consistent with the picture of a relatively polar Ru-Hg bridge bond where the mercury bears more positive charge than the hydride in I. Aside from this difference, the metal carbon framework of the cluster remains almost unchanged with respect to I. For example, the C(10)-C(11) bond length is 1.31 Å in II and 1.315 Å in I. Similarly, the Ru(1)-C(10) bond is 1.96 and 1.947 Å in II and I, respectively.

The reaction of II (X = Br) with $Ag(OOCCH_3)$ gives III in good yield (Table I):

$$(C_6H_9)Ru_3(CO)_9HgX + Ag(OOCCH_3) \xrightarrow{\text{THF}} \underset{\text{III}}{(C_6H_9)Ru_3(CO)_9Hg(OOCCH_3)} + AgX \quad (3)$$

However, direct reaction of $C_6H_5Hg(OOCCH_3)$ with I or I^- with $Hg(OOCCH_3)_2$ did not give III.

Under the reaction conditions for the synthesis of II (X = Br only) by the phenylmercuric halide plus hydride route, a byproduct is always obtained (10-20% yield) whose metal analysis (Ru = 33.0%, Hg = 23.9%, no bromine) and IR and mass spectra[12] are consistent with the formula $Hg_2Ru_6(CO)_{18}(C_6H_9)_2$ (IV). Independent experiments show that this compound is formed by reaction of II with I and is accompanied by cluster decomposition. IV is not formed in the synthesis of II from I^- and HgX_2 and is found in only trace amounts when I is reacted with C_6H_5HgI. IV is thermally unstable even in the solid state, slowly decomposing to mercury metal and a ruthenium containing residue. We are currently investigating the solid-state structure of IV.

Although there are many M-Hg-X and M-Hg-M (M = transition metal) derivatives in the literature,[13] II represents the first example of mercury atom briding two transition metals in a three-center bond. The fact that II is formed by both reaction of a phenylmercuric halide with a hydrido cluster and by reaction of a cluster anion with mercuric halides suggests the possibility that these reaction pathways could be of general use for synthesizing main group metal derivatives of transition metal clusters. The mercury derivatives reported here are interesting candidates for oxo or solvo mercuration catalysts and as intermediates for the synthesis of mixed transition metal clusters by oxidative addition of the mercury halogen bond to zerovalent platinum- and palladium-phosphine complexes.[14] We are currently exploring these possibilities. The chemistry observed here is reminiscent of that seen for the reaction of $(CO)_5MnH$ with $(C_6H_5)_3PAuCH_3$ to give CH_4 and a gold-manganese bond.[15] It is in sharp contrast, however, to the reaction of $HCCo_3(CO)_9$ with phenylmercuric halides where phenylation of carbinyl carbon occurs.[16]

Supplementary Material Available: The final atomic coordinates, the atomic thermal parameters and a complete listing of factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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(2) The amount of benzene was evaluated by GC–MS of the reaction volatiles and compared with volatiles isolated from C_6H_5HgBr refluxing in THF.

(3) Reaction of 95% deuterated I synthesized from I^- with C_6H_5HgX gives C_6H_5D as <10% of the C_6H_6 formed, suggesting that the cleavage of the mercury–phenyl bond is not concerted but must involve either prior dissociation of the phenyl group or exchange with solvent of a protonated phenyl group on C_6H_5HgX. The recovered I from these reactions is still fully deuterated.

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(9) Molecular weight by vapor pressure osmometry for $Ru_3(CO)_9(C_6H_9)HgBr$, 903 (calcd 916.8) in benzene.

(10) Computer programs used on a CYBER 7600 computer of the "Centro di Calcolo Interuniversitario dell' Italia Nord-Orientale," Bologna, were those of SHELX-76 system (G. M. Sheldrick, 1976, University of Cambridge, England). In the last stage of refinement a weighting scheme $1/[\sigma^2(F_o) + 0.003F_o^2]$ was adopted.

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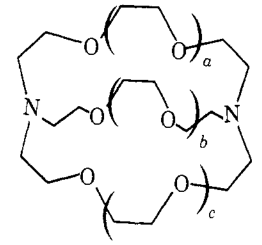
General Acid Catalyzed Dissociation of Metal Cryptates

Sir:

Recent kinetic studies on the dissociation of metal ions from complexes (cryptates) formed between cations and macrobicyclic ligands (cryptands) of the type **1**-**3**,[1] have involved NMR,[2-4] electrochemical,[5,6] relaxation,[7] and flow techniques,[8-10] including the use of strong acids to scavenge the free cryptand in equilibrium with the complex.[9,10]



1, $a = 1; b = c = 0$ (2.1.1)
2, $a = b = 1; c = 0$ (2.2.1)
3, $a = b = c = 1$ (2.2.2)

We have shown[9,10] that the dissociation of cryptates of a number of alkali and alkaline earth cations and Ag^+ are subject to varying degrees of catalysis by strong acids, both in water and methanol.[10] This was attributed to interaction between the proton and the lone pair of one of the nitrogen atoms, presumably in an exo conformation. Weaver and co-workers[6] have also found that the dissociation of europium and ytterbium cryptates is acid catalyzed.

We wish to report that the dissociation reactions are also catalyzed by general acids, HA. The catalytic activity of an

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Table I. Catalytic Constants for the General Acid Catalyzed Dissociation of Li[2.1.1]$^+$ and Ca[2.2.2]$^{2+}$

cryptate	acid (HA)	k_{HA},[a] mol^{-1} dm^3 s^{-1}	pK_a(HA)[b]
Li[2.1.1]$^+$	H$^+$	21.0[c]	−1.70
Li[2.1.1]$^+$	CH_2ClCO_2H	5.25	2.87
Li[2.1.1]$^+$	CH_2ICO_2H	2.90	3.17
Li[2.1.1]$^+$	HCO_2H	1.27	3.75
Li[2.1.1]$^+$	$CH_2ClCH_2CO_2H$	0.86	4.10
Li[2.1.1]$^+$	$HO_2C{\cdot}CO_2^-$ [d]	3.76	4.27
Li[2.1.1]$^+$	$C_6H_5NH_3^+$[d]	0.04	4.60
Li[2.1.1]$^+$	$CH_3{\cdot}CO_2H$	0.31	4.76
Ca[2.2.2]$^{2+}$	H$^+$	550[c]	−1.70
Ca[2.2.2]$^{2+}$	CH_2ICO_2H	85.0	3.17
Ca[2.2.2]$^{2+}$	HCO_2H	40.4	3.75
Ca[2.2.2]$^{2+}$	$CH_2ClCH_2CO_2H$	50.8	4.10
Ca[2.2.2]$^{2+}$	CH_3CO_2H	27.1	4.76

[a] Catalytic constants for the acid catalyzed dissociation of complexes **1**. Individual rate constants were determined conductimetrically as described in ref 9; Li$^+$, Ca^{2+} = ~4 × 10^{-3} to 10^{-2} M, Cry = 10^{-4} to 4 × 10^{-3} M, ionic strength, 0.03–0.06 M. [b] R. A. Robinson and R. H. Stokes, "Electrolytes Solutions", 2nd ed., Butterworths, London, 1965. [c] Reference 9. [d] Corrected to I = 0.

acid depends upon its acid strength, but evidence is also presented that the effectiveness of the catalyst is very dependent upon its charge. Furthermore, we have also found that the dissociation of Ag$^+$ cryptates is very strongly catalyzed by halide ions (Cl$^-$, Br$^-$, and I$^-$) and thiosulfate ions.[11] These results, as well as providing further information on the kinetic process of cryptates, may have significant implications for the more general problem of the transport of cations through membranes.[12] Lehn and co-workers[13,14] have found, for example, that, when cryptands are used as carriers, the relative transport rates for different cations are not proportional to complex stability or extraction efficiency, and in some cases are actually opposite. However, if an effective catalyst for the dissociation process is present, high stabilities and extraction efficiencies may be compatible with rapid release of the cation. Antibiotics of the Nigericin group, which contain carboxylic acid or carboxylate groups and function as mobile carriers exchanging H$^+$ against K$^+$ or Na$^+$,[15] should also be especially suited to catalytic exchange processes.

Figure 1 shows the dependence of the dissociation rate of Ca[2.2.2]$^{2+}$ upon acid concentration in acetic acid/acetate buffers at constant ionic strength (NEt_4ClO_4). Variation of acetate concentration at constant acetic acid concentration showed the effect to be independent of acetate concentration (due allowance was made for the small contribution to the observed rate by H$^+$ catalysis at these pH values of ~4.0–4.5). Similar behavior was observed in other buffers, and the rate law for dissociation may be represented by

$$-\frac{d[MCry^{n+}]}{dt} = k_e[MCry^{n+}] \qquad (1)$$

where

$$k_e = k_d + k_H[H^+] + k_{HA}[HA] \qquad (2)$$

in which HA represents a general acid and k_d, k_H, and k_{HA} represent the rate constants for the uncatalyzed, H$^+$ catalyzed, and HA catalyzed reactions, respectively. Values of k_{HA} for several carboxylic acids, obtained from plots of k_e against [HA] at constant buffer ratio [HA]/[A$^-$], are listed in Table I.

The dissociation of Li[2.1.1]$^+$, which has previously been shown to be strongly catalyzed by H$^+$,[9] is also subject to general acid catalysis. Results in acetic acid/acetate buffers of varying buffer ratios (again corrected for the small contribution from H$^+$ catalysis) are shown in Figure 2. These results are also typical for Li[2.1.1]$^+$ in other buffer systems. It is noticeable that, at higher concentrations of acetic acid (and hence acetate ions), the values fall below those extrapolated from lower concentrations. The effect is more pronounced in buffers containing higher acetate concentrations. A twofold increase in acetate concentration from 0.01 to 0.02 M, for example, leads to a rate reduction of ~10%. The lowering in reaction rate thus presumably results from an interaction between the cryptate and acetate ions, although the mechanism for such a reduction is not clear. Evidence for strong interaction between cryptates and anions has been found by Weaver and co-workers[6] in studies of lanthanide cryptates in the presence of F$^-$ and OH$^-$ ions. ^{7}Li NMR studies[16] suggest that the Li$^+$ in the Li[2.1.1]$^+$ cryptate is well shielded from the surrounding medium, so that direct cation–anion interactions in this case seem unlikely. Catalytic constants quoted in Table I for this system have been obtained from the initial linear portion of the curves.

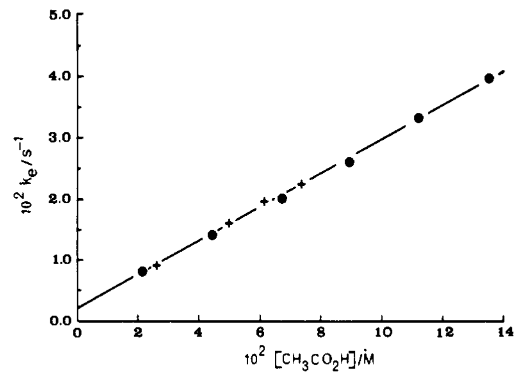

Figure 1. Acetic acid catalyzed dissociation of Ca[2.2.2]$^{2+}$: (●) [HOAc]/[OAc$^-$] = 2.75; (+) [HOAc]/[OAc$^-$] = 1.49.

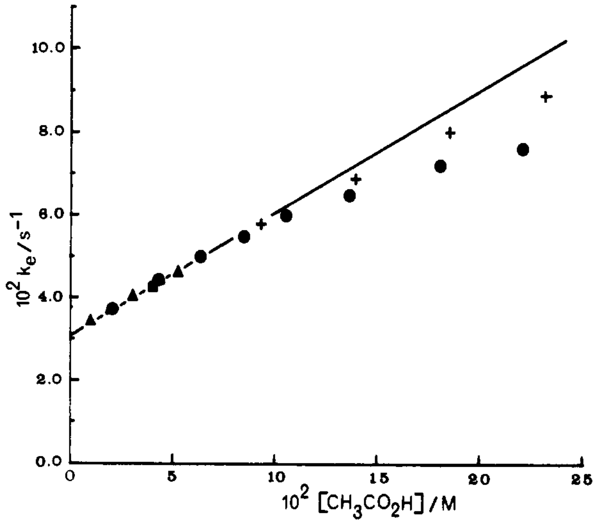

Figure 2. Acetic acid catalyzed dissociation of Li[2.1.1]$^+$: (+) [HOAc]/[OAc$^-$] = 21; (●) [HOAc]/[OAc$^-$] = 8.8; (▲) [HOAc]/[OAc$^-$] = 4.4; (■) [HOAc]/[OAc$^-$] = 2.3.

The dissociation of K[2.2.2]$^+$ was also studied in acetate/acetic acid buffers. The rates were independent of buffer concentration up to [HOAc] = [OAc$^-$] = 0.08 M. The measured dissociation rate constant, k_d, at 25 °C was k_d = 7.8 (±0.2) s^{-1}, in good agreement with that obtained in dilute HCl solutions [k_d = 7.5 (±0.3) s^{-1}].[9] This reaction had also been shown previously to be independent of H$^+$ concentrations (up to 2.5 × 10^{-3} M).

The dependence of the catalytic constants, k_{HA}, for the two systems upon the strength and type of acid HA may be seen more clearly in Figure 3, in which log k_{HA} is plotted against

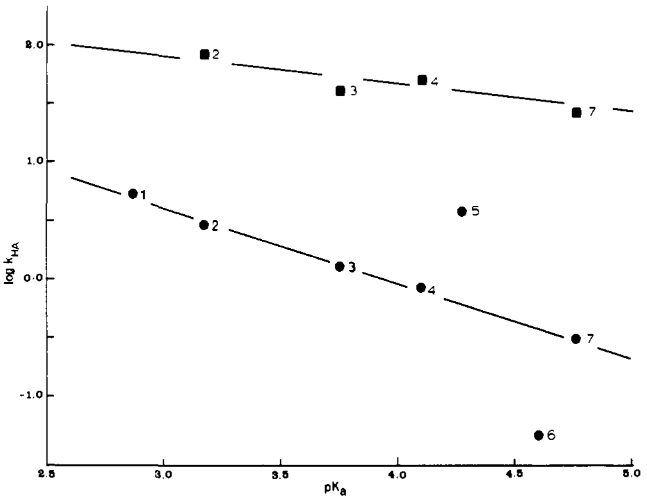

Figure 3. Brønsted plot for the general acid catalyzed dissociation of Ca[2.2.2]$^{2+}$ (■) and Li[2.1.1]$^+$ (●). Catalyzing acids are as follows: 1, CH_2ClCO_2H; 2, CH_2ICO_2H; 3, HCO_2H; 4, $CH_2ClCH_2CO_2H$; 5, $HO_2C{\cdot}CO_2^-$; 6, $C_6H_5NH_3^+$; 7, CH_3CO_2H.

pK_a(HA). For a given acid catalyst, the dissociation of Ca[2.2.2]$^{2+}$ is more strongly catalyzed than that of Li[2.1.1]$^+$, but it is significantly less sensitive to acid strength (Brønsted α values[17] are 0.25 and 0.64, respectively). The very striking difference between the uncharged substituted acetic acids and the charged acids (monooxalate ion, $HCO_2{\cdot}CO_2^-$, and anilinium ion, $C_6H_5NH_3^+$) when used as catalysts for Li[2.1.1]$^+$ is also clearly apparent. It would seem that, although the cations are contained within the cavity of the ligands, the relative charge of the complex and the catalyzing acid plays an important part in these reactions. The catalytic constant, k_H, for proton catalysis is not shown, but log k_H falls well below lines extrapolated from those shown in Figure 3, particularly for Li[2.1.1]$^+$. This may be partly a consequence of the positive charge on the proton, but a relatively low reactivity of the proton in general acid catalyzed reactions is frequently observed.[17]

A detailed mechanism for the acid catalyzed pathway is uncertain. A rate law of the form shown in eq 1 and 2 could arise either from a rate-determining proton transfer from HA to MCry^{n+} (followed by, or even possibly coincidental with, loss of the cation), or a rate-determining dissociation of M^{n+} from an AH···CryM^{n+} complex. It has been claimed,[18] on the basis of a positive kinetic salt effect on the H$^+$ catalyzed dissociation, that the rate-determining step for this reaction is the protonation of the cryptate complex. However, this conclusion seems to be of doubtful validity, as catalysis by H$^+$ should show a positive salt effect whether the mechanism involved a preequilibrium protonation or a rate-determining proton transfer. It is hoped that kinetic hydrogen isotope effect studies, and studies of the proton-transfer reactions between HA and the monoprotonated cryptand, CryH$^+$, might help to resolve this mechanistic question.

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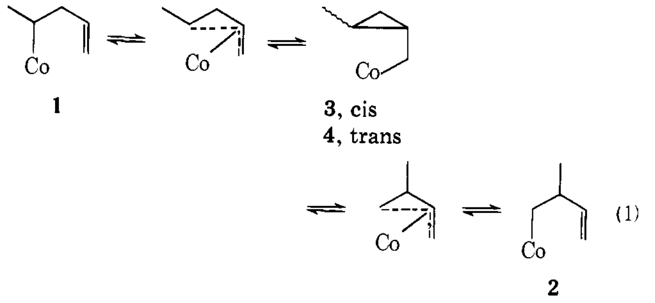
$^3\eta$-Homoallylcobalt Complexes in the Intramolecular Rearrangements of But-3-enylcobaloximes

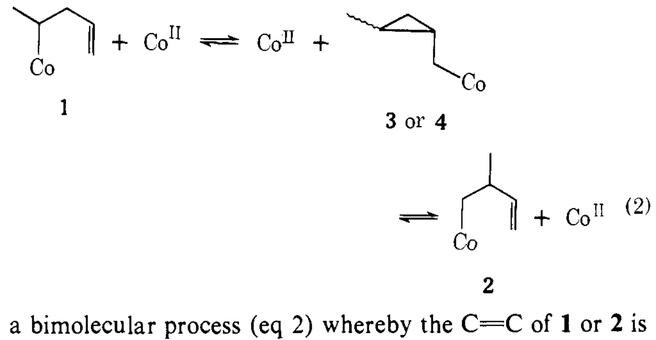
Sir:

We reported[1,2] the thermal and acid-catalyzed equilibrium of 1-methylbut-3-enyl(pyridine)cobaloxime (**1**) with 2-methylbut-3-enyl(pyridine)cobaloxime (**2**). Cyclopropylcarbinylcobalt complexes such as **3** and **4** were postulated as intermediates in this and related rearrangements. Thus **3** and **4** might arise from **1** or **2** either in a unimolecular process (eq 1) via a $^3\eta$-homoallylic imtermediate or transition state or in a bimolecular process (eq 2) whereby the C=C of **1** or **2** is attacked by a cobaloxime(II) species. We now report the syntheses and rearrangements of racemic **3** and **4**, studies of the stereochemical course of the acid-catalyzed equilibration of **1** and **2**, and an investigation of the skeletal rearrangement of isotopically labeled but-3-enylcobaloximes. We demonstrate that the acid-catalyzed equilibration of **1** and **2** is stereospecific and intramolecular, and that methylcyclopropylcarbinylcobalt species are plausible intermediates in this process. This is the first demonstration of the stereospecific and intramolecular character of the rearrangement of a but-3-enyl group attached to a metal.



1
3, cis
4, trans
2
(1)

Co = Co(dmgH)$_2$py



1
3 or **4**
2
(2)

Cobaloximes **3** and **4** were obtained by reacting (pyridine)-

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