*trans* CO) ppm.

[Et₄N][W(CO)₅S₂COH]. Adding 0.08 mL of CS₂ (1 mmol) to a solution of the hydroxo complex prepared as above and stirring the solution for 30 min gave the insertion product. Removal of the solvent *in vacuo* yielded 0.504 g of a yellow-orange solid (a mixture of the η¹ and η² products). IR (MeOH): 2063 (w), 1926 (s), 1880 (m) cm^{−1}. ¹³C NMR: 196.9 (*cis* CO's), 201.1 (*trans* CO), 199.7 (inserted ¹³CS₂) ppm.

[Et₄N][W(CO)₅O₂COH]. When a sample of [Et₄N][W(CO)₅OH] was placed under an atmosphere of CO₂, the insertion product was obtained immediately. An IR spectrum shows peaks at 2067 (w), 1927 (s), and 1866 (m) cm^{−1}. The CO₂ insertion product shows CO₂ stretches at 1647 and 1312 cm^{−1}, while the ¹³CO₂ insertion product shows CO₂

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stretches at 1603 and 1285 cm^{-1} . ^{13}C NMR: 199.3 (*cis* CO's), 203.5 (*trans* CO), 160.4 (inserted $^{13}\text{CO}_2$) ppm. This latter signal split into a doublet with a carbon–hydrogen coupling constant of 15 Hz when the proton decoupler was turned off.

[PPN][W(CO)₅O₂COH]. In a typical synthesis, 0.435 g of W(CO)₆ (1.24 mmol) and 150 mL of dry acetone were photolyzed for 2 h to give W(CO)₅(acetone) and a small amount of W(CO)₄(acetone)₂. This solution was then added to 0.616 g of [PPN][HCO₃] (1.03 mmol) under a CO₂ atmosphere *via* cannula. After the solution was warmed gently and stirred for 1 h, the complex was isolated as an oil upon separation in diethyl ether and hexane. Washing the product with diethyl ether provided a yellow-orange powder. The yield was 0.582 g or 61% (based on PPN(HCO₃)). Anal. Found: 53.19, C; 4.45, H. Calcd for [PPN][W(CO)₅HCO₃]·H₂O: 53.58, C; 4.53, H. IR (acetone): 2063 (w), 1914 (s), 1848 (m) cm^{-1} . ^1H NMR: 11.9 ppm.

[PPN][W(CO)₅CS₂OH]. Dissolving 0.116 g of the bicarbonate complex (0.126 mmol) in 2 mL of acetone under N₂, adding 0.5 mL of CS₂ (8 mmol) immediately, and allowing the mixture to stir for 30 min gave a red-orange solution. Adding diethyl ether and hexane gave an orange-brown powder. The powder was washed three times with diethyl ether and dried *in vacuo* to give a yield of 0.076 g or 63% (based on [PPN][W(CO)₅O₂COH]). IR (acetone): 2065 (w), 1927 (s), 1875 (m) cm^{-1} . Anal. Found: 49.69, C; 3.40, H. Calcd for [PPN][W(CO)₅CS₂OH]·H₂O: 50.06, C; 3.03, H. ^1H NMR: 11.9 ppm.

[PPN][W(CO)₅NO₃]. A mixture of 0.3 g of W(CO)₆ (0.9 mmol) and 150 mL of THF was photolyzed for 30 min to give W(CO)₅(THF) and a small amount of W(CO)₄(THF)₂. This solution was then added to 0.40 g of [PPN][NO₃] (0.7 mmol) *via* cannula. The solution turned orange after a few minutes. After 2.5 h of stirring, the solution showed an IR spectrum with peaks for both the η^1 and η^2 products [2010 (w), 1919 (s), 1875 (sh), 1863 (m), 1829 (w) cm].

Kinetic Measurements. Reaction of [PPN][W(CO)₅O₂COH] and P(OMe)₃. [PPN][W(CO)₅O₂COH] (0.233 g, 0.252 mmol) was dissolved in 10.0 mL of dry acetone under CO₂, and the solution was placed in a thermostated water bath at 36.0 ± 0.1 °C. An IR spectrum of the solution was taken, and 0.50 mL of P(OMe)₃ (>20 equiv) was added. The reaction was monitored by following the disappearance of the IR peak at 1915 cm^{-1} with spectra being taken as quickly as possible (about every 1.5 min). The absorbance at 1915 cm^{-1} was corrected by subtracting the absorbance at 2150 cm^{-1} , where no peaks occur. The reaction of [PPN][W(CO)₅O₂COH] and P(OMe)₃ in CH₃CN was similarly studied.

Reaction of [PPN][W(CO)₅O₂CCH₂CN] and P(OMe)₃. [PPN][W(CO)₅O₂CCH₂CN] (0.018 g, 0.033 mmol) was dissolved in 10.0 mL of dry acetone, and the solution was placed in a thermostated water bath at 36.0 ± 0.1 °C. An IR spectrum of the solution was taken, and 0.50 mL of P(OMe)₃ (>20 equiv) was added. The reaction was monitored by following the disappearance of the IR peak at 1916 cm^{-1} with spectra being taken as quickly as possible (about every 1.5 min). The absorbance at 1916 cm^{-1} was corrected by subtracting the absorbance at 2150 cm^{-1} . The kinetics for this reaction in THF have previously been reported.²⁰

Reaction of [PPN][W(CO)₅O₂COH] and $^{13}\text{CS}_2$. Using the inversion–recovery method, T_1 for CS₂ was determined to be 30.103 s. The optimal 90° pulse width was determined to be 17.5°.

In a typical run, 10 mg of [PPN][W(CO)₅O₂COH] (0.011 mmol) was placed in a 10 mm NMR tube. Three grams of *d*₆-acetone and varying amounts of 4% ^{13}C -enriched CS₂, prepared from CS₂ and a small amount of $^{13}\text{CS}_2$ and measured with a 50 μL syringe, were placed in a small flask. This solution was then added to the NMR tube, and the tube was shaken and placed in the instrument as quickly as possible. The typical delay from preparation of the sample to starting the data collection was 5 min.

The instrument was set to take 15 spectra 2 min apart, with each transient spectrum taking 2 min due to the 110 s relaxation delay. The instrument was set to observe only the range from 219 to 174 ppm. The temperature was regulated to 20.2 ± 1.0 °C.

The peak at 193.1 ppm for free CS₂ was integrated, with all spectra in each run being integrated with the same vertical and integral scales and the same range. Three to nine equivalents of CS₂ could be used, since less was too small to observe and more resulted in no change for the free CS₂ peak.

Table 1. Crystallographic Data and Data Collection Parameters for [PPN][W(CO)₅O₂COH]

formula	C ₄₂ H ₃₁ NO ₈ P ₂ W
formula weight	923.5
space group	triclinic, <i>P</i> 1
<i>a</i> , Å	12.208(2)
<i>b</i> , Å	13.497(2)
<i>c</i> , Å	13.681(2)
α , deg	101.06(2)
β , deg	114.760(10)
γ , deg	98.45(2)
<i>V</i> , Å ³	1942.6(5)
<i>Z</i>	2
density (calcd), g/cm ³	1.579
abs coeff mm ⁻¹	6.804
λ (Å)	1.54178
<i>T</i> , K	296
normlzd transmn coeff	0.9999–0.5978
<i>R</i> , %	4.9
<i>R</i> _w , %	5.1

$$^a R = \sum ||F_o| - |F_c|| / \sum F_o. \quad ^b R_w = \{[\sum w(F_o - F_c)^2 / \sum w(F_o)^2]\}^{1/2}.$$

Exchange of [PPN][W(CO)₅O₂COH] with $^{13}\text{CO}_2$. [PPN][W(CO)₅O₂COH] (0.045 g, 0.049 mmol) was placed in a 10 mm NMR tube under $^{13}\text{CO}_2$. Three vials of *d*₆-acetone were also placed under an atmosphere of $^{13}\text{CO}_2$ and were added to the tube. The solution was allowed to sit at room temperature for 24 min with occasional shaking. The NMR was cooled to -78 °C, and the tube was inserted. After the NMR tube sat for 10 min to allow the temperature of the solution to equilibrate, a spectrum was taken. The tube was removed from the instrument, and the solution was allowed to warm to room temperature and sit for 10 min with occasional shaking. A second spectrum was then taken by the same method as above.

The peak for inserted CO₂ was integrated *versus* the peak at 135 ppm for the para carbons of the [PPN]⁺ counterion. The integration of the inserted CO₂ peak did not increase relative to the counterion peak in the second spectrum.

Reaction of [Et₄N][W(CO)₅OH] and $^{13}\text{CO}_2$. A 30 mL solution of [Et₄N][W(CO)₅OH] was prepared from 0.413 g of W(CO)₆ (1.18 mmol) and 0.53 g of a solution of 25% Et₄N(OH) in methanol (0.90 mmol). A small amount of the cold solution was added to a 10 mm NMR tube containing 0.6 mL of *d*₆-acetone under an atmosphere of CO. The tube was put in the sample holder and cooled in a dry ice/acetone bath. The instrument was cooled to -70.2 ± 1.0 °C. The NMR tube was filled with $^{13}\text{CO}_2$ and inserted into the instrument as quickly as possible. The first spectrum, which shows inserted $^{13}\text{CO}_2$, was complete after 12 min and 11 s from when the sample was prepared. A second spectrum, which shows no change, was complete after 18 min. The NMR tube was then emptied into a graduated cylinder to determine the total volume of the sample, which was 5.4 mL.

Additional Reactivity Studies. A solution of [Et₄N][W(CO)₅OH] was prepared from 0.0595 g of W(CO)₆ (0.169 mmol), 50 mL of methanol, and 0.08 g of a solution of 25% Et₄N(OH) in methanol (0.1 mmol) and cooled to 0 °C. H₂¹⁸O (30.0 μL , 1.66 mmol) was dissolved in 1 mL of methanol and added to the cold solution. The mixture was allowed to stir for 2 h at room temperature under CO, and the IR spectrum did not change. The solution was placed under a slight pressure of CO₂ after a brief vacuum was subsequently pulled on the flask, and the mixture was allowed to stir for 1 h. An IR spectrum showed no change in the CO₂ peak for the incorporation of ¹⁸O.

X-ray Crystal Structure Determination of [PPN][W(CO)₅O₂COH].

Crystals were grown by the slow diffusion of hexane into a concentrated solution of the complex in acetone at -10 °C. Crystal data and details of data collection are given in Table 1. A yellow needle (0.05 × 0.12 × 0.50 mm) was mounted on a glass fiber with epoxy cement at room temperature. The crystal was identified as triclinic, with a space group of *P*1. The unit cell dimensions are *a* = 12.208(2) Å, *b* = 13.497(2) Å, *c* = 13.681(2) Å, α = 101.06(2)°, β = 114.760(10)°, γ = 98.45(2)°, *V* = 1942.580 Å³, *Z* = 2, and *D*_{calc} = 1.579 g cm⁻³. Data were measured using Cu K α radiation (λ = 1.54178 Å) on a Rigaku AFC5R X-ray diffractometer equipped with an oriented graphite monochromator. Data were collected for $5.0^\circ \leq 2\theta \leq 120.0^\circ$. A total of 6081 reflections were collected, and a total of 3926 unique reflections, with $|I| \geq 2.0\sigma I$, were used in further calculations. Lorentz and polarization

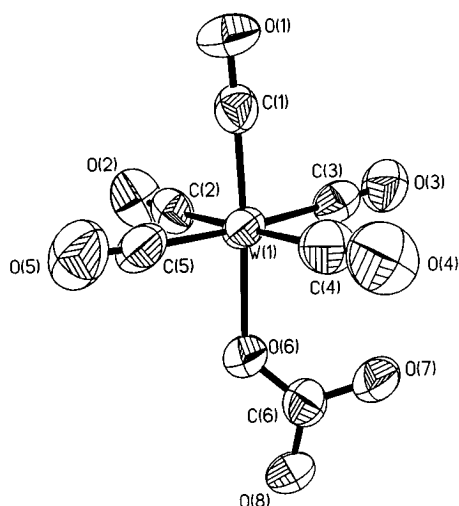


Figure 1. Thermal ellipsoid drawing of the anion of complex 2, $W(CO)_5O_2COH^-$. Ellipsoids are drawn with 50% probability boundaries.

more scarce.^{29,30} $[PPN][W(CO)_5O_2COH]$ (**2**) was prepared from the reaction of $W(CO)_5(\text{acetone})$, photochemically generated from $W(CO)_6$ in acetone, and $[PPN][HCO_3]$ in acetone under an atmosphere of carbon dioxide.^{31–33} The product was isolated as a yellow-orange powder upon precipitation from the reaction solution by the addition of hexane/ether. The complex was stored under CO_2 in order to prevent decarboxylation. The $\nu(CO)$ infrared spectrum of **2** in acetone consists of three bands at 2063 (w), 1914 (s), and 1848 (m) cm^{-1} . Although these are somewhat lower than the $\nu(CO)$ values observed for the complex resulting from the insertion of carbon dioxide into $W(CO)_5OH^-$ in the better hydrogen-bonding solvent methanol, complex **2** exhibits $\nu(CO)$ vibrations in methanol identical to those of the insertion product in that solvent. Correspondingly, the OH proton resonance in **2** appears at 11.9 ppm.

X-ray Structure of $[PPN][W(CO)_5O_2COH]$. Crystals suitable for X-ray crystallography were obtained by the slow diffusion of hexane into a concentrated solution of **2** in acetone at $-10^\circ C$. Figure 1 illustrates a drawing of the anion and its atomic numbering scheme, and selected bond lengths and angles for the anion are listed in Tables 2 and 3, respectively. The structure consists of a central W(0) bound to five carbonyl ligands, and the coordination around the metal is completed by a monodentate bound bicarbonate ligand located 2.19(1) Å away from the metal center. The distal oxygen of the bicarbonate ligand is 3.4 Å away from the tungsten atom, with the dihedral angle between the $W(1)O(6)C(1)C(2)C(4)$ plane (mean deviation = 0.0308 Å) and the CO_3 plane (mean deviation = 0.0069 Å) being 49.6° . In other words, the distal oxygen of the bicarbonate ligand lies almost directly between C(3) and C(4) of the *cis* carbonyl groups. 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 2. Furthermore, it was located in solution by 1H and $^{13}C\{^1H\}$ NMR spectroscopic measurements.

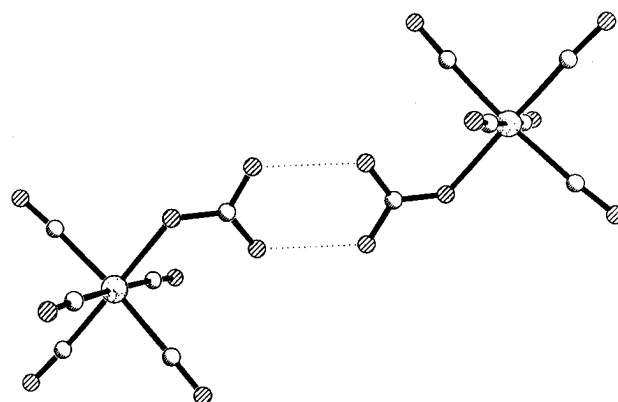


Figure 2. Intermolecular hydrogen bonding between bicarbonate ligands in the two anions of complex **2**.

Table 2. Selected Bond Lengths (Å)^a for $[PPN][W(CO)_5O_2COH]$

W(1)–O(6)	2.19(1)	W(1)–C(1)	1.94(1)
W(1)–C(2)	2.03(1)	W(1)–C(3)	2.03(1)
W(1)–C(4)	2.02(1)	W(1)–C(5)	2.04(1)
O(1)–C(1)	1.16(2)	O(2)–C(2)	1.13(1)
O(3)–C(3)	1.16(1)	O(4)–C(4)	1.14(2)
O(5)–C(5)	1.14(1)	O(6)–C(6)	1.26(1)
O(7)–C(6)	1.25(1)	O(8)–C(6)	1.26(2)

^a Estimated standard deviations are given in parentheses.

Table 3. Selected Bond Angles (deg)^a for $[PPN][W(CO)_5O_2COH]$

O(6)–W(1)–C(1)	177.4(3)	O(6)–W(1)–C(2)	89.5(4)
C(1)–W(1)–C(2)	89.3(5)	O(6)–W(1)–C(3)	94.0(5)
C(1)–W(1)–C(3)	88.3(5)	C(2)–W(1)–C(3)	88.9(4)
O(6)–W(1)–C(4)	90.1(5)	C(1)–W(1)–C(4)	91.2(6)
C(2)–W(1)–C(4)	177.9(3)	C(3)–W(1)–C(4)	89.2(5)
O(6)–W(1)–C(5)	89.8(5)	C(1)–W(1)–C(5)	88.0(5)
C(2)–W(1)–C(5)	90.8(5)	C(3)–W(1)–C(5)	176.2(6)
C(4)–W(1)–C(5)	91.2(5)	W(1)–O(6)–C(6)	129.0(9)
W(1)–C(2)–O(2)	176.0(1)	W(1)–C(1)–O(1)	177.4(9)
W(1)–C(4)–O(4)	177.0(1)	W(1)–C(3)–O(3)	178.0(1)
O(6)–C(6)–O(7)	124.0(1)	W(1)–C(5)–O(5)	176.0(1)
O(7)–C(6)–O(8)	118.0(1)	O(6)–C(6)–O(8)	118.0(1)

^a Estimated standard deviations are given in parentheses.

Table 4. Comparative Interatomic Distances and Angles in Monodentate Bicarbonate Complexes

[M]	<i>trans</i> -PdMe(PEt ₃) ₂ ^a	<i>trans</i> -PtPh(PEt ₃) ₂ ^b	W(CO) ₅ ^c
<i>a</i> (Å)	1.27(4)	1.264(7)	1.26(1)
<i>b</i> (Å)	1.28(3)	1.320(7)	1.26(2)
<i>b'</i> (Å)	1.31(3)	1.249(7)	1.25(1)
O···O	2.60(2)	2.649(6)	2.568(5)
1 (deg)	120(3)	119.9(6)	118.0(1)
2 (deg)	119(2)	115.2(2)	118.0(1)
2' (deg)	121(3)	125.0(6)	124.0(1)

^a Reference 28c. ^b Reference 28a. ^c This work.

The C–O distances within the monodentate bicarbonate ligand are all the same within the limits of the determination (see Table 4). This was previously noted in the *trans*-PdMe-(O₂COH)(PEt₃)₂ complex and ascribed to the fact that each oxygen atom is involved in bonding to either a proton, as a result of hydrogen bonding, or to the metal center.^{28c} On the other hand, in the closely related *trans*-PtPh(O₂COH)(PEt₃)₂ complex one of the C–O bonds was significantly longer than the other two.^{28a} The other reported monodentate structure Pd(O₂COH)₂(dppe), which was not intermolecularly hydrogen bonded, displays C–O bond distances for the oxygens bound to palladium which are much longer than the other two C–O distances.^{28b} Comparative interatomic distances and angles, as defined in structure C, in the three monodentate bicarbonate complexes which are intermolecularly hydrogen bonded are summarized in Table 4.

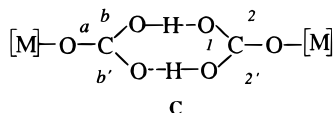
(29) Yoshida, T.; Thorn, D. L.; Okano, T.; Ibers, J. A.; Otsuka, S. *J. Am. Chem. Soc.* **1979**, *101*, 4212.

(30) Baxter, K. E.; Hanton, L. R.; Simpson, J.; Vincent, B. R.; Blackman, A. G. *Inorg. Chem.* **1995**, *34*, 2795.

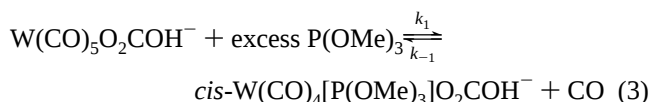
(31) It should be noted parenthetically that attempts to prepare $[PPN][OH]$ by analogy to the published method for $[PPN][OMe]$ ³² were unsuccessful.³³

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(33) (a) Darensbourg, D. J.; Pala, M.; Rheingold, A. L. *Inorg. Chem.* **1986**, *25*, 125. (b) Darensbourg, D. J.; Pala, M.; Simmons, D.; Rheingold, A. L. *Inorg. Chem.* **1986**, *25*, 3537.



CO Ligand Substitution Process. The CO-labilizing ability of the carboxylate ligand in $W(CO)_5O_2CR^-$ anions has been attributed to an involvement of the distal oxygen atom of the monodentate carboxylate in cis CO substitution reactions, with more-electron-donating carboxylate ligands leading to more labile CO groups.^{34,35} Furthermore, it was found that there was a strong correlation between the propensity of the carboxylate to chelate and the rate of cis CO dissociation. That is, chelation of the carboxylate was observed in instances where the distal oxygen is electron-rich (*e.g.*, R = *tert*-butyl, Me, and H) and was not seen for the electron-withdrawing substituents R = CH_2CN or CF_3 . In an effort to ascertain the influence of the bicarbonate ligand on the substitution reaction (eq 3), we have investigated this process under the conditions analogous to those previously employed for the series of $W(CO)_5(\text{carboxylate})^-$.³⁵



Reaction 3 has been established to be first order in metal complex and, when run in the presence of a large excess of $P(OMe)_3$, to be zero order in $P(OMe)_3$.³⁵ The forward rate constant k_1 was determined in acetone to be $7.60 \times 10^{-3} \text{ s}^{-1}$ at 36 °C. This value is an order of magnitude greater than that predicted ($7.88 \times 10^{-4} \text{ s}^{-1}$) from the previously determined linear free energy relationship of $\log k_1$ versus σ^* , where $\sigma^* = 1.34$ for R = OH.³⁵ Indeed, this value is slightly greater than 10 times larger than the value of $4.27 \times 10^{-4} \text{ s}^{-1}$ at 36 °C reported for CO dissociation in $[PPN][W(CO)_5O_2CCH_2CN]$ in THF solvent. That is, since CH_2CN has a σ^* parameter of 1.30, the rate constants for CO dissociation from the $W(CO)_5O_2CR^-$ anion (R = CH_2CN or OH) would be expected to be similar. However, k_1 for the bicarbonate complex is similar to those reported for more-electron-releasing carboxylates, such as $[PPN][W(CO)_5O_2CC(CH_3)_3]$ ($1.09 \times 10^{-2} \text{ s}^{-1}$ at 40 °C) and $[PPN][W(CO)_5O_2CCH_3]$ ($5.55 \times 10^{-3} \text{ s}^{-1}$ at 40 °C) for which the ligands have Taft parameters³⁶ of -0.30 and 0.00 , respectively.

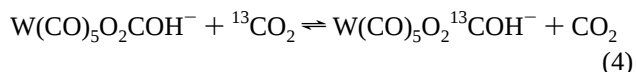
One possible explanation for the larger than expected rate constant is a solvent effect. Therefore, two kinetic studies were undertaken to determine whether or not a solvent effect was at work here. In the first run, the reaction of $[PPN][W(CO)_5O_2CCH_2CN]$ with $P(OMe)_3$ was studied in acetone at 36 °C. The determined rate constant was $4.23 \times 10^{-4} \text{ s}^{-1}$, which is in good agreement with the value of $4.27 \times 10^{-4} \text{ s}^{-1}$ reported for the complex at 36 °C in THF. In the second run, the bicarbonate complex was studied in acetonitrile. The rate constant was found to be $6.08 \times 10^{-3} \text{ s}^{-1}$. This value is only slightly smaller than the corresponding value determined in acetone of $7.60 \times 10^{-3} \text{ s}^{-1}$. The results of these two kinetic studies rule out the faster than expected rate having been caused by a solvent effect.

An alternative explanation for the enhanced rate of CO dissociation from the monodentate bound bicarbonate complex 2 lies in the expected difference in CO-labilizing abilities between the bicarbonate ligand and its deprotonated congener. In proceeding from $-O_2COH^-$ to $-O_2CO^{2-}$, the Taft σ^* parameter decreases from 1.34 to -2.78 . That is, the R

substituent of the $-O_2CR$ group goes from electron withdrawing to highly electron releasing. Hence, the carbonate ligand is anticipated to be very CO labilizing and to provide a stable chelated tungsten carbonyl anion. Both expectations have been realized in that $[PPN]_2[W(CO)_4CO_3]$ is the exclusive product which results from the rapid reaction of $[PPN]_2[CO_3]$ and $W(CO)_5THF$.^{18,37,38} The intermediacy of $W(CO)_5CO_3^{2-}$ was not observed as expected since it has a calculated rate constant for CO dissociation of $4.15 \times 10^{-1} \text{ s}^{-1}$ at 40 °C. Hence, it is likely that the O–H bond in the monodentate bound bicarbonate ligand is lengthened in solution, possibly by hydrogen bonding to the solvent such that it somewhat resembles the carbonate ligand and as a consequence is more CO labilizing.

For $[PPN][W(CO)_5HCO_3]$, no η^2 product is seen, even though there is some $W(CO)_4(\text{acetone})_2$ in the photolytic solution from which it is prepared. By contrast, the reaction of $W(CO)_5(THF)$ and $W(CO)_4(THF)_2$ with $PPN(NO_3)$ produces both the η^1 and η^2 products. The bicarbonate and nitrate ligands are isoelectronic, and bound nitrate has been used as a model for bound bicarbonate;³⁹ nevertheless, their reactivity is different in this case. Although CO dissociation in the $W(CO)_5O_2COH^-$ anion is faster than expected, it is still much slower than CO loss in $W(CO)_5OR^-$ (R = H or alkyl/aryl group). For example, the rate constant for CO dissociation in $W(CO)_5OPh^-$ was measured to be $2.15 \times 10^{-2} \text{ s}^{-1}$ at 5 °C in THF.⁴⁰ Thus, the reactivity of the $W(CO)_5$ unit with regard to CO dissociation is greatly altered (decreased) upon inserting CO_2 into the $(CO)_5W-OH^-$ bond to provide the $(CO)_5WO_2COH^-$ complex. In this regard it is important to note that the CO ligand substitution kinetics for complex 2 were determined in a CO_2 -saturated solution under an atmosphere of carbon dioxide to maintain the complex in its carboxylated form.

Rate of Decarboxylation of $[PPN][W(CO)_5O_2COH]$. An estimate of the rate of decarboxylation of complex 2 was obtained by an examination of the $^{13}CO_2$ exchange reaction (eq 4). A sample of 2 in acetone was allowed to stand for 24 min



under an atmosphere of $^{13}CO_2$ at 20 °C, and its ^{13}C NMR spectrum was recorded at -78 °C. The intensity ratio of the signal at 160.4 ppm for the inserted $^{13}CO_2$ versus that of the *para* carbons of the PPN^+ counterion (135 ppm) was determined. Reaction for an additional 10 min at 20 °C resulted in no change in this intensity ratio, nor did the free to inserted $^{13}CO_2$ intensity ratio change. Hence, the decarboxylation reaction was deemed to be complete within the initial 24 min reaction period. Experiments carried out with different [2] provided similar estimates for the rate of decarboxylation, indicative of first-order behavior in [2].

Since carbon dioxide insertion into the $W-OH^-$ bond in 2 is very fast (*vide infra*), the rate-limiting step in the exchange process defined in eq 4 is decarboxylation. This is in accord with our previous observations on the $^{13}CO_2$ exchange reactions with metalloformate derivatives.^{41,42} From the fact that the

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(37) The structure of the $[Et_4N]_2[W(CO)_4CO_3]$ salt has been defined crystallographically.^{18,38}

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(42) Darensbourg, D. J.; Wiegrefe, H. P.; Wiegrefe, P. W. *J. Am. Chem. Soc.* **1990**, 112, 9252.

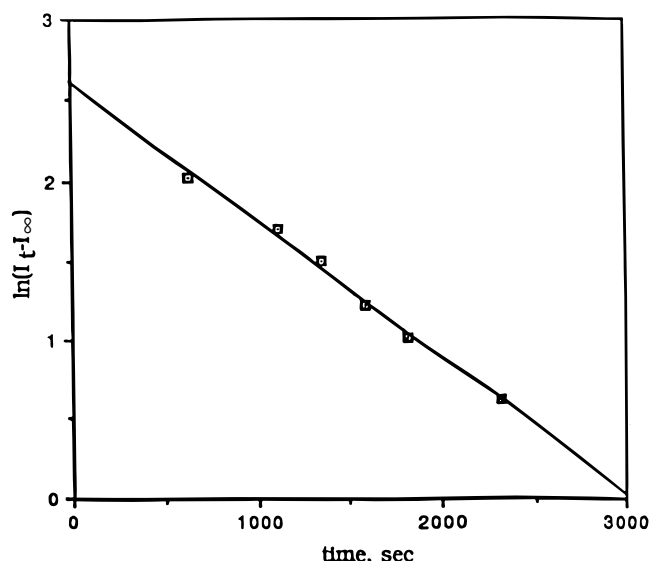
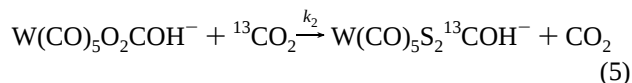


Figure 3. Disappearance of $[\text{CS}_2]$ as indicated by the integrated intensity of the ^{13}C resonance of free CS_2 $\ln[I_t - I_\infty]$, with time for reaction 5.

reaction is essentially complete in at least 24 min, it is possible to conclude that the upper limit for the $^{13}\text{CO}_2$ exchange process is $t_{1/2} = 5.0$ min at 20°C . In an effort to better quantify this reaction, we have repeated the study employing CS_2 , where the reverse, deinsertion reaction does not readily occur.

The exchange reaction indicated in eq 5 was followed utilizing ^{13}C -enriched carbon disulfide, where the decrease in CS_2 concentration with time was monitored by ^{13}C NMR spectroscopy. Nevertheless, employing this method for measuring the rate of reaction 5 required solving other problems. First of all,



the long relaxation delay required to obtain reliable integration data for the free CS_2 peak limits the speed at which spectra can be taken. This problem was solved by taking spectra which consisted of only one transient. While this method undermines the automatic correction for instrumental noise which is performed after every four transients, the amount of noise introduced into the spectra was small and remained constant throughout a given run. However, in order to increase the signal to noise ratio for the free CS_2 peak to a reasonable value, 4% ^{13}C -enriched CS_2 was required. Finally, this method of following the reaction limits the amount of CS_2 which can be used. Normally, the reaction would have been followed under pseudo-first-order conditions (i.e., using more than 20 equiv of CS_2). However, it was found that using more than 9 equiv of carbon disulfide results in immeasurably small changes in the integrations for the free CS_2 peak.

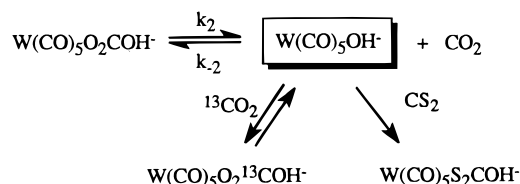
Under these conditions, several kinetic runs were carried out using various quantities of carbon disulfide. From the initial data, the rate constants (k_2) were determined from a plot of $\ln[I_t - I_\infty]$ versus time, where I_t and I_∞ equal the integrated intensity of the free CS_2 ^{13}C resonance at time t and time $= \infty$, respectively. These plots were linear (a representative plot is illustrated in Figure 3), and the rate constants for CS_2 exchange are listed in Table 5. A plot of the observed rate constant as a function of carbon disulfide concentration exhibits curvature indicative of saturation kinetics. This observation would be consistent with decarboxylation of the $\text{W}(\text{CO})_5\text{O}_2\text{COH}^-$ anion being rate limiting. Extrapolation to greater than 20 equiv of CS_2 would indicate a minimum value of k_2 at 20.2°C of about $2.5 \times 10^{-3} \text{ s}^{-1}$. However, it should be noted that the

Table 5. Rate Constants for $^{13}\text{CS}_2$ Exchange with 2 as a Function of $[\text{CS}_2]^a$

$10^3 k_{\text{obs}}, \text{ s}^{-1}$	$10^2 [\text{CS}_2], ^b \text{ M}$
0.971	0.905
1.89	1.81
2.20	2.32

^a Reactions carried out in d_6 -acetone at 20.2°C . ^b 4% ^{13}C -enriched CS_2 utilized.

Scheme 2



actual rate constant could be as much as 50% higher than this estimated value. Nevertheless, a rate constant of this magnitude would be in agreement with its estimate obtained from the reversible $^{13}\text{CO}_2$ exchange study (*vide supra*).

Rate of Carboxylation Reaction of $[\text{Et}_4\text{N}][\text{W}(\text{CO})_5\text{OH}]$ with $^{13}\text{CO}_2$. It is apparent from our qualitative observations reported herein and elsewhere^{18,43} that the CO_2 insertion reaction into tungsten(0) alkoxide or aryloxy bonds is fast in the absence of steric hindrance. We have attempted to better quantify this "very fast" process. Specifically, the rate constant for the insertion of CO_2 into the $(\text{CO})_5\text{W}-\text{OH}^-$ bond is of course highly relevant to the previously discussed decarboxylation studies (Scheme 2), where the rate-limiting step was assumed to be decarboxylation.

An estimate of the time scale for the reaction of $[\text{Et}_4\text{N}][\text{W}(\text{CO})_5\text{OH}]$ with $^{13}\text{CO}_2$ was determined by ^{13}C NMR spectroscopy. Because the reaction was known to occur rapidly at ambient temperature, the sample (0.039 M $[\text{Et}_4\text{N}][\text{W}(\text{CO})_5\text{OH}]$ in methanol) was kept cold in a dry ice/acetone bath at all times, except when it was in the spectrometer at -70.2°C . After the sample was put under an atmosphere of $^{13}\text{CO}_2$, it was placed in the spectrometer as quickly as possible, and the first spectrum was completed after 12.2 min from time of mixing. A second spectrum was completed after a reaction time of 18 min. An intense resonance for the inserted $^{13}\text{CO}_2$ at 159 ppm was seen in the first spectrum, and its integrated intensity did not increase in the second spectrum. Therefore, the reaction was over in the time period required for the acquisition of the first spectrum (12.2 min).

The rate of the insertion reaction of $\text{W}(\text{CO})_5\text{OH}^-$ with CO_2 is assumed to be first order in $[\text{CO}_2]$, since the analogous process involving the $\text{W}(\text{CO})_5\text{R}^-$ anions ($\text{R} = \text{H}, \text{CH}_3$) is second order, first order in [metal complex] and first order in $[\text{CO}_2]$.⁴⁴ The $[\text{CO}_2]$ concentration in methanol at -70.2°C was estimated to be 9.2 M on the basis of comparative measurements carried out in methanol ($0-25^\circ\text{C}$)⁴⁵ and acetone,⁴⁶ where in the latter solvent the $[\text{CO}_2]$ was accurately determined from 0 to -75°C . From this estimated $[\text{CO}_2]$, the initial concentration of the substrate $[\text{W}(\text{CO})_5\text{OH}^-]_0$, and the maximum reaction time, we can establish that the lower limit for k_{-2} for the carboxylation process in Scheme 2 is $4.2 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ at -70.2°C . It should be recognized, however, that the actual value of k_{-2} could indeed greatly exceed this value. Although this rate constant

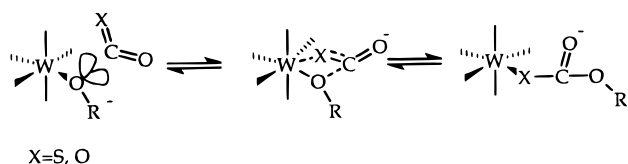
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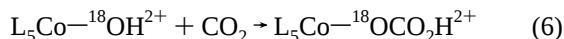
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Scheme 3



would be expected to be much larger at ambient temperature, it is unlikely that it would increase by more than 4 or 5 orders of magnitude. If the rate of the reaction is assumed to increase by a factor of 2 or 3 for every 10 °C increase in temperature, the lower limit for the rate constant (k_{-2}) would lie between 2.2×10^{-1} and $8.3 \text{ M}^{-1} \text{ s}^{-1}$ at 20 °C.

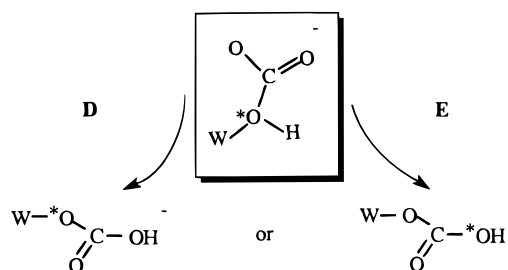
In an experiment designed to examine whether $\text{W}(\text{CO})_5\text{OH}^-$ catalyzes the exchange of oxygen atoms between H_2^{18}O and CO_2 , a sample of $[\text{Et}_4\text{N}][\text{W}(\text{CO})_5\text{OH}]$ in methanol, stabilized by excess carbon monoxide, was stirred in excess H_2^{18}O for several hours. The resultant solution was placed under an atmosphere of CO_2 and agitated for over 1 h at ambient temperature. The solution infrared spectrum of CO_2 exhibited no incorporation of oxygen-18, indicative either of very slow $\text{H}_2\text{O}/\text{OH}^-$ exchange or no $\text{W}-\text{O}$ bond rupture during the insertion process. Nevertheless, due to our inability to assess the level of ^{18}O incorporation in the $\text{W}(\text{CO})_5\text{OH}^-$ derivative, this experiment is equivocal. An observation which indicates the absence of metal-oxygen bond cleavage during the insertion reaction has been reported for the carboxylation process involving cobalt(III) amine hydroxide complexes (eq 6).⁴⁷⁻⁴⁹



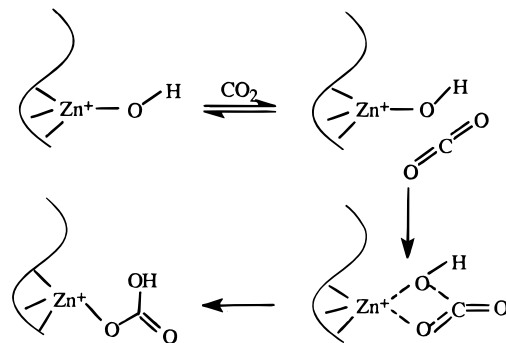
Conclusions

In spite of the fact that the rate constant for carboxylation (k_{-2}) is so imprecisely defined at ambient temperature, it is nevertheless clear that k_{-2} is several orders of magnitude larger than k_2 (the rate constant for decarboxylation). This observation is consistent with the evidence that the equilibrium illustrated in eq 1 lies far to the right in carbon dioxide saturated methanol. It is important to note that the carboxylation reaction was measured under an atmosphere of CO . Similar mechanistic aspects for the insertion of CO_2 into the $\text{W}-\text{OPh}$ bond of $\text{W}(\text{CO})_5\text{O}^-$ have been presented, although this latter process is qualitatively slower. That is, the proposed mechanism involves the prior interaction of the Lewis acid site of CO_2 with the lone pairs on the alkoxide oxygen followed by a concerted transformation to a four-centered transition state (Scheme 3). This transition state appears not to require an open coordination site, as the rate of insertion is not slowed in the presence of additional CO .⁴³ Further studies on the sterically hindered $[\text{W}(\text{CO})_5\text{O}-2,6\text{-Ph}_2\text{C}_6\text{H}_3]^-$ complex found it to be unreactive to CO_2 , although it did insert COS , where $\text{W}-\text{X}$ interaction is significant.

Scheme 4



Scheme 5



Although the reaction of CO_2 with the $\text{W}-\text{OH}$ group of $\text{W}(\text{CO})_5\text{OH}^-$ to provide the bicarbonate complex $\text{W}(\text{CO})_5\text{O}-\text{COH}^-$ is formally similar to the insertion reaction of $\text{W}(\text{CO})_5\text{O}^-$ with CO_2 to afford the aryl carbonate, an important mechanistic feature must be considered in the former process. That is, in the intermediate formed by electrophilic addition of CO_2 at the nucleophilic hydroxide center two pathways are open: a simple proton transfer (D) or CO_2 insertion (E) (Scheme 4). Attempts to distinguish between these two scenarios were not definitive due to our inability to assess the level of ^{18}O incorporation into the OH group of $\text{W}(\text{CO})_5\text{OH}^-$. On the other hand, the insertion process involving COS or CS_2 where $\text{W}-\text{S}$ bond formation occurs clearly involves $\text{W}-\text{O}$ bond rupture.

Contrary to this observation, the $\{\eta^3\text{-HB}(3\text{-Bu}^t\text{-5-Mep})_3\}_2\text{ZnOH}$ complex has been shown to be both a structural and functional model for carbonic anhydrase. That is, this monomeric zinc hydroxide complex serves as an effective catalyst for the exchange of oxygen atoms between CO_2 and H_2^{17}O in benzene solution.⁵⁰ This observation clearly reflects the involvement of the metal center in activating CO_2 during its reaction with the $\text{M}-\text{OH}$ functionality. Indeed, it is this polarization of the CO_2 molecule by the metal center (Scheme 5) which is used to rationalize the much greater second-order rate constant for the attack of CA upon CO_2 ($10^8 \text{ M}^{-1} \text{ s}^{-1}$) as compared to the analogous rate constant for OH^- attack ($8.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$).^{51,52} However, it is clear that other factors, such as indirect ligands, play a role in the catalytic efficiency of the metalloenzyme system.⁵³

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Supporting Information Available: An ORTEP drawing of $[\text{PPN}]^+$ and tables of the atomic coordinates and equivalent isotropic displacement coefficients, bond lengths and angles, and anisotropic thermal parameters for $[\text{PPN}][\text{W}(\text{CO})_5\text{HCO}_3]$ (8 pages). Ordering information is given on any current masthead page.

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