in the reaction of T_{OH}^{0} because this negative charge is (partially) compensated by the positive charge on water (2) or by protonation (3).

Another factor which could reduce the imbalance in the transition state of the water-catalyzed reaction is that in general a very late transition state is less likely to be strongly imbalanced. This is best visualized if one places the reaction coordinate on a diagram with separate axes for C–C bond cleavage and for charge delocalization. As the reaction coordinate approaches the product corner, it inevitably also approaches the diagonal line for balanced reactions. If the larger secondary isotope effects for the water reaction (1.24 to 1.28) compared to that of the k_4 step (1.20) is a true indication of a later transition state, this factor could be significant.

C. Water Addition to the Double Bond, K_1 . We note that the equilibrium isotope effect on K_1 (average $K_1^{\rm H}/K_1^{\rm D} = 0.906$) is substantially smaller than the equilibrium isotope effects for nucleophilic addition to carbonyl carbon.^{36,57,58} Whether this is typical for the addition to activated olefins will have to await further study. Nevertheless, it is noteworthy that this result is consistent with expectations based on fractionation factor calculations.⁶⁵

Experimental Section

Materials. 1-H, 1-NO₂, and 1-OMe were available from a previous study.¹ The deuterated analogues were synthesized by condensation of Meldrum's acid with the respective deuterated benzaldehyde as described by Schuster et al.;⁶⁶ the isotopic purity of the deuterated olefins was 98% or better as shown by NMR analysis. Benzaldehyde- d_1 was prepared by the method of Schowen et al.,⁶⁷ p-methoxylbenzaldehyde- d_1 by the me

Morpholine and triethylamine were purified by refluxing for 8 h over sodium followed by distillation under nitrogen. The other materials were all reagent grade and were used without further purification.

Equilibrium Measurements. K_1^{H} and K_1^{D} were measured spectrophotometrically at λ_{max} of the olefin (325 nm for 1-H, 320 nm for 1-NO₂, 372 nm for 1-OMe); at these wavelengths T_{OH}^{-} does not absorb. pK_1 was obtained as

$$pK_1 = pH + \log \frac{OD}{OD_0 - OD}$$
(21)

where OD refers to the optical density at a pH close to pK_1 while OD_o is the optical density of a solution where all the material is in the olefin form. Since the solutions were unstable owing to the onset of the hydrolysis reaction, the following procedure was adopted. A few microliters of a stock solution of the olefin in Me₂SO as injected into a prethermostated buffer solution placed into a cuvette of a Gilford spectrophotometer. The OD was recorded as a function of time with the time of injection being t = 0. Logarithmic plots of Δ OD vs. time where extrapolated to t = 0 in order to obtain the desired OD.

Kinetic Experiments. The techniques used were the same as the ones reported before.^{1,3}

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Registry No. 1-H, 1214-54-6; 1-NO₂, 15795-62-7; 1-OMe, 15795-54-7.

Supplementary Material Available: Tables S1–S4, observed rate constants for hydrolytic cleavage of $1-NO_2$ and $1d-NO_2$ (S1), of 1-H and 1d-H (S2), and of 1-OMe and 1d-OMe (S3); observed rate constants for hydrolytic cleavage of $1-NO_2$, 1-H, and 1-OMe, additional data (S4); synthesis of *p*-nitrobenzaldehyde- d_1 (9 pages). Ordering information is given on any current masthead page.

Reactivity of Some Transition-Metal Systems toward Liquid Carbon Dioxide

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Abstract: The reactivity of several transition-metal complexes toward liquid CO₂ has been investigated as a means of screening such complexes for their ability to bind CO₂. Although the known Ni(CO₂)(PCy₃)₂ complex was prepared by the reaction of [Ni(PCy₃)₂]₂(μ -N₂) with CO₂(l), the compound Pd(PCy₃)₂ and Pt(PCy₃)₂ do not react with CO₂(l) to afford CO₂ complexes. But the compound Pt(PCy₃)₂ does react with wet CO₂ to afford PtH(O₂COH)(PCy₃)₂, a bicarbonato complex. Similar reactivity was seen for W(CO)₃(PCy₃)₂, which produces WH(O₂COH)(CO)₃(PCy₃)₂ in wet CO₂(l). The compounds Na[Co(N₂)(PEt₂Ph)₃] and [Co(PEt₂Ph)₃]₂(μ -N₂) react with CO₂(l) to form complexes that contain carbonyl and carbonato ligands. Peroxocarbonato complexes, IrR(OCO₃)(CO)(PPh₃)₂ (R = Me, Ph), were prepared from IrR(O₂)(CO)(PPh₃)₂ with CO₂(l).

Carbon dioxide offers an attractive potential alternative to carbon monoxide in the development of a C_1 chemical technology to supplement present petroleum-based technology. Before such a development can be realized, transition-metal-carbon dioxide interactions must be studied, as it is presumed that the catalytic reduction of carbon dioxide, if it is to be accomplished at all, will be carried out in the presence of a transition metal.¹

Eisenberg and Hendriksen¹ recently reviewed the coordination chemistry of carbon dioxide and summarized some examples of metal complexes originally believed to be those of carbon dioxide that on further examination turned out to be otherwise. Because of difficulties of spectroscopic characterization, the unpredictable effects of adventitious water, and the tendency of coordinated CO_2 to react further, it is prudent to accept structural characterization by diffraction methods as the criterion for judging the authenticity of a given class of transition-metal-carbon dioxide complexes

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 $(M-CO_2)$. To our knowledge only three $M-CO_2$ complexes, $Ni(\eta^2-CO_2)(PCy_3)_2^{,2,3} K[Co(Pr-salen)(\eta^1-CO_2)]^4$ and $Nb(\eta^5 C_5H_4Me)_2(CH_2SiMe_3)(\eta^2-CO_2)$,⁵ have been so characterized, despite the intense effort that has been devoted to the preparation of such complexes. The Ni complex appears to have the correct balance of electronic and steric factors for the stabilization of bound CO₂, as the complexes $M(\eta^2$ -CO₂)(PR₃)₂ (M = Pd, Pt; R = Cy (vide infra), Ph⁶) cannot be prepared. The stability of the Nb complex has been ascribed to its coordinative saturation and to the fact that the orientation of the bound CO_2 ligand disfavors an internal decomposition route. The stability of the Co complex has been ascribed to the simultaneous involvement of the Lewis acid site at C with Co and of the Lewis base site at O with K.

The existence of these three M-CO₂ complexes provides meager clues as to how one might develop a general coordination chemistry of CO_2 . What is needed at this stage is a convenient method for surveying the reactivity of CO_2 toward a wide spectrum of transition-metal complexes. While previous studies have used gaseous CO_2 , we describe here some experiments on the reactivity at room temperature of a number of transition-metal complexes toward liquid CO_2 . We believe that the benefits of using liquid CO2 are a greatly increased CO2 concentration and the elimination of solvent competition for a vacant coordination site on the metal. Therefore, the use of liquid CO_2 may be an effective way to survey metal complexes for their ability to bind CO_2 .

In this initial study, each of the metal systems chosen generally has the following characteristics: a low-valent metal atom is surrounded by electron-donating ligands, usually trialkylphosphine ligands; the compound is either coordinatively unsaturated or contains an easily displaceable ligand such as N2 or an olefin; and at least some of the ligands about the metal are sterically demanding.

Experimental Section

All reactions were performed under an atmosphere of prepurified N₂ with standard Schlenkware. Air-sensitive solids were handled in a Vacuum Atmosphere glove box under an Ar atmosphere. Solvents were refluxed under N2 over Na/benzophenone and were distilled immediately prior to use. The compounds PPh₃, PEt₂Ph, and Cy₃PCS₂ were purchased from Strem Chemicals, Inc. The compound PCy₃ was generated by dissolving Cy_3PCS_2 in ethanol and distilling CS_2 from it. All other organic reagents were purchased from Aldrich Chemical Co. The compounds $IrCl(CO)(PPh_{3})_{2}$,⁷ $IrCl(N_{2})(PPh_{3})_{8}$ ⁸ $Ir(CH_{3})(CO)(PPh_{3})_{2}$,⁹ $Ir(C_{6}H_{5})(CO)(PPh_{3})_{2}$,¹⁰ $[RhH(PCy_{3})_{2}]_{2}(\mu-N_{2})$,¹¹ $W(CO)_{3}(PCy_{3})_{2}$,¹² $Mo(CO)_{3}(PCy_{3})_{2}$,¹² $[Co(PEt_{2}Ph)_{3}]_{2}(\mu-N_{2})$,¹³ $[Co(PPh_{3})_{3}]_{2}(\mu-N_{2})$,¹³ $Na[Co(N_{2})(PEt_{2}Ph)_{3}]$,¹³ $[Ni(PCy_{3})_{2}]_{2}(\mu-N_{2})$,¹⁴ $Pd(PCy_{3})_{2}$,¹⁵ and Pt_{3} $(PCy_3)_2^{15}$ were prepared as described in the literature. Coleman Instrument Grade CO₂ was obtained from Matheson and dried by passage through a 2×40 cm column of activated 3-Å molecular sieves (Davison).

- (2) Abbreviations used: Cy = cyclohexyl, $Pr-salen = o-HOC_6H_4C(Pr)=$
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Table I. Reactivity of Some Transition-Metal Systems toward Liquid CO,

complex	reacts with dry CO ₂	reacts with wet CO ₂
$IrCl(N_2)(PPh_3)_2$	no	
$Ir R(CO)(PPh_3)_2$, R = Me, Ph	no	
$IrR(O_2)(CO)(PPh_3)_2$ R = Me, Ph	yes	
$[RhH(PCy_3)_2]_2(\mu-N_2)$	no	
$[Ni(PCy_3)_2]_2(\mu - N_2)$	yes	
$Pd(PCy_3)_2$	no	
$Pt(PCy_3)_2$	no	yes
$Mo(CO)_{3}(PCy_{3})_{2}$	no	
$W(CO)_3(PCy_3)_2$	no	yes
$[Co(PPh_3)_3]_2(\mu N_2)$	no	
$[Co(PEt_2Ph)_3]_2(\mu-N_2)$	yes	
$Na[Co(N_2)(PEt_2Ph)_3]$	yes	

A Perkin-Elmer 283 spectrometer was used to record IR spectra. The NMR spectra were obtained from a JEOL FX90O spectrometer on samples in 10-mm tubes. ¹H spectra are referenced to external Me₄Si and the ${}^{31}P{}^{1}H$ NMR spectra to external 85% $H_{3}PO_{4}$ with positive chemical shift values to lower field.

A Parr Instruments, Inc., 45-mL pressure vessel was used for the liquid CO₂ experiments. A typical run consisted of placing 0.1-0.15 g of starting metal complex and a stirring bar into the quartz-lined pressure vessel under an inert atmosphere. A measured amount of $CO_2(g)$ (\approx 3500 cm³, enough to yield ~10 mL CO₂(l)) was condensed into the vessel cooled by a dry ice/ether bath (-100 °C). This corresponds roughly to about a 1000-fold molar excess of CO₂ to metal complex. The system was then sealed, placed behind a blast shield, and brought to room temperature (pressure in vessel 60-70 atm). Since the critical temperature of CO₂ is 31 °C and the pressure limit in the vessel is \approx 120 atm, experiments at elevated temperatures were not carried out. The reaction mixture was stirred for 1 h to 2 weeks, depending on the compound under study. The CO₂ was then vented, the pressure vessel opened under an inert atmosphere, and the nature of the metal complex probed spectroscopically. The presence of trace amounts of H₂O in CO₂ must be considered when one evaluates the nature of the products obtained, whether with gaseous or liquid CO₂. Therefore, if on the basis of spectroscopic examination of the products a reaction was judged to have occurred, the experiment was repeated with water deliberately added to the reaction mixture. If the yield of the same product increased, then the reaction was assumed to require wet CO₂; if the yield of product did not change, the reaction was assumed to occur with dry CO₂.

Results

We divide our findings on the reactivity at room temperature of transition-metal complexes toward liquid CO₂ into three categories: no reaction; reaction with dry CO_2 ; and reaction with wet CO_2 . The various reactivities are summarized in Table I.

No Reaction. As Table I indicates, a number of the complexes studied show no reactivity toward liquid CO₂. These compounds were recovered unchanged from the reaction vessel, although the fact that they were generally dispersed over the quartz liner argues for their having been dissolved in liquid CO_2 . Although the experimental conditions did not enable us to observe or probe the reaction mixtures under pressure, at least for the N2-containing complexes of Table I, the persistence of N_2 as a ligand argues against CO₂ reactivity at high pressure. Thus, CO₂ did not displace N_2 from IrCl(N_2)(PPh₃)₂. There is no evidence that CO₂ will insert into the Ir-R bond of $IrR(CO)(PPh_3)_2$, R = Me, Ph. Moreover, in a separate experiment, the addition of CH₃I to $IrCl(CO)(PPh_3)_2$ in liquid CO₂ proceeded smoothly to afford IrClI(CH₃)(CO)(PPh₃)₂, as judged by comparison of the spectral properties of an authentic sample prepared in toluene. Thus, there is no evidence of CO₂ insertion into the Ir-CH₃ bond.

Speier et al.¹⁶ report that $Co(N_2)(PPh_3)_3$ reacts with CO_2 in toluene to produce $[Co(CO_2)(PPh_3)_2]_n$. However, we find that $[Co(PPh_3)_3]_2(\mu-N_2)$ shows no reactivity toward CO₂, although the corresponding PEt₂Ph complex does. The results for the Ph complexes may not be at variance, for it seems doubtful if a CO₂

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complex was prepared by Speier et al.¹⁶ They assign to the coordinated CO_2 molecule an IR vibration at 1890 cm⁻¹. This is well beyond the range of 1550–1740 cm⁻¹ observed in authentic CO₂ complexes.¹

Although [Ni(PCy₃)₂]₂(μ -N₂) is known to react with CO₂(g) to afford Ni(η^2 -CO₂)(PCy₃)₂,³ and indeed this same complex is formed with CO₂(l) (vide infra), the closely related complexes Pd(PCy₃)₂ and Pt(PCy₃)₂ do not react with dry CO₂, although the Pt compound does react with wet CO₂. Nor does the related Rh system, [RhH(PCy₃)₂]₂(μ -N₂), display any reactivity toward CO₂. Finally, the earlier transition-metal systems, M(CO)₃-(PCy₃)₂, M = Mo, W,¹² do not react with dry CO₂, although the W complex does react with wet CO₂.

Reactions with Dry CO₂. The compound $Ir(CH_3)(O_2)$ - $(CO)(PPh_3)_2$, prepared by exposing $Ir(CH_3)(CO)(PPh_3)_2$ to the atmosphere for 24 h, shows reactivity toward dry $CO_2(l)$. The oxygen complex shows a ν_{CO} band at 1968 cm⁻¹ and a ν_{OO} band at 826 cm⁻¹. The ³¹P{¹H} NMR spectrum consists of a singlet at -2.56 ppm. The ¹H NMR spectrum displays a triplet resonance at 0.40 ppm ($J_{PH} = 4.9$ Hz). The product of the reaction with dry CO₂ shows a ν_{CO} band at 2015 cm⁻¹ and absorption bands at 1680 and 772 cm⁻¹. Its ³¹P{¹H} NMR spectrum consists of a singlet at 8.58 ppm. Its ¹H NMR spectrum displays a triplet resonance at 0.51 ppm ($J_{PH} = 4.9$ Hz). The compound Pt-(O₂)(PCy₃)₂ reacts with CO₂ to afford Pt(OCO₃)(PCy₃)₂,¹⁷ which displays vibrations at 1680 and 822 cm⁻¹ that have been assigned to the C=O and O-O stretching vibrations of the peroxycarbonato ligand. The close correspondence of the vibrational spectra of the Ir and Pt systems, along with the NMR evidence on the Ir system, leads us to suggest that the complex formed between Ir(CH₃)(O₂)(CO)(PPh₃)₂ and CO₂(1) is Ir(CH₃)- $(OCO_3)(CO)(PPh_3)_2$, in which the phosphines are trans to one another. Comparisons of the spectra suggest similarly that the product of $Ir(C_6H_5)(O_2)(CO)(PPh_3)_2$ with $CO_2(1)$ is also a peroxycarbonate.

The ready displacement of the N_2 ligand from $[Ni(PCy_3)_2]_2$ - $(\mu - N_2)$ led us to examine other first-row transition-metal dinitrogen complexes. The compound $[Co(PEt_2Ph)_3]_2(\mu-N_2)$ reacts with liquid CO₂ to yield a highly air-sensitive red oil. The reaction is accompanied by the release of PEt₂Ph. The IR spectrum of the product displays intense bands at 1910, 1855, and 1715 cm⁻¹ and no evidence of OPEt, Ph formation. The red compound is paramagnetic, making NMR spectral measurements impossible. Exposure of the product to air converts it into a very insoluble purple solid containing $Co(CO_3)$, as judged by comparison of the IR spectrum with that of an authentic sample of $Co(CO_3)$ prepared from $Co(ClO_4)_2$ and Na_2CO_3 . The infrared bands at 1910 and 1855 cm⁻¹ might arise from carbonyl vibrations, and the band at 1715 cm⁻¹ could be assigned to a metal-carbonato vibration (compare the 1680 cm⁻¹ band in $Pt(CO_3)(PPh_3)_2^{18}$). The reductive disproportionation of CO_2 to CO and $CO_3^{2^2}$ has been observed previously in $[Mo(CO_3)(CO)(PMe_2Ph)_3]_2$,¹⁹ $[Ti(C_5 H_5)_2]_4(CO_3)_2^{20}$ and the reaction of Na[Fe(C₅H₅)(CO)₂] with CO_2 ²¹ The intermediacy of a C_2O_4 ligand, as observed in $IrCl(C_2O_4)(PMe_3)_3$ ²² is an attractive idea but has not been conclusively demonstrated for any system to date.

Similar chemistry was seen for $Na[Co(N_2)(PEt_2Ph)_3]$ in liquid CO₂. The starting metal complex displays a NN stretching frequency at 1840 cm⁻¹. This is absent in the reaction product, and new bands are present at 1974, 1910, and 1715 cm⁻¹. These can again be assigned to metal-carbonyl and metal-carbonate vibrations. No OPEt₂Ph was detected, and the compound again



Figure 1. ³¹P[¹H] NMR spectral changes observed upon adding CO₂ to a toluene- d^8 solution of Ni(N₂)(PCy₃)₂ and then cooling the Ni(CO₂)-(PCy₃)₂ solution that is formed.

decomposed in air to a purple solid containing $Co(CO_3)$.

The reaction of $[Ni(PCy_3)_2]_2(\mu-N_2)$ with $CO_2(g)$ was first reported to afford $[Ni(PCy_3)_2]_2(\mu-CO_2)$.¹⁴ Later, $Ni(\eta^2-CO_2)$. $(PCy_3)_2$ was isolated from this reaction, as characterized by a single-crystal X-ray diffraction study.³ We find that this complex may be prepared in high yield in liquid CO_2 . In N₂-saturated toluene solution, the equilibrium

$$[\text{Ni}(\text{PCy}_{3})_{2}]_{2}(\mu-\text{N}_{2}) \xrightarrow[-N_{2}]{+N_{2}}_{-N_{2}} 2\text{Ni}(\text{N}_{2})(\text{PCy}_{3})_{2}$$
(1)

is confirmed from the observation of an N-N stretching vibration.¹⁴ This vibration is absent in the solid-state IR spectrum, as expected for a symmetrical dimer. We have studied this equilibrium with the use of ${}^{31}P{}^{1}H$ NMR spectroscopy. The ³¹P{¹H} NMR spectrum of $[Ni(PCy_3)_2]_2(\mu-N_2)$ in toluene-d⁸ solution at 30 °C consists of a singlet at 46.5 ppm that is assignable to $Ni(N_2)(PCy_3)_2$. If argon is bubbled through the solution, N_2 is displaced, and a signal arising from $Ni(PCy_3)_2$ is observed at 44.2 ppm. When an N₂-saturated solution of $Ni(N_2)(PCy_3)_2$ is cooled, the resonance assigned to $[Ni(PCy_3)_2]_2(\mu-N_2)$ appears at 7.35 ppm. Even at -88 °C the equilibrium is not completely shifted to the left, and observable amounts of $Ni(N_2)(PCy_3)_2$ persist. There is a spectral change when CO_2 is bubbled through a solution of $[Ni(PCy_3)_2]_2(\mu-N_2)$ (Figure 1). The resonance arising from the starting material disappears, and a signal assigned to Ni(CO₂)(PCy₃)₂ is observed. At 30 °C the spectrum consists of a singlet at 36.16 ppm, but upon cooling the sample the signal coalesces at -50 °C and then sharpens into the expected doublet-of-doublets pattern for two mutually coupled inequivalent cis phosphine ligands (51.5, 20.0 ppm; $J_{PP} = 40.3$ Hz). The ΔG_c^4 for this exchange process is $9.8 \pm 0.2 \text{ kcal/mol.}^{23}$

Reactions with Wet CO₂. The presence of adventitious water has resulted in the misformulations of several "CO₂" compounds.²⁴⁻²⁸ Consequently, as we indicated above, if a given

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transition-metal complex appeared to react with dry $CO_2(1)$, we repeated the experiment with water deliberately added to the reaction mixture (M:H₂O = 1:1) to ascertain if the reaction was really occurring not with dry CO_2 but with wet CO_2 . As Table I indicates, we have found that both $Pt(PCy_3)_2$ and $W(CO)_3$ - $(PCy_3)_2$ react with wet CO_2 .

The compound $Pt(PCy_3)_2$, which is known to react with H_2O ,²⁹ reacts with wet CO₂ to produce trans-PtH(O₂COH)(PCy₃)₂. This formulation is based on IR, ¹H NMR, and ³¹P{¹H} NMR spectroscopy. The IR spectrum displays a Pt-H stretching vibration at 2240 cm⁻¹, together with a CO vibration at 1609 cm⁻¹ and an OH vibration at 2660 cm⁻¹ that may be assigned to the bicarbonato ligand. The ¹H NMR spectrum displays a signal at -23.59 ppm $(J_{\rm PH} = 14.2 \text{ Hz}, J_{\rm PtH} = 1178 \text{ Hz})$ assignable as the hydride resonance and a broad peak at 11.78 ppm attributable to the bicarbonato proton. The trans arrangement of the phosphine ligands is confirmed by the observation of a singlet at 39.91 ppm accompanied by ¹⁹⁵Pt satellites ($J_{PtP} = 2920 \text{ Hz}$) in the ³¹P{¹H} NMR spectrum. Two closely related compounds, *trans*-PtH- $(\eta^1-O_2COCH_3)(PCy_3)_2^{30}$ and trans-Pd(CH₃)(η^1-O_2COH)- $(PEt_3)_2^{27}$ are known.

We find that $W(CO)_3(PCy_3)_2$ reacts both with H_2O and with CO_2/H_2O mixtures. The product with H_2O is highly labile and reverts to $W(CO)_3(PCy_3)_2$ in a dry atmosphere or in vacuo. Since the compound is insoluble in hydrocarbon solvents and reacts with donor or chlorinated solvents, no NMR spectral measurements were possible. Its IR spectrum consists of two peaks in the v_{OH} region at 3635 and 3662 cm^{-1} and a series of bands at 1925, 1862, 1800, 1709, and 1678 cm⁻¹. Treatment of $W(CO)_3(PCy_3)_2$ with D_2O produces the deuterated analogue. Its IR spectrum lacks the bands at 3635, 3662, 1709, and 1678 cm^{-1} and displays new vibrations at 2718, 2698, 1696, and 1242 cm⁻¹. The question arises whether the complex is better formulated as $W(H_2O)(CO)_3$ - $(PCy_3)_2$ or as $WH(OH)(CO)_3(PCy_3)_2$. The IR vibrations expected for a metal-coordinated H_2O^{31} are a stretching mode below 3500 cm⁻¹ and a bending mode near 1600 cm⁻¹, both of weak intensity. For a hydrido-hydroxo complex, a M-OH stretching vibration above 3500 cm^{-1 31} and a M-H stretching mode should be observed. Thus, we believe the compound is WH(OH)- $(CO)_3(PCy_3)_2$. The two peaks in the ν_{OH} region probably arise from intermolecular interactions; two peaks are also seen for $Pt(CH_3)(OH)(PPh_3)_2^{32}$ and $Pd(OH)(CClCCl_2)(PPh_3)_2^{32}$. Deuteration again produces two bands in the v_{OD} region at 2718 and 2698 cm⁻¹ ($\nu_{OH}/\nu_{OD} = 1.35$). Assignment of the ν_{H} vibration can be made on the basis of a v_D band at 1242 cm⁻¹, assuming $v_{\rm H}/v_{\rm D} \sim 1.4$. The W-H vibration is then expected to be at ~ 1700 cm⁻¹. The hydride complex displays two bands in this region $(1709, 1678 \text{ cm}^{-1})$. The compound WH(OH)(CO)₃(PCy₃)₂ is a member of a small class of hydrido-hydroxo complexes formed by oxidative addition of H₂O. The compounds $PtH(OH)(P(i-Pr)_3)_2^{29}$ [RhH(OH)(en)₂]^{+,33} and Os₃H(OH)(CO)₁₀³⁴ have been reported. Addition of NaOH to RuHCl(PPh₃)₂ produces RuH- $(OH)(S)(PPh_3)_2^{35}$ (S = solvent). The reaction of Pt(PR_3)_3 (R = i-Pr, Et) with H₂O affords [PtH(PR₃)₃][OH] and [PtH(S)-

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 $(PR_3)_2$ [OH].²⁹ Likewise, RhH(P(*i*-Pr)₃)₃ oxidatively adds H₂O to afford $[RhH_2(S)_2(P(i-Pr)_3)_2][OH]$,³⁶ which can be isolated as the BPh₄⁻ salt.

Reaction of $WH(OH)(CO)_3(PCy_3)_2$ in liquid CO_2 produces $WH(O_2COH)(CO)_3(PCy_3)_2$, a labile bicarbonato complex, which in vacuo reverts to $W(CO)_3(PCy_3)_2$. The formulation as WH- $(O_2COH)(CO)_3(PCy_3)_2$ is made on the basis of the disappearance of the v_{OH} and v_{H} vibrations and the appearance of a new v_{H} vibration of 2010 cm⁻¹ and a ν_{O_2COH} vibration at 1615 cm⁻¹. Deuteration shifts these frequencies to 1380 and 1605 cm⁻¹, respectively. In both complexes there are bands at 1894, 1860, and 1795 cm⁻¹ in the CO stretching region. The OH stretching vibration could not be located for the bicarbonato ligand. These absorptions are usually broad and weak if there is any intermolecular hydrogen bonding.²⁸ There is no sign of insertion into the W-H bond. Other cases are known²⁸ in which insertion into M-OH bonds occurs preferentially over insertion into M-H bonds.

Discussion

Even under the forcing conditions of liquid CO_2 , with no solvent present and a CO₂:M ratio of perhaps 1000:1, most metal complexes examined remained unreactive toward CO₂. But in the course of this survey of the reactivity of some transition-metal systems toward $CO_2(l)$, several interesting reactions were found, as deduced from the nature of the products.

The formation of $IrR(OCO_3)(CO)(PPh_3)_2$ from $IrR(O_2)$ - $(CO)(PPh_3)_2$ is probably an example of external attack by CO_2 on a coordinated species. The compounds $IrR(O_2)(CO)(PPh_3)_2$ are coordinately saturated, and even if an open coordination site were provided by PPh_3 dissociation, CO_2 coordination to the iridium atom would seem unlikely because of the demonstrated inertness of $IrCl(N_2)(PPh_3)_2$ and $IrR(CO)(PPh_3)_2$ to CO_2 . Kinetic measurements for the reaction of hexafluoroacetone with IrCl- $(O_2)(CO)(PPh_3)_2^{37}$ to form $IrCl(O_2C(CF_3)_2O)(CO)(PPh_3)_2$ are consistent with a similar external attack mechanism for this reaction.

Similarly, the formation of $WH(O_2COH)(CO)_3(PCy_3)_2$ from $WH(OH)(CO)_3(PCy_3)_2$ and $CO_2(l)$ probably results from external attack of the CO₂ molecule on the W-OH linkage, as its seems unlikely that prior to insertion CO2 could coordinate to a sevencoordinate W atom. But the formation of trans-PtH- $(O_2COH)(PCy_3)_2$ from the reaction of $Pt(PCy_3)_2$ with wet $CO_2(1)$ could proceed through CO_2 attack on a *trans*-PtH(OH)(PCy₃)₂ intermediate, formed by oxidative addition of H_2O to $Pt(PCy_3)_2$, or by oxidative addition of H_2CO_3 to $Pt(PCy_3)_2$.

Spectroscopic evidence for CO and CO_3^{2-} in the products of the reactions of $[Co(PEt_2Ph)_3]_2(\mu-N_2)$ and $Na[Co(N_2)(PEt_2Ph)_3]$ with $CO_2(l)$ suggests that in these instances intermediate CO_2 complexes were formed. Such complexes, not stabilized by steric bulk, are open to attack by additional CO₂, ultimately leading to reductive disproportionation to CO and CO_3^{2-} . The use of steric bulk to stabilize highly reactive CO_2 complexes is clearly important.

But the results for the Ni triad provide the most dramatic illustration of the importance of electronic factors in CO₂ coordination. The compound $[Ni(PCy_3)_2]_2(\mu-N_2)$, which in solution is in equilibrium with $Ni(N_2)(PCy_3)_2$, readily forms the modestly stable compound Ni(η^2 -CO₂)(PCy₃)₂ with CO₂(g)³ or CO₂(l). It does not matter whether the CO_2 is dry or wet. The analogous Pd complex, $Pd(PCy_3)_2$, is unreactive toward either dry or wet $CO_2(l)$. And the complex $Pt(PCy_3)_2$, while unreactive toward dry $CO_2(l)$, reacts with wet $CO_2(l)$ to afford trans-PtH(O₂COH)- $(PCy_3)_2$.

Although the preparation of new, stable, isolable M-CO₂ complexes has not been realized in this initial study, we are encouraged by the ease with which we were able to prepare the known complex Ni(η^2 -CO₂)(PCy₃)₂ with CO₂(l), rather than $CO_2(g)$, and by the ease with which we were able to screen

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transition-metal systems for their reactivity toward CO2 through the use of $CO_2(l)$.

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Registry No. IrCl(N₂)(PPh₃)₂, 15695-36-0; IrMe(CO)(PPh₃)₂,

Fission Fragment Ionization Mass Spectrometry of Alamethicin I

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Abstract: Positive and negative Cf-252 fission fragment ionization spectra have been obtained for a natural and a synthetic sample of alamethicin I. The positive spectra of the two samples are identical to within an experimental error, and the negative spectra are identical except for the presence of a trace amount of impurity in the natural sample. The spectra provide strong evidence that the natural and synthetic samples are identical and thus that natural alamethicin I has the same structure as the known structure of the synthetic sample. The fragmentation occurring in the positive ion spectra is analyzed, and several series of sequence ions are identified. Reaction mechanisms producing the several series of sequence ions are suggested. Two of the sequence ions series involve addition of sodium ion to the alamethicin I molecule followed by fragmentation with retention of the sodium in the charged fragment.

Alamethicin $(ALA)^2$ is a peptide antibiotic produced by the fungus *Trichoderma viride.*³ The primary interest in alamethicin stems from the fact that it affects the electrical properties of artificial bilayer membranes.^{4,5} Some controversy has surrounded the elucidation of the structure of natural alamethicin,⁶ which is a mixture of closely related compounds. Using the solid-phase technique,⁷ one of us has recently concluded the chemical synthesis of the major component of alamethicin (ALA I) and has demonstrated identity of the synthetic with the natural product.⁸

Rinehart and co-workers9 have made an extensive investigation of alamethicin using various mass spectrometric procedures, and their work provides strong evidence concerning the amino acid sequences in alamethicin I and II. Our main analytical goal in the work reported here is to demonstrate by fission fragment ionization mass spectrometry that separated and purified alamethicin I from natural sources is identical with synthesized alamethicin I. Such a comparison provides further evidence about the structure of natural alamethicin I. Fission fragment ionization

mass spectrometry^{10,11} has been little used for the determination of the identity and structure of peptides, and consequently we give the results of our findings. In addition, we present details of the novel and interesting ionic chemistry giving rise to the observed spectra.

At present there exists only a very limited set of published data on polypeptides using fission fragment ionization mass spectrometry¹⁰⁻¹² or the related ionization techniques involving bombardment by keV ions¹³ and intense laser pulses.¹⁴ Macfarlane and co-workers have given in the open literature the spectra of two peptides, β -endorphin¹² and gramicidin A.¹⁰ The spectrum of the 31-residue peptide β -endorphin covers the mass range from 900 to the quasi-molecular ion region at m/z 3487 ((M + Na)⁺). This spectrum is remarkable in that a distinct $(M + Na)^+$ ion is observed (signal to noise fluctuation ratio of approximately 20:1), while virtually no fragmentation is seen above m/z 900. The hints of fragment ion peaks that are to be seen have very low signal to noise fluctuation ratios ($\sim 1:1$). The spectrum given for gramicidin A (15 residues) is restricted to the molecular ion region where $(M + Na)^+$ ions at m/z 1904 and 1918, respectively, are observed for the two variants studied. Macfarlane and co-workers also describe¹⁰ certain aspects of the spectra of γ -glutathione (six residues) and a series of di- and tripeptides.

Positive and negative mass spectra for the tripeptide Ala-Ala-Ala have been obtained in this laboratory.¹¹ Quasi-molecular ions are observed in the positive ion spectrum, and the fragmentation is representative of the peptide structure. By contrast,

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⁽²⁾ Abbreviations: ALA, alamethicin; Aib, α -aminoisobutyric acid; Phol, phenylalaninol.

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