O, 90083-20-8; $CH_3(CH_2)_5CH{=}CHCHO$, 2463-53-8; *t*-BuOK, 865-47-4.

Supplementary Material Available: ^1H and ^{13}C NMR data for compounds **4a–f** and **6a–d** (1 page). Ordering information is given on any current masthead page.

Metal-Induced Transformations of Carbon Dioxide. Carbon–Carbon Bond Forming Processes Involving Anionic Group 6B Metal Derivatives and the X-ray Structure of [PNP][*cis*-$CH_3W(CO)_4P(CH_3)_3$]

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Received March 9, 1984

The reaction of carbon dioxide with metal alkyls represents a fundamental step in the eventual exploitation of carbon dioxide in the catalytic synthesis of organic substances derived from this most abundant C_1 feedstock. Although much effort has been expended in organometallic chemistry in characterizing migratory CO insertion processes,[1] systematic investigations of the corresponding processes involving CO_2 are lacking.[2] One aspect of our program in carbon dioxide chemistry is centered around gaining a more definitive knowledge of what factors affect CO_2 insertion reactions into M–H and M–C bonds.[3] Specifically we have shown that alkyl and aryl derivatives, $M(CO)_5R^-$ (M = Cr, W; R = CH_3 or Ph), smoothly undergo insertion reactions wtih carbon dioxide to provide the corresponding carboxylates (eq 1).

$$M(CO)_5R^- + CO_2 \rightarrow M(CO)_5OC(O)R^- \qquad (1)$$

We report herein mechanistically on these reaction processes, along with the effects on these reactions of modification of the electron affinity at the metal center as mediated by the ancillary ligands.

Observations on the intimate details of carbon dioxide insertion into $CH_3W(CO)_5^-$ to generate $CH_3CO_2W(CO)_5^-$ are consistent with a concerted (I_a) mechanism. The reaction was found to be first order in both metal substrate and carbon dioxide. A plot of the pseudo-first-order rate constant (k_{obsd}) for CO_2 insertion at ambient temperature (23 °C) as a function of CO_2 pressure[4] was linear up to a total CO_2 pressure of ca. 200 psi, beyond which Henry's law does not apply.[5]

A significant acceleration of CO_2 insertion was noted in the presence of alkali metal counterions which serve to neutralize the buildup of negative charge on the incipient carboxylate ligand. For example, reactions that occur only slowly (days) at high pressures of CO_2 in the absence of these alkali metal ions take place in hours and at low CO_2 pressures in the presence of a slight excess of lithium ions. Unfortunately, reactions subsequent to the CO_2 insertion process, i.e., alkali metal assisted displacement of the carboxylate ligand by other nucleophiles (e.g., eq 2), result in removal of the carboxylate ligand from the metal center.[6]

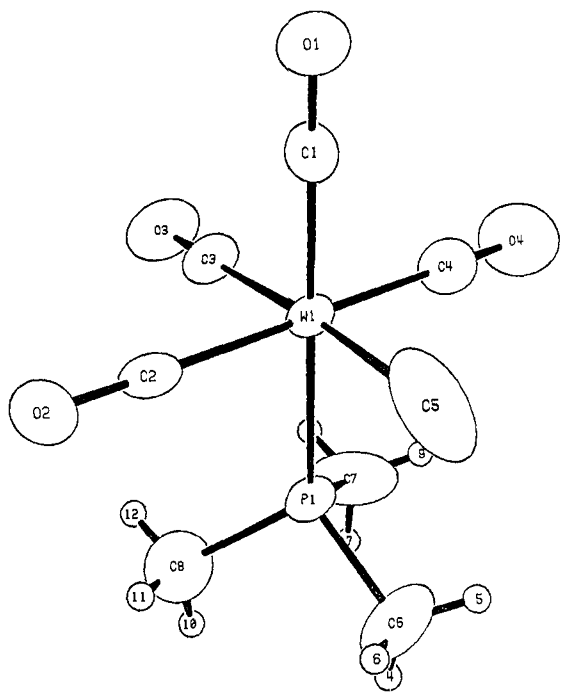

Figure 1. ORTEP drawing of the *cis*-$CH_3W(CO)_4PMe_3^-$ anion. Some bond lengths are as follows: W–C(CH_3), 2.18 (3) Å; W–P, 2.532 (3) Å; W–C_1, 1.941 (13) Å; W–C_2, 2.005 (13) Å; W–C_3, 2.09 (2) Å; W–C_4, 2.008 (15) Å.

$$CH_3CO_2M(CO)_5^- + LiCl \rightarrow ClM(CO)_5^- + CH_3CO_2^-Li^+ \quad (2)$$

This enhanced rate of carbon dioxide insertion into M–C bonds in the presence of alkali metal ions has allowed us to investigate the effects of added carbon monoxide on the rate of the CO_2 insertion process. This is of importance since in the absence of alkali promoters, CO insertion into the M–C bond to afford acyls derivatives is much faster than CO_2 insertion to yield carboxylates. When reaction 1 where M = W and R = CH_3 was carried out in a mixture of carbon dioxide/carbon monoxide (100 psi/400 psi) in the presence of excess LiCl, no retardation of the reaction rate was noted when compared to the same reaction conditions in the absence of 400 psi of carbon monoxide.

In further compliance with an I_a reaction pathway the rate of carbon dioxide insertion into the M–C bond as described in eq 1 is Cr < W and CH_3 > Ph. This latter dependence on the nature of the R group has been noted by Casey and Polichnowski[7] for carbon monoxide insertion reactions of $RW(CO)_5^-$, and is seen as well for analogous processes involving the neutral $RMn(CO)_5$ derivatives.[8]

Since the interaction of carbon dioxide with metal centers is anticipated to intensify at electron-rich metal centers, we have synthesized alkyltungsten carbonyl derivatives with phosphorus donor ligand substituents. These derivatives were synthesized by alkylation of $Na_2W(CO)_4PR_3$ (derived from sodium naphthalenide reduction of *cis*-$W(CO)_4[PR_3]NC_5H_{11}$[9,10]) by methyl tosylate, followed by addition of [PNP][tosylate] to precipitate the [PNP][*cis*-$CH_3W(CO)_4PR_3$] salt. One of the derivatives was fully characterized by X-ray crystallography at −99 ± 1 °C in order to accurately define the W–C(CH_3) bond distance.[11] Figure 1

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[4] Carbon dioxide insertion reactions requiring pressure greater than atmospheric were carried out in a 300-mL Parr reactor fitted with a glass linear and a dip tube to allow sampling of the solution during the reaction. Temperatures were maintained by immersing the reactor in a constant temperature bath. The reactions were monitored by infrared spectroscopy in the ν(CO) region.

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Table I. Second-Order Rate Constants for Carbon Dioxide Insertion into *cis*-$CH_3W(CO)_4L^-$ Derivatives[a]

L	k_2, s^{-1} M^{-1}	relative rates
CO	3.46×10^{-6}	1
$P(OMe)_3$	2.00×10^{-4}	57.8
PMe_3	8.40×10^{-4}	243

[a] Reactions carried out in tetrahydrofuran at 25 °C at a carbon dioxide pressure of 760 torr. The products, *cis*-$CH_3CO_2W(CO)_4L^-$, have been prepared by more conventional approaches elsewhere and characterized spectroscopically as well as X-ray crystallographically.[15]

contains an ORTEP drawing of the anion, *cis*-$CH_3W(CO)_4PMe_3^-$, along with pertinent bond distances. Unfortunately we have not thus far been able to obtain X-ray quality crystals of the parent salt containing the $CH_3W(CO)_5^-$ anion for comparative purposes. However, the structure of the isoelectronic neutral species, $CH_3Re(CO)_5$, has been determined by electron diffraction.[12] The Re–C(CH_3) bond distance was found to be 2.308 (17) Å, or somewhat longer than that found in *cis*-$CH_3W(CO)_4PMe_3^-$, where the W–C(CH_3) distance is 2.18 (3) Å. On the basis of the expected effect on the M–C(CH_3) bond upon going from $CH_3Re(CO)_5$ to $CH_3W(CO)_5^-$, the W–C(CH_3) bond in the latter species is anticipated to be somewhat *longer* than that observed in the analogous neutral rhenium species and the herein reported tungsten PMe_3 substituted derivative. This similarity in metal–ligand bond distances is seen in the $(CO)_5ReCl$[13] and $(CO)_5WCl^-$[14] species, where the M–Cl bond distances are 2.515 (2) and 2.566 (2) Å, respectively.

Substitution at the metal center by phosphorus donor ligands is found to greatly expedite the CO_2 insertion process, where the second-order rate constant (Table I) increases in value by 2 orders of magnitude upon replacing CO by PMe_3 or $P(OMe)_3$.[15,16] As expected the more basic PMe_3 ligand has a greater effect. Temperature-dependent studies were carried out at atmospheric CO_2 pressure employing the *cis*-$CH_3W(CO)_4P(OMe)_3^-$ substrate, resulting in activation parameters of $\Delta H^* = 10.2$ kcal mol^{-1} and $\Delta S^* = -43.3$ eu. These parameters are quite consistent with the proposed concerted mechanism for carbon dioxide insertion.

A similar rate enhancement was noted for CO_2 insertion into the W–C bond in the chelating $(CO)_4\overline{WCH_2CH_2CH_2P}Ph_2^-$ derivative. This latter species was prepared by thermal decarbonylation of the stable $(CO)_4\overline{WC(O)CH_2CH_2CH_2P}Ph_2^-$ species[17] which resulted from reaction 3.[18,19]

$$(CO)_5W^{2-} + Ph_2PCH_2CH_2CH_2Cl \rightarrow (CO)_5WCH_2CH_2CH_2PPh_2^- \rightarrow (CO)_4\overline{WC(O)CH_2CH_2CH_2P}Ph_2 \quad (3)$$

Since crystallographic data do not indicate a weakening of the W–C(CH_3) bond upon substitution by sterically nonencumbering phosphine ligands, the propensity for CO_2 insertion into M–C bonds involving electron-rich metal centers can be assumed to arise from an enhanced interaction of the CO_2 molecule with these centers. Studies are continuing to further assess the details of these carbon dioxide insertion processes.

Acknowledgment. The financial support of this research by the National Science Foundation (Grant CHE 83-08281) is greatly appreciated.

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(11) Single crystals of [PNP][*cis*-$CH_3W(CO)_4PMe_3$] were grown from THF/toluene/hexane (1:1:1) at 0 °C. They belong to the monoclinic space group C_c with $a = 16.538$ (8) Å, $b = 17.102$ (9) Å, $c = 16.106$ (7) Å, $\beta = 115.26$ (3)°, $V = 4119.7$ Å^3. R(weighted) = 4.35% for 4034 reflections with $I > 3\sigma(I)$. Crystallographic analysis was carried out by the crystallographic staff of Molecular Structure Corp.: Dr. M. W. Extine, R. A. Peascoe, Dr. J. M. Troup, and B. B. Warrington (details to be published separately).

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(17) The chelating acyl derivative has been characterized by X-ray crystallography. Crystals of this salt suitable for X-ray analysis were grown from THF/toluene at 10 °C. They belong to the monoclinic space group $P2_1/c$ with $a = 9.444$ (1) Å, $b = 22.654$ (5) Å, $c = 21.279$ (4) Å, $\beta = 96.00$ (1) Å^3, R(weighted) = 6.1% for 1693 reflections with $I > 3\sigma(I)$. Crystallographic analysis was carried out by Dr. Terry Delord at TAMU. Details to be published separately.

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Electrochemical Reduction of Aqueous Bicarbonate to Formate with High Current Efficiency Near the Thermodynamic Potential at Chemically Derivatized Electrodes

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Received February 6, 1984

We wish to report results that show that the electrochemical reduction of aqueous CO_3H^- to HCO_2^-, eq 1, can be effected with

$$CO_3H^- + 2e^- + 2H^+ \rightarrow HCO_2^- + H_2O \quad (1)$$

high current efficiency and near the thermodynamic potential using chemically derivatized metallic electrodes represented by Figure 1. We note that CO_3H^-(aq) is a CO_2 equivalent: $H_2O + CO_2 \rightleftarrows H_2CO_3 \rightleftarrows CO_3H^- + H^+ \rightleftarrows CO_3^{2-} + 2H^+$. The reduction of aqueous CO_2 is known to occur at many electrode surfaces,[1-4] but generally the reduction requires a significantly more negative electrode potential than thermodynamically demanded. Our work was stimulated by the discovery[5,6] that supported Pd is an effective catalyst for the reaction of CO_3H^- with H_2 to form HCO_2^-. The Pd-impregnated polymer, $[(PQ^{2+})_n]_{surf}$, on semiconductor or metallic electrodes illustrated in Figure 1 has been shown to be an effective catalyst for H_2 evolution.[7] We have subsequently shown[6] that the Pd-impregnated $[(PQ^{2+})_n]$ system is capable of catalyzing the reaction of H_2 with CO_3H^- to form HCO_2^-. In the electrochemical experiments described below, the $[(PQ^{2+})_n]$ redox polymer provides a mechanism to bring the reducing equivalents to the high surface area Pd catalyst sites. The $E°$'s of the $[(PQ^{2+/+/0})_n]_{surf}$ system are −0.55 and −0.90 V vs. SCE,[7-9] negative enough to bring the Pd particles to a sufficiently reducing

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