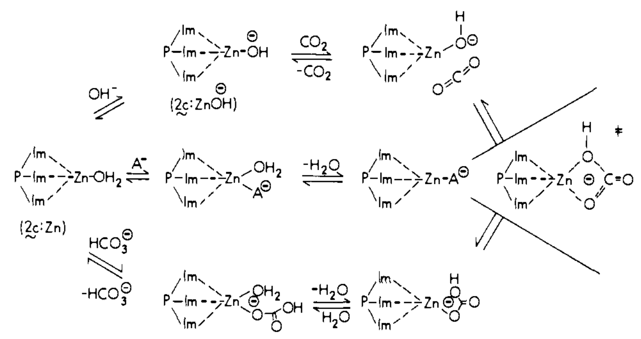
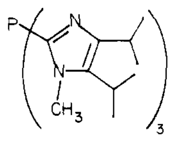
Scheme I



Basically mechanisms for CA can be categorized into two main types. In the first category the primary purpose of the metal is to reduce the pK_a of an attached group (OH_2 or imidazole)[26,27] such that it becomes an effective nucleophile (or general base) toward CO_2. The metal may also serve an additional role as Lewis acid which sufficiently polarizes the CO_2 to render it more susceptable to nucleophilic attack.

Alternatively, for the second category, attendant to the above metal function, an additional required function of the protein is to provide catalytically important groups to assist in proton transfer from the metal-bound H_2O or to act as general bases to assist in delivering free H_2O to CO_2.[1d,5d,e,i] Since **2c**:Zn^{2+} shows catalytic behavior but mimics only the metal-binding site, it may be tempting in the most generous extrapolation to favor the first mechanistic category. Of course since the catalysis afforded by **2c**:Zn^{2+} is modest relative to the enzyme,[28] protein interactions could be fine tuning its catalysis. In fact, it now seems certain enzymically, the rate-determining step is not the actual metal-catalyzed CO_2 hydration, but a subsequent proton transfer involving two or more equivalent hydrogens in the transition state.[29]

In the case of **2c**:Zn^{2+}, one must propose either a $Zn^{2+}OH^-$ mechanism[1] or a Zn^{2+} imidazolate mechanism,[26,27] neither being distinguished by the above observations. In principle, these could be distinguished if it were observed that the corresponding *N*-methyl derivative **3** could be catalytically viable. However we



3

are convinced that **3** would not bind Zn^{2+} as well as **2c** since preliminary work in related systems[9a] shows each N-H to N-CH_3 substitution reduces a ligand's p$K_{M^{2+}}$ by 1-1.5 units. Additionally, **3** is very difficult to purify, most operations leading to the easily formed phosphine oxide.

For reasons of simplicity we favor a mechanism as in Scheme I, akin to that proposed by Lövgren et al.[6b] for the enzyme, the difference here being that the H-bonding network between Zn-OH_2 and the protein is absent. In this mechanism, the transition state (‡) involves a five-coordinate Zn^{2+}, the purpose of the metal being to serve as a template for delivery of a bound ^-OH and stabilizing the incipient change on CO_2. That the low coordination numbers for Zn^{2+} are required for activity is supported by observations[9b] which indicate that neither **2a**.Zn^{2+} nor **2b**:Zn^{2+} appear to catalyze the $CO_2 \rightleftharpoons HCO_3^-$ interconversion,[30] and their corresponding Co^{II} complexes do not show evidence of four- (five-) coordination. The inhibition of activity by anions is most easily rationalized in Scheme I as a nonproductive association of A^- with the Zn^{2+} which blocks further access of CO_2 (HCO_3^-). The above rationalization indirectly supports the Zn hydroxide mechanism[1] since it is less satisfying (but not impossible if one invokes a severe reduction of the Zn^{2+} electropositive character on its association with anion) to explain the effect of anionic inhibition in terms of the Zn imidazolate mechanism.[26]

Acknowledgment. We thank the University of Alberta and National Science and Engineering Council of Canada for support of this work. In addition we acknowledge Professor H. B. Dunford, Professor M. N. G. James, and Mr. R. Read for helpful discussions and Professor R. B. Jordan for the use of his stopped-flow machine.

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(26) For evidence supporting this mechanism see ref 1g,h and 9d.

(27) For criticisms of this mechanism see: Martin, R. B. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 4346-4347.

(28) We have avoided strict numerical comparison of catalysis by **2c**:Zn^{2+} and CA for several reasons. First, the medium used in this study is very different from those employed for enzyme studies[13] as is the present kinetic procedure which monitors $k_{obsd} = k_{hyd} + k_{dehyd}$. Also, there is an obvious problem of units in comparing the present second-order catalytic process, with the enzymic process which involves Michaelis-Mentin kinetics. Previous work in model CA systems[7a,9b] has attempted such comparison by using $k_{cat}/K_M = 10^7$ and 8×10^7 M^{-1} s^{-1} for human CA-B and CA-C, respectively.

(29) (a) Venkatasubban, K. S.; Silverman, D. N. *Biochemistry* **1980**, *19*, 4984-4991. (b) Silverman, D. N.; Tu, C. K.; Lindskog, S.; Wynns, G. C. *J. Am. Chem. Soc.* **1979**, *101*, 6734-6740. (c) Steiner, H.; Jonsson, B. H.; Lindskog, S. *Eur. J. Biochem.* **1975**, *59*, 253.

(30) Our preliminary studies with **2a-c** showed the former two Zn^{2+}-bound species to be completely inactive toward $CO_2 \rightleftarrows HCO_3^-$ interconversion.[9b] While suggestive of the importance of reduced coordination of Zn^{2+}, these experiments are not strictly comparable to those with **2c**:Zn^{2+} since the former species required solvent systems of a more highly aqueous content.[9b]

Communications to the Editor

Carbon Monoxide Activation by Organoactinides. Migratory CO Insertion into Metal-Hydrogen Bonds to Produce Mononuclear Formyls

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Although the migratory insertion of CO into a metal-hydrogen bond to produce a formyl[1,2] (A, eq 1) has been much discussed

$$\underset{\text{A}}{M\text{-}H + CO \rightarrow M(CHO)} \qquad (1)$$

as a primary event in the heterogeneous catalytic hydrogenation of carbon monoxide,[3] there is little unambiguous evidence for this

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(1) (a) Steinmetz, G. R.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 1278-1279. (b) Thorn, D. L. *Ibid.* **1980**, *102*, 7109-7110. (c) Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Rinz, J. E. *Ibid.* **1980**, *102*, 1927-1933. (d) Wong, W.-K.; Tam, W.; Gladysz, J. A. *Ibid.* **1979**, *101*, 5440-5442. (e) Brown, K. L.; Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *Ibid.* **1979**, *101*, 503-505. (f) Collman, J. P.; Winter, S. R. *J. Am. Chem. Soc.* **1973**, *95*, 4089-4090. (g) Pearson, R. G.; Walker, H. W.; Mauermann, H.; Ford, P. C. *Inorg. Chem.* **1981**, *20*, 2741-2743. (h) To our knowledge, the first suggestion of the possibility of such an insertion process was in: Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions"; 2nd ed.; John Wiley: New York, 1968; Chapter 7. (i) **Note Added in Proof**: For the formation of an unstable formyl via carbonylation of a rhodium porphyrin hydride, see: Wayland, B. B.; Woods, B. A. *J. Chem. Soc., Chem. Commun.* **1981**, 700-701.

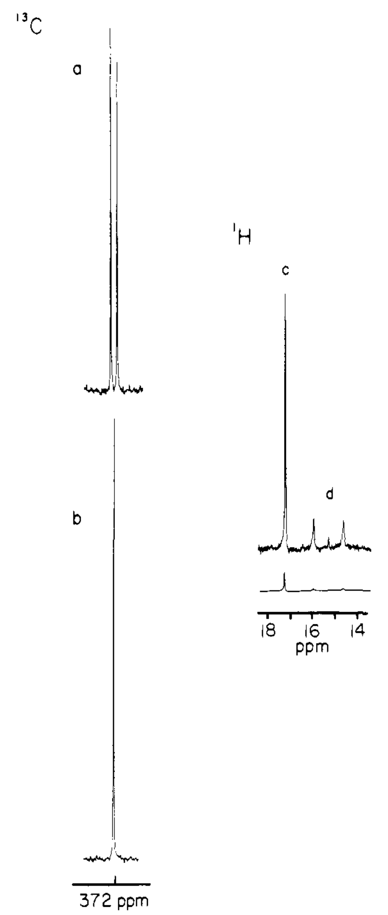
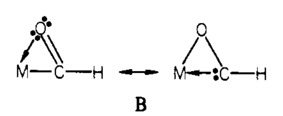


Figure 1. FT–NMR spectra of $Th[\eta^5\text{-}(CH_3)_5C_5]_2\{OC[C(CH_3)]_2H\}H$ (**1b**) as a toluene-d_8 solution in the presence of 0.5-atm ^{13}CO at −80 °C. (a) ^{13}C spectrum showing the formyl carbon resonance at 372 ppm. (b) ^{13}C spectrum after selective decoupling of the formyl proton resonance at 15.2 ppm. ^1H spectrum showing (c) the hydride (17.2 ppm) and (d) the formyl (15.2 ppm) resonances, respectively. From these data, $^1J_{^{13}C-H} = 114$ Hz.

simple reaction under homogeneous conditions. To the degree that this situation reflects thermodynamic constraints,[1,2,4] it would be of great interest to determine whether eq 1 could be rendered favorable by providing a metallic center with sufficient unsaturation and oxygen affinity to stabilize a mononuclear formyl via conjunctive metal–oxygen bonding (B).[5] We report here that such an insertion is both spontaneous and rapid for selected organoactinide hydrides and describe some of the interesting properties of the resulting formyls.



B

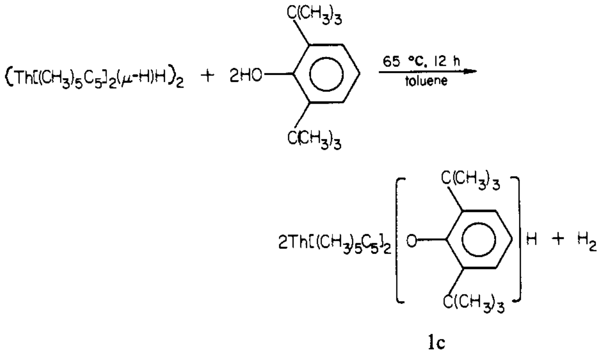
Sterically unencumbered bis(pentamethylcyclopentadienyl) 5f hydrides such as $\{Th[(CH_3)_5C_5]_2(\mu\text{-}H)H\}_2$[6] react rapidly with excess CO at −78 °C to yield, inter alia, dimeric enediolate derivatives (eq 2) with no identifiable intermediates.[7] Far more

$$2Th\text{–}H + \text{excess } CO \xrightarrow{\text{toluene}} ThOC(H){=}C(H)OTh) \quad (2)$$

informative is the carbonylation chemistry of the alkoxy hydrides prepared in 80–90% yields via the routes of eq 3–5.[8]

$$Th[(CH_3)_5C_5]_2[OC(CH_3)_3]CH_3 \xrightarrow[\text{toluene, 24 h}]{H_2,\ 100 °C} \underset{\mathbf{1a}}{Th[(CH_3)_5C_5]_2[OC(CH_3)_3]H} \quad (3)$$

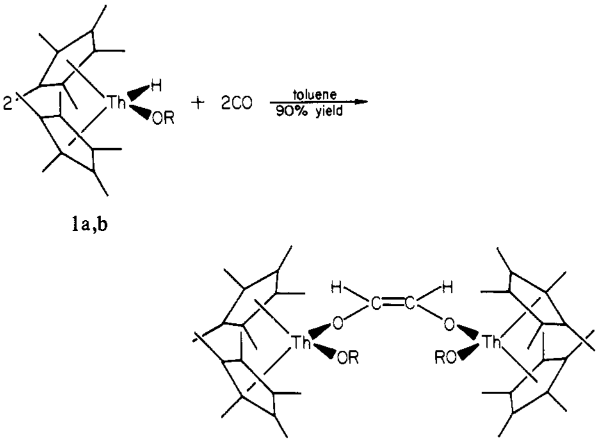
$$\{Th[(CH_3)_5C_5]_2(\mu\text{-}H)H\}_2 + 2(CH_3)_3CC({=}O)C(CH_3)_3 \xrightarrow[\text{toluene}]{65 °C,\ 2\ h} \underset{\mathbf{1b}}{2Th[(CH_3)_3C_5]_2\{OC[C(CH_3)_3]_2H\}H} \quad (4)$$



(5)

1c

At 25 °C and 0.7 atm of CO pressure, 0.010 M solutions of **1a** and **1b** react to form enediolates **2a** and **2b** with half-lives of ca. 3 min and 5 h, respectively (eq 6).



1a,b

(6)

2a, R = $C(CH_3)_3$
b, R = $C[C(CH_3)_3]_2H$

The structures of **2a** and **2b** were established by the usual techniques[8] and cryoscopic molecular weight measurements in benzene; the cis stereochemistry of the C=C double bond follows from analysis of the AA′XX′ ^1H and ^{13}C NMR spectra of analogues prepared with ^{13}CO.[9] The formation

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(2) For polynuclear complexes where a CHO fragment is bound to several metal atoms, see: (a) Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 2650–2659. (b) Churchill, M. R.; Wasserman, H. J. *J. Chem. Soc., Chem. Commun.* **1981**, 274–275. (c) Belmonte, P.; Schrock, R. R.; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 2868–2860.

(3) (a) Biloen, P.; Sachtler, W. M. H. *Adv. Catal.*, in press. (b) Kung, H. *Catal. Rev.-Sci. Eng.* **1980**, *22*, 235–259. (c) Muetterties, E. L.; Stein, *J. Chem. Rev.* **1979**, *79*, 479–490. (d) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61–103. (e) Ponec, V. *Catal. Rev.-Sci. Eng.* **1978**, *18*, 151–171.

(4) Fagan, P. J.; Manriquez, J. M.; Vollmer, S. H.; Day, C. S.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 2206–2220.

(5) (a) Fagan, P. J.; Maatta, E. A.; Marks, T. J. *ACS Symp. Ser.* **1981**, *No. 152*, 52–78. (b) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, V. W.; Vollmer, S. H.; Day, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 5393–5396.

(6) (a) Fagan, P. J.; Maatta, E. A.; Manriquez, J. M.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.*, in press. (b) Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3939–3941. (c) Broach, R. W.; Schultz, A. J.; Williams, J. M.; Brown, G. M.; Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *Science (Washington, D.C.)* **1979**, *203*, 172–174.

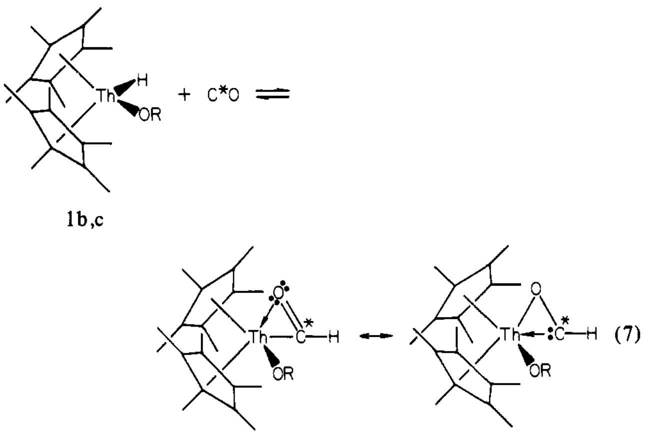
(7) (a) Fagan, P. J. Ph.D. Thesis, Northwestern University, 1980. (b) Fagan, P. J.; Maatta, E. A.; Manriquez, J. M.; Marks, T. J.; Day, C. S.; Day, V. W.; Vollmer, S. H., submitted for publication.

(8) All isolable new compounds gave satisfactory elemental analyses as well as expected ^1H NMR and infrared spectra.

(9) (a) For **2a**, $J_{H-H} = 4.5$, $J_{C-C} = 89.4$, $^1J_{H-C} = 172.4$ and $^2J_{H-C} = 20.2$ Hz. (b) For **2b**, $J_{H-H} = 4.2$, $J_{C-C} = 98.0$, $^1J_{H-C} = 187.0$, and $^2J_{H-C} = 22.0$ Hz. (c) JEOL FX-90Q spin simulation program. (d) Becker, E. D. "High Resolution NMR", 2nd ed.; Academic Press: New York, 1980; Chapter 5. (e) Levy, G. C.; Lichter, R. L.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance Spectroscopy", 2nd ed.; Wiley-Interscience: New York, **1980**; Chapter 3. (f) Wray, V.; Hansen, P. E. *Annu. Rep. NMR Spectrosc.* **1981**, *11A*, 99–181.

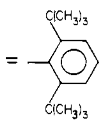
of an enediolate from **1c** is immeasurably slow under these conditions.

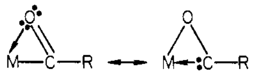
Although the bulky alkoxy functionalities impede enediolate formation, the reaction of these hydrides with CO is remarkably rapid (and reversible). Exposure of colorless toluene solutions of **1b** or **1c**[10] to 0.7 atm of CO at −78 °C results in an immediate yellow coloration and rapid CO uptake. The CO uptake can be quantitatively reversed at −78 °C (Toepler pump) and **1b,c** recovered unchanged. We ascribe these changes to reversible migratory CO insertion, producing mononuclear thorium dihaptoformyls (eq 7). The nature of **3b** and **3c** follows from chemical and spectroscopic data correlated with previous observations on the carbene-like organoactinide dihaptoacyls (C), e.g., $Th[(CH_3)_5C_5]_2[\eta^2\text{-}COCH_2C(CH_3)_3]Cl$ (**4**).[5] In toluene-d_8 or THF-d_8 solution (<−50 °C), ^1H and ^{13}C NMR spectra of **3b**, **3b***, **3c**, and **3c***, exhibit, in addition to $\eta^5\text{-}(CH_3)_5C_5$ and OR resonances in the proper intensity ratios,[11] characteristic proton resonances at δ 15.2 (**3b**, **3b***) and 14.7 (**3c**, **3c***), and ^{13}C resonances at δ 372 (**3b***) and 360 (**3c***). Unreacted alkoxy hydride is also evident under these conditions.[12] The low field ^1H data compare favorably with values for other mononuclear formyls[1] while the ^{13}C data are in the range found for thorium dihaptoacyls (cf. δ 362 in **4**).[5,13] Selective heteronuclear decoupling experiments (Figure 1) indicate $^1J_{^{13}C\text{-}H}$ = 114 (**3b***) and 117 Hz (**3c***), parameters in accord with the expected carbenoid character of actinide dihaptoformyls (B).[14] Low-temperature infrared spectra of **3b** and **3b*** (<−50 °C, THF or THF-d_8 solution) provide further support for the mononuclear formyl structure shown in eq 7. Addition of CO diminishes the intensity of $\nu_{Th\text{-}H}$ (1355 cm^{-1}), and a new transition appears at 1477 cm^{-1} (1443 in **3b***) which is assigned to ν_{CO}; these parameters agree favorably with those in **4** (ν_{CO} 1469, $\nu_{^{13}CO}$ = 1434 cm^{-1})[5] and are not compatible with a dinuclear bis(carbene) complex.[15–17]



1b,c

3b, R = $C[C(CH_3)_3]_2H$, C* = ^{12}C; 3b*, C* = ^{13}C

3c, R =  , C* = ^{12}C; 3c*, C* = ^{13}C



C

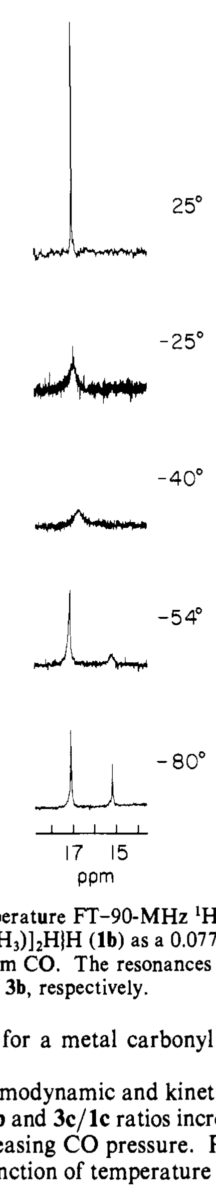


Figure 2. Variable temperature FT-90-MHz ^1H NMR spectra of Th-$[\eta^5\text{-}(CH_3)_5C_5]_2\{OC[C(CH_3)]_2H\}H$ (**1b**) as a 0.077 M toluene-d_8 solution in the presence of 0.7-atm CO. The resonances at 17.2 and 15.2 ppm are attributed to **1b** and **3b**, respectively.

There is no evidence for a metal carbonyl[18] in the 2000-cm^{-1} region.

As regards the thermodynamic and kinetic aspects of eq 7, it is found that the **3b**/**1b** and **3c**/**1c** ratios increase with decreasing temperature and increasing CO pressure. Preliminary analysis of these data[19] as a function of temperature yields $\Delta H = -4.5 \pm 0.9$ kcal/mol, $\Delta S = -11.7 \pm 4.3$ eu (**1b** ⇌ **3b**) and $\Delta H = -5.9 \pm 1.5$ kcal/mol, $\Delta S = -23.9 \pm 7.4$ eu (**1c** ⇌ **3c**) in toluene solution. The great rapidity with which CO insertion/extrusion occurs is dramatically illustrated in Figure 2; for the sample shown, equilibration is rapid on the NMR time scale by −40 °C. Magnetization transfer studies on mixtures of **1b**/**3b** with **1c**/**3c**

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[10] These observations appear also to apply to **1a**, but the rapidity of the subsequent coupling reaction complicates the spectral analysis; further studies are in progress.

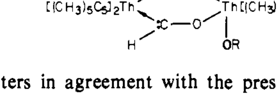
[11] ^1H data for **3b**: δ 1.07 (18 H, s), 2.17 (30 H, s), 3.70 (1 H, s), 15.2 (1H, s). **3c**: δ 1.65 (18 H, s), 1.93 (30 H, s), 7.0 (3 H, m), 14.7 (1 H, s).

[12] ^1H data for **1b**: δ 1.18 (18 H, s); 2.23 (30 H, s); 3.50 (1H, s), 17.2 (1H, s). **1c**: δ 1.52 (18 H, s); 2.03 (30 H, s); 7.0 (3 H, m), 19.1 (1 H, s).

[13] Mintz, E. A.; Marks, T. J.; manuscript in preparation.

[14] (a) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98–104. (b) Messerle, L. W.; Jennische, P.; Schrock, R. R.; Stucky, G. *J. Am. Chem. Soc.* **1980**, *102*, 6744–6752.

[15] Based upon published spectral data,[2a,16] a dinuclear bis(carbene) structure[17] such as that shown below would not be anticipated to display ν_{CO}



or δ^1H parameters in agreement with the present results. Furthermore, inspection of diffraction-derived molecular models indicates unreasonable nonbonded repulsions in such a dimer containing the R groups of **3b** and **3c**. The rapidity of CO exchange also appears incompatible with such a formulation. Thorium(IV) η^1-carbene complexes are as yet unknown.

[16] (a) Green, M. L. H.; Mitchard, L. C.; Swanwick, M. G. *J. Chem. Soc. A* **1971**, 794–797. (b) Fischer, E. O.; Maasbol, *A. Angew, Chem. Int. Ed.*, **1964**, *3*, 580–581.

[17] Lindley, P. F.; Mills, O. S. *J. Chem. Soc. A* **1969**, 1279–1285.

[18] (a) Marsella, J. A.; Curtis, C. J.; Bercaw, J. E.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 7244–7246. (b) The magnitude of $^1J_{^{13}C\text{-}H}$ also appears to be incompatible with a carbonyl in the present case.

[19] Experiments were performed at constant CO pressure using an NMR tube equipped with a mixing device and a large gas reservoir. CO solubilities were taken from the literature.[20]

argue that *intermolecular* hydride transfer to coordinated CO[21] is not important in eq 7. Exchange is only observed between hydride and formyl protons of species bearing the same alkoxide group, whereas intermolecular hydride transfer would reasonably be expected to permute all hydride environments. Further studies of the kinetic/thermodynamic aspects of the migratory CO insertion process and the chemical reactivity of organoactinide formyls are in progress.

Acknowledgment. We thank the National Science Foundation (CHE8009060) for generous support of this research and Joseph F. Lomax for experimental assistance.

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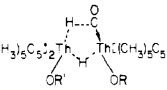
(20) Gjaldbaek, J. C.; Andersen, E. K. *Acta Chem. Scand.* **1965**, *8*, 1398-1413 and references therein.

(21) Presumably via a hypothetical transition state such as



Molecular models suggest that such structures would be prohibitively high in energy.

Formation Constants of Ion Pair-Ligand Complexes. Application of Crown Ether Network Polymers

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College of Environmental Science and Forestry
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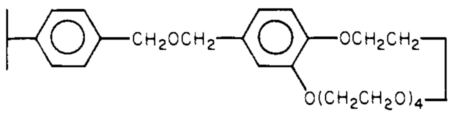
Received June 17, 1981

Crown ethers, cryptands, podands, and other cation-binding ligands, when used in anion-activated catalysis or mediated ion transport, are usually operating in an apolar environment where ionic species tend to associate into ion pairs. Quantitative information on complexation between ligands and ion pairs in apolar solvents (e.g., dioxane, toluene) is frequently hard to obtain because of the large formation constants of the complexes. We now wish to report that crown ether network polymers can serve as reliable probes in the study of ion pair-ligand complexes, including the determination of their association constants in apolar media. Moreover, the measurements can also furnish quantiative information on ion pair binding to crown ether network polymers, materials employed in anion-activated catalysis[1-3] and the separation of solutes.[4,5] Crown ether resin I, synthesized from 2% cross-linked chloromethylated polystyrene and [(hydroxymethyl)benzo]-18-crown-6 is added to a solution of a metal picrate in dioxane, conditions being such that nearly all picrate salt is bound to the insoluble crown polymer (crown to picrate ratio ~40). Addition of a soluble ligand (e.g., 18-crown-6, cryptand 2.2.2) releases the network-bound salt into the solution according to reaction 1 where the starred species are network bound. If f_1



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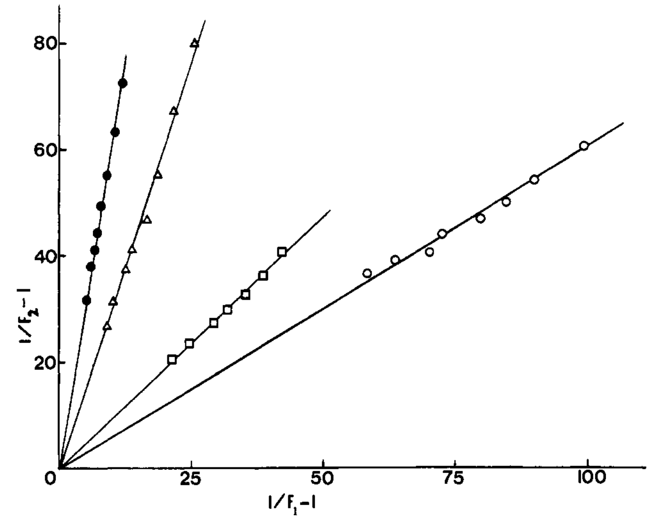

Figure 1. Plots of $(1/f_2) - 1$ vs. $(1/f_1) - 1$ in dioxane for the equilibrium $Pi^-,K^+,Cr^* + L \rightleftharpoons Pi^-,K^+,L + Cr^*$ (see text) for different ligands L: (●) 18-crown-6; (▲) dicyclohexano-18-crown-6 (□) 4'-(methylbenzo)-18-crown-6; (○) (dimethyldibenzo)-18-crown-6.

Table I. Association Constants, K_L, of Macroheterocyclic Ligands to Potassium Picrate in Dioxane at 25 °C

ligand	K	$K_L \times 10^{-5}$, M^{-1}
(dimethyldibenzo)-18-crown-6	0.596	1.03
4'-(methylbenzo)-18-crown-6	0.908	1.56
dicyclohexyl-18-crown-6	3.13	5.38
18-crown-6	5.62	9.67
cryptand 2.2.2.	1230	2000

$$Pi^-,M^+,Cr^* + L \underset{K}{\rightleftharpoons} Cr^* + Pi^-,M^+,L \qquad (1)$$

is the fraction of the ligand L bound to the picrate salt ($f_1 = Pi^-,M^+,L/L_0$) and f_2 the fraction of the network crown bound to the salt ($f_2 = Pi^-,M^+,Cr^*/Cr_0^*$), then the following relationship holds.

$$[(1/f_2) - 1] = K[(1/f_1) - 1] \qquad (2)$$

Since the total concentrations of picrate (Pi_0^-), ligand (L_0), and crown (Cr_0^*, in equivalents) are known, f_1 and f_2 can be determined by measuring spectrophotometrically the concentration of Pi^-,M^+,L in dioxane, since $Pi^-,M^+Cr^* = Pi_0^- - Pi^-,M^+,L$. Figure 1 depicts plots of $(1/f_2) - 1$ vs. $(1/f_1) - 1$ for four different crown ethers. K values calculated from these plots are collected in Table I, including the value for cryptand 2.2.2. Note that K for 4'-(methylbenzo)-18-crown-6 is 1.03. This implies that the cation affinity of this crown is essentially the same whether anchored to a dioxane-swollen network or a free ligand in dioxane. Increased ion pair loading or higher crown densities on the network (I contains on the average 1 crown ether for 11 monomer units) may well result in differences in cation affinities. Also, preliminary data in THF as solvent yield K about 4.0, indicating a decreased affinity of the network-bound benzo-18-crown-6 relative to that of the free ligand.

Equilibrium 1 can be analyzed in terms of reactions 3 and 4

$$Cr^* + Pi^-,M^+ \underset{K_N}{\rightleftharpoons} Pi^-,M^+,Cr^* \qquad (3)$$

$$L + Pi^-,M^+ \underset{K_L}{\rightleftharpoons} Pi^-,M^+,L \qquad (4)$$

where

$$K = K_L/K_N \qquad (5)$$

The formation constants, K_L, for ion pair-ligand complexes in solution can be calculated from (5) if K_N in known. The latter represents the binding constant of an ion pair to the crown network

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