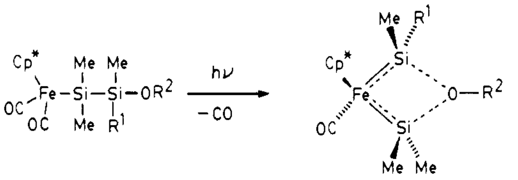
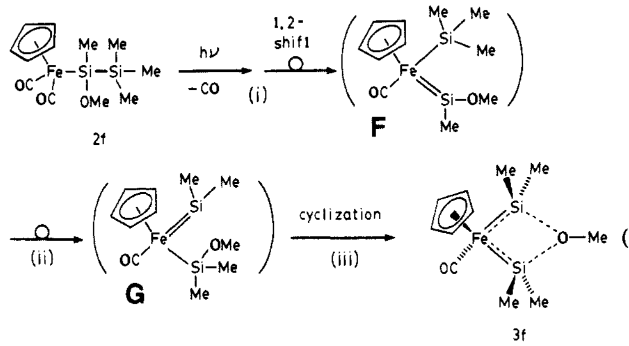
only one product **3e** was obtained from the photolysis of (di-*tert*-butoxydisilanyl)iron complex **2e**, in contrast to the formation of two geometric isomers, **3b** and **3b′**, from the photolysis of **2b**. The structure of **3e** is assignable to the less sterically hindered isomer shown in eq 2.



(2)

2a, 3a: Cp* = Cp′; R¹ = R² = Me
2c, 3c: Cp* = Cp′; R¹ = Me; R² = Bu^t
2d, 3d: Cp* = Cp; R¹ = Me; R² = Bu^t
2e, 3e: Cp* = Cp; R¹ = OBu^t; R² = Bu^t



(3)

The mechanism for the photoreactions of **2a**, **2c**, **2d**, and **2e** is considered to be similar to that of **2b** (Scheme I). However, for the formation of **3f** from **2f**, migration of a methyl group from one silicon atom to another is required to yield two $SiMe_2$ moieties. Such migration of substituents on silicon atoms has already been noted in the photochemical conversion of $CpFe(CO)_2SiR_2SiR_3$ (R = alkyl, aryl) to $CpFe(CO)_2SiR_3$ and it has been proposed that such migration occurs in silyl(silyene)iron intermediates.[6,7] Thus, **3f** is formed from **2f** via methyl group migration in the silyl(silylene)iron intermediate (eq 3) in the following manner: (i) formation of a silyl(methoxysilylene)iron intermediate F; (ii) methyl group migration from the silyl group to the silylene ligand; formation of a methoxysilyl(silylene)iron intermediate G; and (iii) cyclization to form **3f**.

The bis(silylene)iron complexes, **3a**, **3c**, **3d**, **3e**, and **3f**, as well as **3b** and **3b′**, show ^{29}Si NMR signals at very low field (90–125 ppm; see Table I). Particularly, each of the photolytic products, **3a**, **3c**, **3d**, and **3f**, which were derived from (monoalkoxydisilanyl)iron complexes, gives only one signal at low field, exemplified by the spectrum of **3a** in Figure 3. The result indicates that the two silicon atoms in each starting complex become equivalent in the corresponding product and is consistent with the structure of the alkoxy-stabilized bis(silylene)iron complex.

There are some other characteristic spectral differences between the starting materials and the products (Table I). As stated above for **2b**, **3b**, and **3b′**, the ^1H NMR signals assigned to the bridged alkoxy groups in the bis(silylene)iron complexes appear at appreciably high field compared to those for the terminal alkoxyl groups of the starting materials. The chemical shift difference amounts to approximately 0.8 ppm for the methoxy-bridged complexes, **3a** and **3f**, and 0.2 ppm for the *tert*-butoxy-bridged complexes, **3c**, **3d**, and **3e**. The IR spectrum of each of the bis(silylene)iron complexes shows only one terminal ν_{CO} band below 1900 cm^{-1} consistent with the structure with a single CO ligand.

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Note Added in Proof. After this paper was submitted for publication, there appeared a paper by K. H. Pannell et al. (*J. Am. Chem. Soc.* **1989**, *111*, 4482) that is closely related to the work of refs 6 and 7.

Supplementary Material Available: Tables of fractional coordinates and thermal parameters for **3b** (2 pages); observed and calculated structure factors for **3b** (9 pages). Ordering information is given on any current masthead page.

Effects of Redox Potential, Steric Configuration, Solvent, and Alkali Metal Cations on the Binding of Carbon Dioxide to Cobalt(I) and Nickel(I) Macrocycles

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Abstract: The binding of CO_2 to metal macrocycles has been determined electrochemically by using cyclic voltammetry or differential pulse polarography. The CO_2 binding constants, K_{CO_2}, for a series of Co(I) tetraazamacrocycle complexes in $(CH_3)_2SO$ showed a strong correlation with the Co(II/I) redox potential. Although meso and *d,l* stereoisomers of $[Co^I(Me_6[14]4,11\text{-diene})]^+$ had identical redox potentials, K_{CO_2} differed by a factor of 10^2 for these stereoisomers, suggesting a large steric effect on CO_2 binding. Binding of CO_2 to Ni(I) tetraazamacrocycles in $(CH_3)_2SO$ yielded a redox potential dependence similar to that of Co(I) macrocycles. A weak correlation between K_{CO_2} and the solvent dielectric constant was found for *d,l*-$[Co(Me_6[14]\text{-}4,11\text{-diene})]^+$. In tetrahydrofuran (THF), *d,l*-$[Co(Me_6[14]4,11\text{-diene})]^+$ was found to bind CO_2 more strongly in the presence of 0.1 M Li^+ than in the presence of 0.1 M tetrabutylammonium (TBA^+). Electrochemically determined K_{CO_2}'s for $Co(salen)^-$ and $Co(Me_2salen)^-$ in THF indicated a strong dependence on redox potential and electrolyte cation.

Much recent work has been focussed on the catalytic activation of CO_2,[1,2] including many electrocatalytic schemes involving macrocyclic complexes of cobalt and nickel.[3,4] Although several mechanistic studies have been performed on thermal CO_2 acti-

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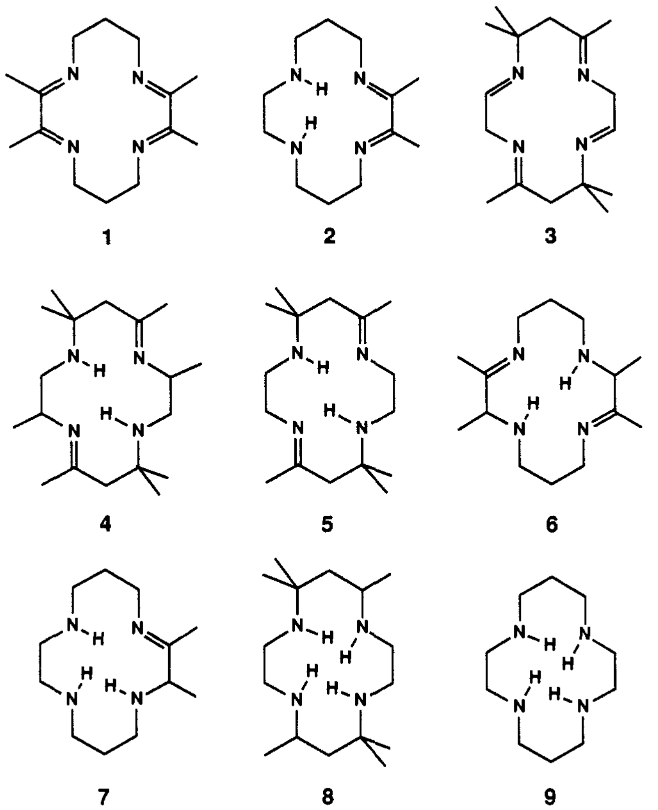

Figure 1. Macrocyclic ligands used in this study: **1** = Me$_4$[14]-1,3,8,10-tetraene, **2** = Me$_2$[14]1,3-diene, **3** = Me$_6$[14]1,4,8,11-tetraene, **4** = Me$_8$[14]4,11-diene, **5** = Me$_6$[14]4,11-diene, **6** = Me$_4$[14]1,8-diene, **7** = Me$_2$[14]1-ene, **8** = Me$_6$[14]ane, **9** = [14]ane or cyclam.

vation processes,[1,2] there have been only a few detailed studies of possible mechanistic steps in the electrocatalytic activation of CO_2.[5,6] In particular, although CO_2 binding to metal complexes has received much attention,[7-9] relatively little quantitative information is available on the factors influencing the binding of CO_2 to transition-metal complexes.[10,11] Trends in CO_2 binding strength as a function of the metal basicity,[8a,12] the steric properties of the coordinated ligands,[4] and the presence of additional Lewis acid sites in the medium[8a,b,13] are of particular interest, since these factors have been invoked to explain the wide variety of reaction pathways observed in CO_2 activation processes. To address these issues in a quantitative fashion, we have determined the CO_2 binding constants (K_{CO_2}) for a series of structurally similar Co(I) and Ni(I) macrocycles and have also examined the effects of solvent and electrolyte on the binding of CO_2 to Co(I) macrocycles and salen complexes.

Our work has focussed on tetraazamacrocycle complexes of Ni and Co because these complexes have been used in schemes for the catalytic reduction of CO_2 to CO.[3,4] CO_2 binding by $[Co(\mathbf{5})]^+$ (**5** = Me$_6$[14]4,11-diene, see Figure 1) has been observed previously.[10,11] A K_{CO_2} of 7×10^4 M^{-1} for CO_2 binding to this complex was obtained electrochemically in 0.1 M tetrabutylammonium perchlorate (TBAClO$_4$) in $(CH_3)_2SO$,[10] while a K_{CO_2} of 1.2×10^4 M^{-1} was measured in acetonitrile by using spectroscopic methods.[11] Additionally, pulse radiolysis studies of $[Co(\mathbf{5})]^+$ in aqueous solution have suggested a binding constant of 1.6×10^8 M^{-1} for this complex.[6] The strong binding of CO_2 to this Co macrocycle complex and the existence of many similar macrocycle complexes provided an excellent opportunity to explore CO_2 binding as a function of redox potential, solvent properties, and ligand structure.

Studies by Floriani and co-workers of Co(salen)$^-$ and related complexes indicated that the stability of CO_2 adducts of these complexes was influenced by the nature of the alkali metal cation present.[8] The Co(7,7′-diethylsalen)Li(CO_2) complex was found to be the most stable in the solid state, since it did not lose CO_2 in vacuo or in the air. This was in contrast to the $[Co(7,7'\text{-dipropylsalen})K(CO_2)(THF)]_n$ complex, which had to be crystallized and studied while under a CO_2 atmosphere. The exceptional stability of the Li$^+$ complexes, however, seemed to be limited to the solid state; in solution, complexation seemed to be favored by

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Na^+ and K^+ ions. These observations have prompted our attempts to quantify the effects of electrolyte cation on K_{CO_2} in THF solutions.

Experimental Section

All compounds were synthesized according to literature procedures. Ligand **5** was synthesized as the $HClO_4$ salt.[14] The *d,l* Co complex of this ligand was prepared in methanol by using an excess of ligand to maintain solution acidity and prevent isomerization.[15] The meso diastereomer was prepared in CH_3CN.[16] Product recovery from the CH_3CN preparation was difficult, and recrystallization from CH_3CN resulted in substantial product loss unless performed anaerobically. Metathesis of this complex with aqueous NH_4PF_6 yielded the *meso*-$[Co(\mathbf{5})][PF_6]_2$. This product could be more easily recrystallized and was used in preliminary studies. The *d,l*-$[Co(\mathbf{5})][CF_3SO_3]$ salt was synthesized because it dissolved more rapidly in THF. This product was made by dissolving the *d,l* ClO_4^- salt in acetonitrile and adding an excess of $K(CF_3SO_3)$. $KClO_4$ precipitated, and the filtrate was reduced to dryness under vacuum. Addition of THF dissolved the $[Co(\mathbf{5})][CF_3SO_3]$ while leaving most of the $K(CF_3SO_3)$ undissolved. Filtration, evaporation, and redissolution in THF were repeated until orange crystals of the $[Co(\mathbf{5})][CF_3SO_3]_2$ could be isolated independently of the colorless $K(CF_3SO_3)$ crystals.

Complexes of **4**,[17] **2**,[18] **3**,[19] **1**,[20] **6**, and **7**[21] were prepared according to published procedures. Dihalo complexes of **2** and **7** were prepared and converted to the bis-acetonitrile complexes before performing electrochemical measurements on these complexes.[22] Salen complexes were prepared according to literature procedures.[23] Ni complexes of ligand **9** were obtained from Bryan Balazs of Caltech.

All electrolytes were dried at > 80 °C in vacuo (<0.1 mmHg) for at least 12 h, except for $LiClO_4$, which was fused in a quartz tube at 270–300 °C in vacuo. $TBA(ClO_4)$ (Southwestern Analytical) was ground to a fine powder before drying. $TBA(CF_3SO_3)$ was made by neutralization of dilute CF_3SO_3H with TBA(OH). Recrystallization of this complex was accomplished by dissolving the salt in a minimum of acetonitrile or acetone, adding a large excess of water (ca. 15 volumes), and boiling for several hours to remove the volatile organic solvent. After the solution cooled overnight, a crystalline product formed and was isolated by filtration. Alkali metal $CF_3SO_3^-$ salts were synthesized by neutralization of dilute CF_3SO_3H by the appropriate hydroxide, followed by evaporation of water under vacuum on a rotary evaporator. These salts were dried without recrystallization. $Li(CF_3SO_3)$ was obtained from Aldrich.

All electrochemistry was performed in dried solvents. Dimethyl sulfoxide and dimethylformamide were stirred over CaH_2 for ca. 12 h, vacuum distilled, and stored under dry N_2. Due to the rapid decomposition of dimethylformamide, it was used within 48 h of distillation. Propylene carbonate was stirred and heated over $KMnO_4$ and Na_2CO_3, vacuum distilled, and used shortly after distillation. THF was distilled over Na/benzophenone under a dry N_2 atmosphere. The acetonitrile used in UV–visible spectroscopy was distilled under dry N_2 from CaH_2 or P_2O_5.

Electrochemistry was performed on 5-mL samples in a two-necked, 50-mL pear-shaped flask. A reference electrode (0.1 M $TBA(ClO_4)$, CH_3CN, Ag wire, ca. 0.001 M $AgCF_3SO_3$) with a ground glass joint and a Vycor frit was fitted to one neck; the other neck was fitted with a rubber septum accommodating working and counter electrodes and gas intake and exhaust needles. The working electrode in all cases was basal plane pyrolytic graphite (0.02–0.10 cm^2) which was sealed in white epoxy (Hysol). A Pt mesh counter electrode was used. After binding constants were measured, dry, sublimed ferrocene was added to the solution, in order to determine values of $E^{\circ\prime}$ relative to this internal reference by cyclic voltammetry of both the ferrocene and the complex of interest. Because the ferrocene/ferricinium couple appears near the $Co(salen)^{0/+}$ and $Co(dimethylsalen)^{0/+}$ couples, decamethylferrocene was used as a reference for these complexes. The Co macrocycle and Co salen complexes were used in concentrations between 5×10^{-4} and 5×10^{-3} M.

A flow of N_2 or CO_2 was maintained to the cell at all times. For determinations of K_{CO_2}, N_2 and CO_2 gases were mixed in a simple glass tee, with >0.5 m of tubing between the tee and the needle entering the cell. For some experiments, gases were passed through a deoxygenating column (Ridox, Fisher Scientific) and a drying column (3 Å molecular sieves, Davison) before entering the cell. These columns had no observable effect on the electrochemistry. The columns were not used for most experiments, because the sieves retained CO_2 and long purges of the columns were necessary to reestablish a nitrogen atmosphere after using CO_2.

For experiments involving THF, the gases were presaturated with THF vapor in a gas-washing bottle to prevent evaporation of the solvent in the electrochemical cell. The vapor-saturated gas was conducted to the cell in $^1/_4$ in. automobile fuel line, which was found to be more resistant to THF vapor than Tygon tubing. After the CO_2/N_2 mixture was adjusted, the tip of a syringe needle was immersed in the solution, and the solution was sparged with the new gas mixture for at least 10 min before taking electrochemical measurements. The cell headspace was then sampled with a gastight syringe (Precision Scientific) to determine the CO_2 partial pressure. These samples were injected into a gas chromatograph designed for gas analysis (Carle). The integrated response (HP 3390A integrator) was found to be linear for CO_2/N_2 mixtures from 0.02 to 1.0 mol fraction CO_2. Sparging all CO_2 from the solution took much longer (approximately 1 h for most solvents) than it took to saturate the solutions with CO_2. Because of the slow displacement of CO_2, measurements with less than 1 atm of CO_2 were taken by increasing the CO_2 partial pressure by steps until 1 atm was reached. The cell was then sparged with N_2, and $E^{\circ\prime}$ was remeasured.

Solubility coefficients for CO_2 in various solvents were obtained by titration of electrolyte solutions saturated wiih CO_2.[24] One milliliter aliquots of the CO_2-saturated electrolyte solutions were added to 10 or 20 mL of a standardized 0.05 M $Ba(OH)_2$ solution to precipitate the CO_2 as $BaCO_3$. The solution was then back-titrated with a standardized 0.1 M HCl solution, by using *m*-cresol purple as the indicator. The saturation concentration of CO_2 in $(CH_3)_2SO$ was found to be higher than that reported in ref 25, which was the value used in previous determinations of K_{CO_2} for $[Co(\mathbf{5})]^+$.[10]

Determination of the saturation concentration of $[CO_2]$ in propylene carbonate could not be performed as described above due to hydrolysis of the solvent by the $Ba(OH)_2$. The amount of CO_2 dissolved in a saturated solution was determined by degassing a sample under vacuum and measuring the volume of gas liberated with a Toepler pump. The value achieved by this method was very close to the value obtained by removing the CO_2 under vacuum with several freeze–pump–thaw cycles and weighing the amount of liberated CO_2 by condensing it into a tared flask cooled with liquid nitrogen.

Electrochemistry was performed using a PAR Model 174A polarographic analyzer or other standard electrochemical instrumentation. Voltammograms were recorded using Houston Instruments Model 2000 recorders.

UV–visible spectra were taken by using a Hewlett-Packard Model 8452A diode array spectrophotometer. Infrared spectra were taken by using a Perkin-Elmer 1600 series fourier transform infrared spectrophotometer. IR spectra were obtained as mineral oil mulls on NaCl plates.

Results

In this study, binding constants of CO_2 to Co and Ni complexes, K_{CO_2}, were determined by measuring the shift in the half-wave potential, $E_{1/2}$, as a function of $[CO_2]$. This approach relies on the following relationship derived from the Nernst equation and the equilibrium constant expression for K_{CO_2}:[10,26]

$$M^{I}\text{-}L + qCO_2 \rightleftharpoons M^{I}\text{-}L(CO_2)_q$$

$$E_{1/2} = E^{\circ\prime} + \frac{RT}{nF}\ln(K_{CO_2}) + q\frac{RT}{nF}\ln[CO_2]$$

where q is the number of CO_2 molecules binding to each metal center. Cyclic voltammetry of the metal complexes indicated that the diffusion coefficients of the oxidized and reduced forms were sufficiently close so that $E_{1/2}$ in the absence of CO_2 could be used

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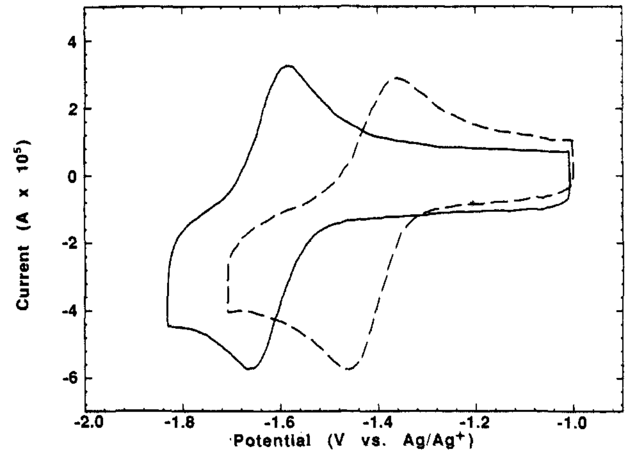

Figure 2. Cyclic voltammetry of $[Co(\mathbf{1})]^{2+/+}$ in $(CH_3)_2SO$–0.1 M $TBA(ClO_4)$: solid line under N_2 atmosphere and dashed line $[CO_2]$ = 0.132 M. Potential measured vs Ag/Ag$^+$ reference, approximately −0.14 V vs ferrocene/ferrocinium.

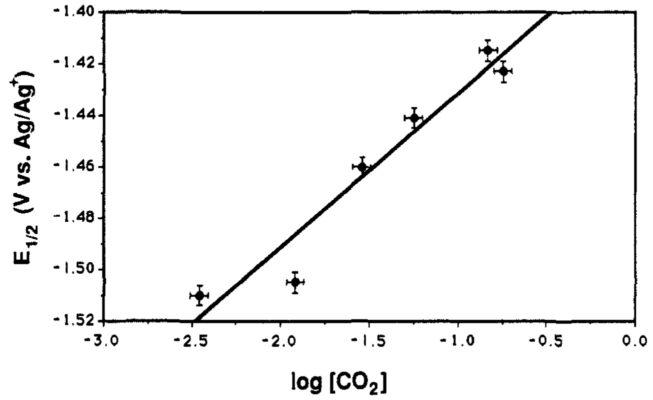

Figure 3. A plot of $E_{1/2}$ vs $[CO_2]$ for $[Co(\mathbf{1})]^{2+/+}$ in dimethylformamide/0.1 M $TBA(ClO_4)$. The least-squares line through the data points shown has a slope = 59 mV/decade $[CO_2]$.

as $E^{\circ\prime}$ in the above equation. Cyclic voltammetry and differential pulse polarography were both used to determine the shift in $E_{1/2}$, and the results for the two techniques were generally in good agreement. Linear plots of $E_{1/2}$ vs $[CO_2]$, with slopes of 59 ± 5 mV, were obtained for all complexes that bound CO_2 reversibly with $K_{CO_2} > 100\ M^{-1}$. This indicated that only one CO_2 molecule was binding to each metal center. The voltammetry of $[Co(\mathbf{1})]^{2+/+}$ in dimethyl sulfoxide/0.1 M $TBA(ClO_4)$ in the presence and absence of CO_2 is shown in Figure 2, and a plot of $E_{1/2}$ vs $[CO_2]$ for this couple in dimethylformamide/0.1 M $TBA(ClO_4)$ is shown in Figure 3.

The K_{CO_2} values for binding constants presented herein are based on the maximum shift in $E_{1/2}$ at a saturation concentration of CO_2, assuming an ideal slope of 59 mV. This method of calculating binding constants is more accurate than using a best-fit line because it utilizes the most reliable measurements of $[CO_2]$ and is not sensitive to small variations in the $E_{1/2}$ vs $[CO_2]$ slope. The ease of measuring the shift in $E^{\circ\prime}$ at saturation also allows for more determinations of K_{CO_2}, increasing confidence in the measurements. The greatest uncertainty in the reported values for K_{CO_2} results from the uncertainty in the measurement of redox potentials by cyclic voltammetry (±5 mV). Uncertainties reported in the tables are generous estimates based on the spread of experimental values.

For complexes with $K_{CO_2} < 100\ M^{-1}$, the assumption used in the derivation of eq 3, that $K_{CO_2}[CO_2] \gg 1$, is no longer valid. In these cases, an expression for the redox potential change for a given $[CO_2]$ was used to derive K_{CO_2} from the $E_{1/2}$ measured in a CO_2-saturated solution, with q assumed to be 1:

$$E_{1/2} = E^{\circ\prime} + \frac{RT}{nF} \ln (K_{CO_2}[CO_2] + 1)$$

Table I. Binding Constants, K_{CO_2}, of CO_2 to Co and Ni Tetraazamacrocycles in $(CH_3)_2SO$/0.1 M $TBA(ClO_4)$

complex	ligand	$E^{\circ\prime}$ $(M^{II/I})^a$	K_{CO_2}, M^{-1}
$[Co(Me_4[14]1,3,8,10\text{-tetraene})]^+$	**1**	−0.76	$<4^b$
$[Co(Me_2[14]1,3\text{-diene})]^+$	**2**	−1.31	$<4^b$
$[Co(Me_6[14]1,4,8,11\text{-tetraene})]^+$	**3**	−1.42	<4
$[Ni(Me_6[14]ane)]^+$	**8**	−1.69	<4
$[Co(Me_8[14]4,11\text{-diene})]^+$	**4**	−1.70	7 ± 5
meso-$[Co(Me_6[14]4,11\text{-diene})]^+$	**5**	−1.74	$(2.6 \pm 0.5) \times 10^2$
d,l-$[Co(Me_6[14]4,11\text{-diene})]^+$	**5**	−1.74	$(3.0 \pm 0.7) \times 10^4$
$[Co(Me_4[14]1,8\text{-diene})]^+$	**6**	−1.80	$(1.0 \pm 0.3) \times 10^5$
$[Ni([14]ane)]^+$	**9**	−1.89	irreversible
$[Co(Me_2[14]1\text{-ene})]^+$	**7**	−2.00	irreversible

[a] Measured vs ferricinium/ferrocene internal reference. [b] An irreversible reaction with CO_2 occurs upon reduction to Co^0.

The ligands used in this study (Figure 1) were selected because they provided a wide variation in redox potential, implying a wide variation in electron density on the metal center. Binding constants, K_{CO_2}, were measured for these complexes in $(CH_3)_2SO$ solution, with $TBA(ClO_4)$ (TBA = tetrabutylammonium) as the supporting electrolyte (Table I). The complexes used all displayed reversible electrochemistry under these conditions. The reported values for K_{CO_2} in Table I are means of two or more independent determinations. These data suggest that metal basicity, as reflected in the $Co^{II/I}$ redox potential, has a large influence on CO_2 binding. From Table I it can be seen that no detectable binding was observed for complexes with $E^{\circ\prime} > -1.70$ V vs the ferrocene/ferricinium couple $(Fc^{+/0})$.

The complex with the most negative redox potential, $[Co(\mathbf{7})]^{2+/+}$, yielded irreversible voltammetric behavior. Shifts of 250–300 mV in the cathodic peak were observed for this complex, but no anodic current peak was observed. This behavior could represent irreversible CO_2 binding, in which case the cathodic peak shift is determined by the rate at which CO_2 is bound, and the rate of CO_2 loss is too slow to establish equilibrium concentrations of the bound and unbound species during the anodic scan. This would eliminate anodic current, since the CO_2-bound species probably oxidizes at a much more positive potential. However, no anodic peak other than the $Co^{III/II}$ peak was observed under CO_2 in the potential window (−2.0 to +0.5 V vs $(C_5H_5)_2Fe^{+/0}$) of the $(CH_3)_2SO$ solvent.

Another possible explanation for the lack of reversibility would be the subsequent chemical reaction of the CO_2-bound species to another product which cannot be oxidized in the accessible potential window. One possibility is the reductive disproportionation of the CO_2 adduct to form a bound CO complex and free CO_3^{2-}, a reaction which has been observed with the $[Co(\mathbf{5})]^+$ complex.[11] This possibility can be eliminated on the basis of cyclic voltammetry of $[Co(\mathbf{7})]^+$ under CO, which shows reversible oxidation and reduction waves >500 mV positive of the waves observed under N_2. This indicates strong binding of CO to the Co^I species and also suggests that the oxidation of $[Co(\mathbf{7})(CO)]^+$ should be easily observed in the CO_2 voltammograms if $[Co(\mathbf{7})(CO)]^+$ were the product of the reaction with CO_2. Catalytic reduction of CO_2 can also be eliminated as a reason for the observed voltammetric response because the cathodic current peak is the same height under CO_2 as under N_2.

In this study, the meso and *d,l* diastereomers of $[Co(\mathbf{5})]^{2+}$ were identified by UV–visible spectra of CH_3CN solutions and by solid-state IR spectra of the ClO_4^- salts. The spectral features of the two diastereomers have been identified by Szalda et al.:[27] a UV maximum at 310 nm for the *d,l* isomer and a maximum at 322 nm for the meso isomer, and IR peaks at 1308 cm^{-1} for the *d,l* isomer and 1300 cm^{-1} for the meso isomer. UV–visible spectra of the compounds used in this study showed peaks at 312 nm for the *d,l* isomer and 320 nm for the meso isomer; additionally, IR peaks were observed at 1305 cm^{-1} for the *d,l* isomer and 1298 cm^{-1} for the meso isomer. Complexes having the *d,l*

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(27) Szalda, D. J.; Schwarz, C. L.; Endicott, J. F.; Fujita, E.; Creutz, C. *Inorg. Chem.* **1989**, *28*, 3214.

Table II. Binding Constants of CO_2 to *d,l*-[Co(**5**)]$^+$ in a Variety of Solvents[d]

solvent	$E^{\circ\prime a}$ (V)	[CO_2] (M)	K_{CO_2} (M^{-1})	K_g	$\epsilon/\epsilon_0{}^b$
propylene carbonate	−1.54	0.14	$(4.0 \pm 0.7) \times 10^4$	$(5.6 \pm 0.7) \times 10^3$	64.4
dimethyl sulfoxide	−1.74	0.132	$(3.0 \pm 0.7) \times 10^4$	$(4.0 \pm 0.8) \times 10^3$	46.7
dimethylformamide	−1.77	0.175	$(1.8 \pm 0.6) \times 10^4$	$(3.2 \pm 0.7) \times 10^3$	36.7
acetonitrile	−1.74	0.28[c]	$(1.2 \pm 0.5) \times 10^{4}$[c]	$(3.4 \pm 1.4) \times 10^{3}$[c]	37.5
tetrahydrofuran					
0.10 M TBA(ClO_4)	−1.77	0.211	$(3.0 \pm 0.8) \times 10^3$	$(6.3 \pm 1.6) \times 10^2$	7.6
0.50 M $TBACF_3SO_3$	−1.78	0.167	$(2.7 \pm 1.3) \times 10^3$	$(4.5 \pm 0.5) \times 10^2$	
0.50 M $LiCF_3SO_3$	−1.75	0.181	$(1.0 \pm 0.2) \times 10^4$	$(1.8 \pm 0.3) \times 10^3$	

[a] Measured vs ferricinium/ferrocene internal reference. [b] From Sawyer, D. T.; Roberts, J. L., Jr. *Experimental Electrochemistry for Chemists*; Wiley: New York, 1974; pp 204–205. [c] From ref 11. No electrolyte was used. [d] K_{CO_2} is with respect to the concentration of dissolved CO_2, while K_g is with respect to 1 atm of CO_2(g). Electrolyte is 0.10 M TBA(ClO_4) except where noted.

configuration were found to bind CO_2 over two orders of magnitude more strongly than those having the meso configuration (Table I).

CO_2 binding properties of two Ni macrocycles in $(CH_3)_2SO$–0.10 M TBA(ClO_4) were also investigated. The voltammetry for [Ni(**9**)]$^+$ ($E^{\circ\prime} = -1.89$ V) was similar to that observed for [Co(**7**)]$^+$, suggesting irreversible binding of CO_2 to this complex, while [Ni(**8**)]$^+$ ($E^{\circ\prime} = -1.69$ V) showed no observable binding ($K_{CO_2} < 4$ M^{-1}). Once again, a redox potential threshold for CO_2 binding between −1.7 and −1.9 V vs $Fc^{+/0}$ is evident from these data.

The influence of solvent on the binding of CO_2 to [Co(**5**)]$^+$ was investigated by using the aprotic solvents shown in Table II. The values of K_{CO_2} presented in this table are means of at least two K_{CO_2} determinations. Somewhat irreversible voltammetric behavior was noted when propylene carbonate was the solvent, so the binding constant in this solvent was based on the shift of the cathodic peak rather than the average of the cathodic and anodic current maxima. The value obtained may therefore be higher than the true value, since equilibrium concentrations of the Co^I and Co–CO_2 species may not be established. The value for acetonitrile was taken from ref 11, because electrochemistry in this solvent was quite irreversible, which precluded an accurate electrochemical measurement of K_{CO_2}. The value obtained in this work for K_{CO_2} in $(CH_3)_2SO$ is somewhat smaller than that reported in ref 10, due to a revised value for the solubility of CO_2 and due to our use of the redox potential data at CO_2(g) saturation as the primary measure of K_{CO_2}.

The effect of electrolyte cation on K_{CO_2} in $(CH_3)_2SO$ was investigated by remeasuring K_{CO_2} for the meso and *d,l* diastereomers of [Co(**5**)]$^+$ by using 0.1 M $LiClO_4$ as the electrolyte in $(CH_3)_2SO$. The values obtained for K_{CO_2} under these conditions were identical within experimental error to those obtained with TBA(ClO_4) as the electrolyte, indicating that solution cations have little or no influence on the binding of CO_2 to these complexes in $(CH_3)_2SO$.

In contrast to these results, a cation effect on K_{CO_2} for *d,l*-[Co(**5**)]$^+$ was found when THF was the solvent. In this solvent, a higher binding constant was observed when Li(CF_3SO_3) was used as the electrolyte than when TBA(CF_3SO_3) was used (Table II).

In order to quantify the effects of alkali metal cations on Co(salen) complexes observed by Floriani and co-workers,[8b] the CO_2 binding constants of Co(salen)$^-$ and Co(dimethylsalen)$^-$ were measured in different electrolytes. Initial attempts to measure binding in $(CH_3)_2SO$ solution indicated $K_{CO_2} < 4$ M^{-1} with Na^+, Li^+, and TBA^+ electrolytes. In THF, however, substantial CO_2 binding constants could be obtained for both complexes, Table III, and these binding constants indicate a strong dependence on electrolyte cation. In addition, a correlation between $Co^{II/I}$ redox potential and K_{CO_2} was found. This is in contrast to the assertion by Floriani et al. that substitution on the salen has little or no effect on CO_2 binding.[8b] The $E^{\circ\prime}$ values reported for these complexes were measured vs decamethylferrocene$^{+/0}$ but are expressed vs ferrocene/ferricinium for the purpose of comparison with the other data obtained in this work.

Discussion

1. Redox Potential. The large variation in redox potentials that can be obtained with simple metal tetraazamacrocycles make these complexes an ideal system for studying the effect of metal basicity on CO_2 binding.[22,28] Ligand unsaturation affects the redox potential by providing π systems for delocalization of electron density onto the macrocycle, thus stabilizing the Co^I state. Conjugated unsaturation provides for even greater electron delocalization onto the ligand.[22] Methyl substituents on the macrocycle can also affect the redox potential by inductive effects or by steric interactions with the axial ligands.[22] The results reported above demonstrate that CO_2 binding is strongly dependent on the metal basicity as reflected by the $Co^{II/I}$ potential. This suggests that the CO_2 is bound through the carbon, in agreement with other structurally characterized complexes of Co^I containing CO_2 ligands.[8,11]

A redox potential threshold for CO_2 binding to the Co macrocycles occurs at ≈−1.70 V vs ferrocene/ferricinium, which corresponds to −1.40 V vs the saturated calomel electrode or −1.16 V vs the normal hydrogen electrode. A similar threshold is seen for the Ni complexes. Co(salen) complexes bind CO_2 at more positive potentials, probably as the result of greater participation by alkali-metal cations in binding. Nevertheless, all of these potentials are considerably negative of the thermodynamic potentials for conversion of CO_2 to CO ($E^{\circ\prime} = -0.52$ vs NHE), CH_3OH ($E^{\circ\prime} = -0.38$), or other products.[3h] This suggests that initial CO_2 binding to the metal center is not a favorable mechanism for energy-efficient CO_2 reduction with cobalt macrocycle catalysts.

2. Steric Configuration. The *d,l* and meso diastereomers of [Co(**5**)]$^{2+}$ differ in the configuration at the two saturated nitrogens of the macrocycle.[29] In the *d,l* complex, the axial geminal methyl groups on the six-membered rings are both on the same face of the macrocycle, and the amine hydrogens are on the opposite face. In the meso diastereomer, each face of the macrocycle has one axial geminal methyl group and one amine hydrogen.

It is difficult to determine the reason for the stereosensitivity of K_{CO_2} for [Co(**5**)]$^+$ without X-ray diffraction data for both diastereomers of the CO_2 adduct. Nevertheless, X-ray diffraction data of the μ-CO_2 dimer of the *d,l* diastereomer isolated by Fujita et al. indicates hydrogen bonding between one of the amine hydrogens and a CO_2 oxygen.[11] Similar hydrogen-bonding interactions might explain the greater stability of the CO_2 complex of the *d,l* diastereomer, since both of the amine hydrogens are on the same face of the macrocycle in this diastereomer. These results suggest the possibility of introducing acidic hydrogens into complexes with more positive potentials to increase H-bonding interactions and thus stabilize CO_2 adducts. Steric hindrance from the axial methyl groups may also influence K_{CO_2}; in the *d,l* complex, one face of the complex is completely unhindered by these methyl groups.

This large effect of steric factors on K_{CO_2} indicates that caution must be taken in interpreting the correlation between K_{CO_2} and redox potential shown in Table I. Because many of the macrocycles used have numerous possible stereoisomers, the binding constants obtained may differ from other stereoisomers of the same complex which have identical redox potentials. However, for all

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(28) Busch, D. H.; Pillsbury, D. G.; Lovecchio, F. V.; Tait, A. M.; Hung, Y.; Jackels, S.; Rakowski, M. C.; Schammel, W. P.; Martin, L. Y. *ACS Symp. Ser.* **1977**, *38*, 32.

(29) Schwarz, C. L.; Endicott, J. F. *Inorg. Chem.* **1989**, *28*, 4011.

Table III. Binding Constants, K_{CO_2}, of Co(salen)$^-$ Complexes in THF with a Variety of Electrolytes

ligand and electrolyte	$E^{\circ\prime a}$ (V)	$[CO_2]$ (M)	K_{CO_2} (M^{-1})
Salen			
1.0 M $NaCF_3SO_3$	−1.59	0.162	8 ± 2
1.0 M $LiCF_3SO_3$	−1.53	0.147	3 ± 1
1.0 M $(C_4H_9)_4NCF_3SO_3$	−1.60	0.143	<2
7,7′-Dimethylsalen			
1.0 *M* $NaCF_3SO_3$	−1.73	0.162	500 ± 200
1.0 *M* $LiCF_3SO_3$	−1.65	0.147	120 ± 20
1.0 *M* $(C_4H_9)_4NCF_3SO_3$	−1.84	0.143	2 ± 1

[a] Measured vs ferricinium/ferrocene internal reference.

Table IV. UV-vis Peak Maxima of $[Co(\mathbf{5})]^{2+}$ in Various Solvents with and without 0.1 M TBA(ClO_4) Electrolyte

solvent	electrolyte	λ
propylene carbonate	none	324, 438
propylene carbonate	0.10 M TBA(ClO_4)	324, 438
dimethyl sulfoxide	none	288, 338, 448
dimethyl sulfoxide	0.10 M TBA(ClO_4)	290, 338, 450
dimethylformamide	none	286, 334, 444
dimethylformamide	0.10 M TBA(ClO_4)	282, 334, 444
acetonitrile	none	312, 444
acetonitrile	0.10 M TBA(ClO_4)	312, 444
tetrahydrofuran	none	282, 342, 430
tetrahydrofuran	0.10 M TBA(ClO_4)	280, 326, 430
tetrahydrofuran	0.10 M TBA(PF_6)	280, 328, 434
tetrahydrofuran	0.10 M TBA(CF_3SO_3)	280, 332, 342 (sh), 438

the complexes listed in Table I, cyclic voltammograms showed single, unbroadened peaks under a CO_2 atmosphere, indicating that no mixtures of stereoisomers having large differences in binding constant were used in this study.

The effect of steric hindrance on the binding of CO_2 has been also considered by Sauvage and co-workers in studies of $[Ni(\mathbf{9})]^+$ as a CO_2 reduction catalyst.[4b-d] In aqueous media, CO_2 reduction by $[Ni(\mathbf{9})]^+$ was reported to yield only CO as a product,[4b-d] whereas other catalysts, such as $[Ni(\mathbf{8})]^+$, often yield H_2 as a side product.[4a] The selective reaction of $[Ni(\mathbf{9})]^+$ with CO_2 was ascribed to direct CO_2 binding to the catalyst, and steric hindrance was suggested as a possible reason for the lack of CO_2 binding or selectivity when the $[Ni(\mathbf{8})]$ catalyst was used. Our electrochemical studies in $(CH_3)_2SO$ solvent indicated no observable reaction of CO_2 with $[Ni(\mathbf{8})]^+$, while the $[Ni(\mathbf{9})]^+$ electrochemistry indicated irreversible CO_2 binding (Table I). Thus, as Sauvage et al. suggested, $[Ni(\mathbf{9})]^+$ is more reactive toward CO_2, and this difference may explain the greater selectivity of the cyclam catalyst in aqueous media. But as we noted above, the difference in redox potentials between the two complexes may be sufficient to explain the difference in reactivity, and steric effects need not be invoked. It is important, then, to consider both steric and electronic factors in studies of potential catalysts.

3. Solvent. Possible roles for solvent in the binding of CO_2 to Co^I macrocycles might include acting as trans axial ligands, acting as ligands competing with CO_2 for binding sites, or preferentially solvating reactants or products. Our interest in the effects of solvent on CO_2 binding was piqued by the report of Creutz et al. that a K_{CO_2} of 1.6×10^8 M^{-1} was obtained for $[Co(\mathbf{5})]^+$ in water.[6] Because Co^I species tend to form hydrides in protic solvents, the electrochemical method of determining K_{CO_2} cannot be used in such solvents. Therefore investigations herein were limited to aprotic solvents.

A trend with the dielectric constant (ϵ/ϵ_0) of the solvent is noticeable (Table II), but no clear relationship with solvent donor or acceptor numbers is seen.[30] Because K_{CO_2} expresses the stability of the solvated Co–CO_2 complex relative to the solvated Co^I complex and solvated CO_2, the positive correlation with solvent dielectric constant may reflect the greater stability of a polar metal carboxylate species in more polar solvents. However, the correlation may also be largely due to trends in CO_2 solubility. In order to account for variable CO_2 interactions with different solvents, Fujita et al. have suggested that binding constants should be expressed relative to 1 atm of gaseous CO_2 as the standard state.[11] A binding constant reflecting this approach can be formulated in terms of K_{CO_2} and the saturation concentration of CO_2, $[CO_2]_{sat}$:

$$K_g = K_{CO_2}[CO_2]_{sat}$$

Mean values of K_g are also listed in Table II. The same general relationship between K_{CO_2} and dielectric constant can be inferred from these data, but they also suggest that K_g may be roughly the same for all solvents except THF.

Because THF is not a very polar solvent, the possibility of ion pairing or anion coordination in this solvent was explored. UV-visible spectra of $[Co(\mathbf{5})]^{2+}$ in the various solvents were taken with and without electrolyte. With the exception of THF, no difference in peak position was observed upon the addition of electrolyte (Table IV). The shift in the charge-transfer band near 342 nm[22] in THF can be attributed to ion pairing of the $[Co(\mathbf{5})]^{2+}$ and electrolyte anion in the rather nonpolar solvent. Different shifts are observed with different electrolyte anions, further suggesting a close interaction between the anion and the metal center.

Because $[Co(\mathbf{5})]^{2+}$ has been shown to be five-coordinate,[15] it may be more appropriate to consider the anions to be ligands coordinated to the Co in THF. In this interpretation, the other solvents would be better ligands than the anions, while THF would be a worse ligand, less able to compete with the anions for the axial coordination site. The anions may remain coordinated to the metal center when the complex is reduced to the Co^I state, especially in the rather nonpolar THF solvent. The coordinated anions would then block sites otherwise available for CO_2 binding and thereby reduce the measured K_{CO_2}. No difference in K_{CO_2} was observed with TBA(CF_3SO_3) or TBA(ClO_4) as electrolyte, but this does not imply that ion pairing or anion coordination is not the cause of the lower binding constant.

In summary, the binding of CO_2 is favored in more polar solvents, but this may be largely the effect of these solvents having a smaller affinity for CO_2. Ion pairing may interfere with CO_2 binding in solvents of extremely low dielectric constants such as THF. Nothing uncovered in this study of solvent effects on the binding of CO_2 to $[Co(\mathbf{5})]^+$ can explain the high value of K_{CO_2} observed in H_2O.[6] From the observed lack of trends with solvent donor or acceptor numbers, it is unlikely that the solvents act as competing or trans ligands.

4. Alkali Metal Cations. The studies of Floriani and co-workers indicated that alkali metal cations could have a large influence on reactivity of metal complexes toward CO_2 and on the stability of the resulting CO_2 complexes.[8b] Because the CO_2 ligand in these complexes is bent, the complexes were viewed as "metal carboxylates" having excess electron density on the CO_2 oxygens. Coordination of the alkali metal cations to these oxygens was directly observed in crystal structures, and this coordination provided a mechanism for explaining the effect of different cations on the complex stability.[8b]

Similarly, the higher K_{CO_2} observed for $[Co(\mathbf{5})]^+$ in the presence of Li^+ than that observed in the presence of TBA^+ (Table II) can be explained by the greater charge density on the small unipositive cation providing greater stabilization of electron density on CO_2 oxygens. The fact that this effect is observed in THF but not in $(CH_3)_2SO$ is probably the result of a greater solvation of the Li^+ cation by $(CH_3)_2SO$, which is a good donor solvent (donor number DN = 29.8 for $(CH_3)_2SO$; for THF, DN = 20.0).[30]

Much larger effects of cation size on K_{CO_2} were evident for the salen complexes ($>10^2$) than for $[Co(\mathbf{5})]^+$ in the same solvent, implying that alkali metal cations play a more important role in CO_2 binding for the salen complexes than for the tetraazamacrocycle complexes. The lack of CO_2 binding to the salen complexes in $(CH_3)_2SO$ may be attributed to the greater solvation of the alkali metal cations in this solvent, making them unavailable for assisting CO_2 binding. If this were true, similar binding constants should be found in $(CH_3)_2SO$ and THF with TBA^+ electrolytes. Unfortunately, the lower limit on measurable K_{CO_2}'s

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(30) Gutmann, V. *Chimia* **1977**, *31*, 1.

in $(CH_3)_2SO$ is limited by the low solubility of CO_2 in this solvent and is greater than the K_{CO_2} observed in THF.

It is interesting to note that K_{CO_2} is significantly larger for both salen complexes in the presence of Na^+ than in the presence of Li^+. This is in agreement with the trends in reactivity found by Floriani and co-workers, who attributed the lower reactivity with Li^+ to the greater solvation of this ion by THF.[8b] Experiments with K^+ were not possible due to the low solubility of K^+ electrolytes in THF.

Conclusions

The work described above demonstrates that CO_2 binding to cobalt(I) macrocycle complexes is a general phenomenon that follows predictable trends in metal basicity as reflected by $Co^{II/I}$ redox potentials. Steric factors were found to have a large effect on the binding strength of CO_2 to one cobalt macrocycle complex, suggesting that hydrogen-bonding and/or steric bulk may be important factors in CO_2 binding.

For nonprotic solvents, the strength of CO_2 binding was weakly correlated with solvent dielectric constants. This can be explained to a great extent by the differences in the solvation of CO_2, and ion pairing in the most nonpolar solvents may explain the low binding constants obtained in those solvents. Finally, the role of alkali-metal cations in stabilizing CO_2 adducts of Co(salen) complexes was quantified and was found to be more important for CO_2 binding to these complexes than for CO_2 binding to the cobalt tetraazamacrocycles.

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Clusters Containing Carbene Ligands. 7. Preparation of $Os_3(CO)_8[C(H)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$ and the Nature of Its Reactions with Secondary and Tertiary Amines

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Abstract: $Os_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ and $Os_3(CO)_{10}(\mu\text{-}SPh)(\mu\text{-}H)$ were found to react with NMe_3 to yield the complex $Os_3(CO)_8[C(H)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$ (**1a**) in yields of 31% and 26%, respectively. $Os_3(CO)_{10}(\mu\text{-}CNMe_2)(\mu\text{-}H)$ was found to react with H_2S to yield **1a** in 36% yield. Compound **1a** was analyzed by a single-crystal X-ray diffraction analysis and was found to contain a secondary (dimethylamino)carbene ligand terminally coordinated to a sulfur-bridged triosmium cluster. The amino group in the carbene ligand was exchanged by reactions of **1a** with NEt_2H and $NPr_2{}^nH$ at 56 and 80 °C and by reaction with NEt_3 or $NPr_3{}^n$ at 145 °C in MeOH solvent. Significant amounts of $[Os_3(CO)_9(\mu_3\text{-}S)(\mu\text{-}H)]^-$ (**3**) are also formed in the latter reactions. The diamine $HN(Et)(CH_2)_2NMe_2$ reacted with **1a** at 80 °C to give $Os_3(CO)_8[C(H)N(Et)(CH_2)_2NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$ (**1e**) in 42% yield. **1e** was decarbonylated at 145 °C to give $Os_3(CO)_7[C(H)N(Et)(CH_2)_2NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$ (**2e**) in 41% yield. Compound **2e** was characterized by a single-crystal X-ray diffraction analysis and was found to contain a terminally coordinated $C(H)N(Et)(CH_2)_2NMe_2$ carbene ligand chelated to the cluster through coordination of the NMe_2 group. Labeling studies have shown that the reactions of the carbene complexes with tertiary amines involve C–H activation processes in the alkyl groups and exchange of the amino group of the carbene ligand. A mechanism is proposed that involves iminium ligand intermediates that couple to the carbene ligand to form a nitrogen-containing metallacycle. Solutions of **1a** in methanol were found to catalyze the exchange of alkyl groups between NEt_3 and $NPr_3{}^n$, but analyses of the catalyst mixtures have shown that most of the catalysis was produced by **3**, a decomposition product of the carbene-containing cluster complexes. Crystal data: (for **1a**) space group $P\bar{1}$, $a = 8.703$ (1) Å, $b = 12.226$ (2) Å, $c = 18.980$ (4) Å, $\alpha = 85.30$ (1)°, $\beta = 78.65$ (1)°, $\gamma = 72.29$ (1)°, $R = 0.043$ for 3554 reflections; (for **2e**) space group $P2_1/n$, $a = 11.774$ (3) Å, $b = 12.712$ (2) Å, $c = 14.712$ (4) Å, $\beta = 104.82$ (2)°, $R = 0.050$ for 1866 reflections.

Although amine-substituted carbene ligands, $C(R)NR_2$ (R = alkyl or aryl), are not uncommon to the field of organometallic chemistry,[1,2] there are still comparatively few examples of polynuclear metal carbonyl complexes containing them.[3] In recent studies, we have discovered that bis(dialkylamino)methanes are effective reagents for the introduction of secondary (dialkylamino)carbene ligands, $C(H)NR_2$, into a variety of osmium carbonyl cluster complexes through a process that involves the cleavage of one dialkylamino group and one hydrogen atom from the bis(dialkylamino)methane molecule (e.g., eq 1).[4-6] These carbene complexes possess considerable stability but have been shown to engage in novel multicenter transformation processes in certain cases.[4]

Several years ago, Deeming and Shapley investigated the reactions of NMe_3 with $Os_3(CO)_{12}$, eq 2,[7] and NEt_3 with $Os_3(CO)_{10}(NCMe)_2$, eq 3,[8] respectively. In this report, we describe

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