any organometallic compounds with C_6F_5I.

The ethers coordinated to $M(C_6F_5)_2$ (M = Ni, Co, Fe) themselves are quite labile and can be readily displaced with a variety of other ligands. The solvated $Ni(C_6F_5)_2$ reacts instantly at room temperature with $(C_6H_5)_2PH$ to yield, upon workup and recrystallization from toluene, amber-yellow, diamagnetic crystals of $Ni(C_6F_5)_2[(C_6H_5)_2PH]_2 \cdot C_6H_5CH_3$[23] in 31% yield based on nickel.

The preparation of $Ni(C_6F_5)_2[(C_6H_5)_2PH]_2 \cdot C_6H_5CH_3$ via $Ni(C_6F_5)_2$ is noteworthy in that the reaction of a nickel halide with $(C_6H_5)_2PH$ results in $Ni[(C_6H_5)_2P][(C_6H_5)_2PH]_2$.[24] Thus, this organonickel compound would not be directly available via standard arylating reagents.

The displacement of the ether molecule from $Ni(C_6F_5)_2$ is not limited to phosphines. Addition of pyridine to the orange-brown mixture of solvated $Ni(C_6F_5)_2$ and NiI_2 immediately results in a greenish-yellow mixture and the formation of $Ni(C_6F_5)_2(C_5H_5N)_2$.[25] Preliminary evidence indicates that other amines as well as isocyanides also react to yield derivatives of $Ni(C_6F_5)_2$.

$FeCl_2$ reduced in the usual manner with Li in glyme results in a black slurry in a colorless or lightly brown solution. The black iron powder, though, differs from other transition metals reported by us in that it is pyrophoric. The reaction of this powder with C_6F_5I is very exothermic; hence, the slurry is cooled to about 0 °C for the slow addition of 1 equiv of C_6F_5I. The mixture is stirred at 50 °C for 20 h even though it appears most of the reaction is complete in about 2 h. The deep brown solution contains solvated $Fe(C_6F_5)_2$ and FeI_2. This mixture absorbs CO at room temperature and atmospheric pressure without any color change and results in the formation of $Fe(C_6F_5)_2(CO)_2(C_4H_{10}O_2)_2$[26] in 60% yield.

This compound undoubtedly is 6-coordinate with one of the glymes being a molecule of crystallization. On the NMR time scale ($CDCl_3$), both molecules of glyme are equivalent. The IR spectrum of this compound in the carbonyl region is more complex than would be expected for either a cis or a trans arrangement of the carbonyl groups and suggests a mixture of isomers. Such mixtures of isomers have been observed in related compounds of iron.[27] The analogous reaction employing C_6F_5Br as the organic halide yields the same compound.

The reactivity of these metal powders is not limited to activated halides. For example, a 2:1 mixture of a nickel slurry and iodobenzene reacted quantitatively (98% conversion) after 1 h at 85 °C and resulted in a 65% yield of biphenyl, with the remainder benzene. A Ni/THF slurry prepared by codeposition of nickel vapor and THF has been reported to react with iodobenzene and yield 8% biphenyl.[28] The reaction of a nickel slurry, obtained from $NiBr_2$, and bromobenzene resulted in 90% of the bromobenzene reacting after 24 h at 85 °C. The yield of biphenyl was 20% with the remainder benzene. As far as we known, this is the first report of an Ullman-type coupling of an unactivated aryl bromide with nickel under such mild conditions.

In reaction mixtures containing a haloarene and a halogen different than that of the haloarene, we observe halogen–halogen exchange of the haloarene. For example, in a reaction mixture of iodobenzene and a nickel slurry derived from $NiBr_2$, some bromobenzene forms before it reacts further. Similarly, bromobenzene and a nickel slurry containing iodide result in some iodobenzene forming prior to its subsequent reaction. The facile halogen–halogen exchange we observe may allow coupling of very nonreactive haloarenes by employing slurries obtained by reducing NiI_2.

The reactions of the nonactivated haloarenes, iodobenzene, and bromobenzene with the nickel slurry were carried out under relatively dilute and mild conditions. This nickel slurry appears so far to be an exceptional coupling reagent. We are presently conducting further studies of these systems, which we will report on in the near future, as well as on the chemistry of these and other metals.

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(23) Crystals were completely black before melting: mp 161–162 °C; IR (Nujol) ν (P–H) 2360 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.28 (aromatic m, 25 H), 2.32 (aliphatic s, 3 H). Anal. Calcd for $C_{43}H_{30}F_{10}NiP_2$: C, 60.24; H, 3.53; F, 22.16. Found: C, 59.74; H, 3.70; F, 21.71.

(24) Issleib, K.; Wenschuh, E. *Z. Anorg. Allg. Chem.* **1960**, *305*, 15.

(25) The small amount of light green crystals, presumably $NiI_2(C_5H_5N)_4$, which may also be obtained is washed out with water and the remaining material recrystallized from CH_2Cl_2 to yield small, straw-yellow diamagnetic crystals of $Ni(C_6F_5)_2(C_5H_5N)_2$ in 40% yield; mp >280 °C, discolors at about 250 °C. Anal. Calcd for $C_{22}H_{10}F_{10}N_2Ni$: C, 47.95; H, 1.83; F, 34.48; N, 5.08. Found: C, 47.81; H, 1.83; F, 34.26; N, 5.07.

(26) A slow stream of CO was bubbled through the stirred solution for about 2 h (tenfold excess), and then all volatiles were removed under vacuum. The crude material was dissolved in 15 mL of CH_2Cl_2 and anaerobically filtered. Slow solvent evaporation under an inert atmosphere resulted in diamagnetic, yellow, and moisture-sensitive crystals. The crystals often are covered with a brown oily residue which is readily removed by washing the crystals with a small amount of 2:1 hexane–CH_2Cl_2 mixture: mp (sealed tube) dec >90 °C; IR (Nujol) 2090 (s), 2076 (w), 2020 (vs), 1993 (m), 1976 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.58 (s, 4 H), 3.41 (s, 6 H). Both resonances are shifted downfield from those of free glyme in $CDCl_3$. Anal. Calcd for $C_{22}H_{20}F_{10}FeO_6$: C, 42.19; H, 3.22; F, 30.34. Found: C, 42.35; H, 3.30; F, 30.54.

(27) Hensley, D. W.; Steward, R. P., Jr. *Inorg. Chem.* **1978**, *17*, 905.

(28) Klabunde, K. J.; Murdock, T. O. *J. Org. Chem.* **1979**, *44*, 3901.

Role of Ferryl (FeO^{2+}) Complexes in Oxygen Atom Transfer Reactions. Mechanism of Iron(II) Porphyrin Catalyzed Oxygenation of Triphenylphosphine

Sir:

For some time, it has been suspected that under certain circumstances oxygen can react with $P\mathrm{Fe}^{\mathrm{II}}$ (P = a porphyrin dianion) to yield the ferryl complex $P\mathrm{Fe}^{\mathrm{IV}}\mathrm{O}$.[1-3] Ferryl complexes have been postulated to exist as stable intermediates in enzymatic reactions (peroxidase compound II),[4] as the active oxidants in mixed-function oxidases,[5] and as a reactive species in aliphatic hydroxylation by hydrogen peroxide–ferrous ion.[6] Recent work in this laboratory has indicated that transient ferrylporphyrin complexes are present during the decomposition of iron(III) peroxoporphyrin complexes via reaction 1[7,8] and has allowed

$$2P\mathrm{Fe}^{\mathrm{III}}\mathrm{OOFe}^{\mathrm{III}}P \rightarrow 2P\mathrm{Fe}^{\mathrm{III}}\mathrm{OFe}^{\mathrm{III}}P + \mathrm{O}_2 \qquad (1)$$

low-temperature spectroscopic observation of a moderately stable (at −80 to −30 °C) ferryl complex, $\mathrm{B}P\mathrm{Fe}^{\mathrm{IV}}\mathrm{O}$ (B = *N*-methylimidazole, pyridine, piperidine), which is formed via reaction 2.[9] We now present evidence for the role of ferryl complexes in oxygen atom transfer reactions.

$$P\mathrm{Fe}^{\mathrm{III}}\mathrm{OOFe}^{\mathrm{III}}P + 2\mathrm{B} \rightarrow 2\mathrm{B}P\mathrm{Fe}^{\mathrm{IV}}\mathrm{O} \qquad (2)$$

$\mathrm{B}P\mathrm{FeO}$ reacts with triphenylphosphine at −80 °C in toluene solution over a period of several hours to give triphenylphosphine

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(1) Alben, J. O.; Fuchsman, W. H.; Beaudreau, C. A.; Caughey, W. S. *Biochemistry* **1968**, *7*, 624–635.

(2) Cohen, I. A.; Caughey, W. S. *Biochemistry* **1968**, *7*, 636–641.

(3) Collman, J. P. *Acc. Chem. Res.* **1977**, *10*, 265–272.

(4) Dunford, H. D.; Stillman, J. S. *Coord. Chem. Rev.* **1976**, *19*, 187–251.

(5) Sharpless, K. B.; Flood, T. C. *J. Am. Chem. Soc.* **1971**, *9*, 3, 2316–2318.

(6) Groves, J. T.; Van Der Puy, M. *J. Am. Chem. Soc.* **1976**, *98*, 5290–5297.

(7) Chin, D. H.; Del Gaudio, J.; La Mar, G. N.; Balch, A. L. *J. Am. Chem. Soc.* **1977**, *99*, 5486–5488.

(8) Chin, D. H.; La Mar, G. N.; Balch, A. L. *J. Am. Chem. Soc.*, **1980**, *102*, 4344–4350.

(9) Chin, D. H.; Balch, A. L.; La Mar, G. N. *J. Am. Chem. Soc.* **1980**, *102*, 1446–1448.

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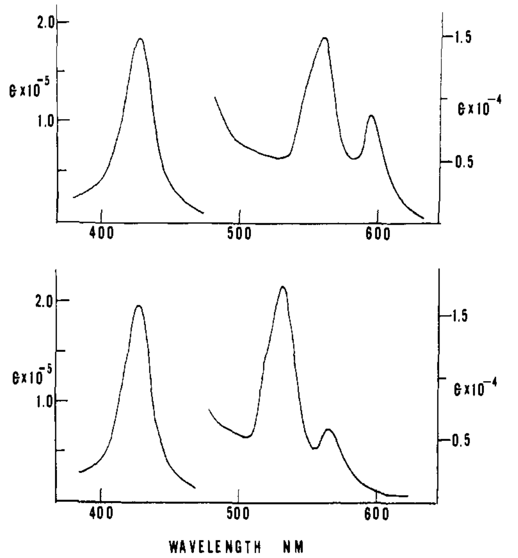


Figure 1. The electronic spectrum of a solution of *N*-MeImTmTPFeO in the presence of excess *N*-MeIm at -80 °C. (Top) Before addition of triphenylphosphine; (Bottom) 2 h after the addition of triphenylphosphine. The bottom spectrum is that of $(N\text{-MeIm})_2\text{TmTPFe}^{II}$.

oxide quantitatively, according to eq 3.[10,11] Electronic spectral changes due to this reaction are shown in Figure 1.

$$\mathrm{B}P\mathrm{Fe}^{IV}\mathrm{O} + \mathrm{B} + \mathrm{Ph_3P} \rightarrow \mathrm{B}_2P\mathrm{Fe}^{II} + \mathrm{Ph_3PO} \qquad (3)$$

$P\mathrm{Fe}^{II}$ catalyzes the oxidation of triphenylphosphine to triphenylphosphine oxide in toluene solution at 25 °C. After exposure of a solution initially containing 1.2×10^{-3} M TPPFe^{II} (TPP = anion of *meso*-tetraphenylporphyrin) and 6×10^{-2} M triphenylphosphine to a stream of dioxygen for 10 min, 27 mol of triphenylphosphine oxide are formed per mol of TPPFe^{II} before the catalyst becomes inactive. Decreasing the concentration of triphenylphosphine lowers the number of successful turnovers of the catalyst. Under otherwise identical conditions but with 6×10^{-3} M triphenylphosphine, only 4 turnovers are accomplished before inactivation occurs. The inactive solution that results contains TPPFeOFeTPP as the only detectable iron porphyrin species.

Since B*P*FeO is capable of oxidizing triphenylphosphine to triphenylphosphine oxide, we suspect that *P*FeO is the active oxidant in reaction. In contrast, Fe(III) species do not serve as oxidants for triphenylphosphine. *P*FeOFe*P*, which is observed in the inactivated catalyst solutions, does not react with triphenylphosphine. Other iron(III) porphyrin species, including *P*FeCl and $\mathrm{B}_2P\mathrm{Fe}^+$, are also unreactive toward triphenylphosphine although more basic phosphines such as tri-*n*-butylphosphine are capable of reducing *P*FeCl.

Further information has been gained by examination of the reacting species at low temperature. Addition of excess triphenylphosphine to $P\mathrm{Fe}^{II}$ in toluene solution at -80 °C produces a diamagnetic complex which we formulate as $(\mathrm{Ph_3P})_2P\mathrm{Fe}^{II}$. Introduction of dioxygen into this solution produces the peroxo-bridged dimer *P*FeOOFe*P*. Solutions of triphenylphosphine and *P*FeOOFe*P* are stable at -80 °C for several days and show no evidence for coordination of *P*FeOOFe*P* by triphenylphosphine. However, when a carefully degassed solution of these two materials is warmed, the iron is reduced to Fe(II), and triphenylphosphine oxide is produced. The ratio of final concentration of $\mathrm{Ph_3PO}$ to initial concentration of *P*FeOOFe*P* is 2.0.[12] The rate of reduction of TmTPFeOOFeTmTP (TmTP = dianion of *meso*-tetra-*m*-tolylporphyrin) has been measured. The reduction rate is first order in *P*FeOOFe*P* and independent of the concentration of triphenylphosphine in the absence of dioxygen.[13] At -27.5 °C, the rate constant is 0.0073 min^{-1} while at -20.5 °C it is 0.020 min^{-1}. In comparison, the rate constant for spontaneous decomposition[8] of TmTPFeOOFeTmTP is twice as great at each temperature (0.015 at -27.5 °C and 0.044 at -20.5 °C). These data suggest that a common rate-limiting step is involved in both the reaction of *P*FeOOFe*P* with triphenylphosphine and the self-decay of *P*FeOOFe*P*. We have presented evidence that suggests that the mechanism of decay of *P*FeOOFe*P* follows eq 4-6.[8] This

$$P\mathrm{Fe}^{III}\mathrm{OOFe}^{III}P \rightarrow 2P\mathrm{Fe}^{IV}\mathrm{O} \qquad (4)$$

$$P\mathrm{Fe}^{IV}\mathrm{O} + P\mathrm{Fe}^{III}\mathrm{OOFe}^{III}P \rightarrow P\mathrm{Fe}^{III}\mathrm{OFe}^{III}P + \mathrm{O}_2P\mathrm{Fe}^{II} \qquad (5)$$

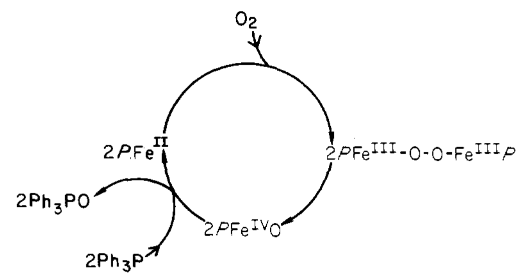
$$P\mathrm{Fe}^{IV}\mathrm{O} + \mathrm{O}_2P\mathrm{Fe}^{II} \rightarrow P\mathrm{Fe}^{III}\mathrm{OFe}^{III}P + \mathrm{O}_2 \qquad (6)$$

mechanism causes the destruction of two molecules of *P*FeOOFe*P* for each O-O bond break, and consequently, the rate constant for loss of *P*FeOOFe*P* is two times the rate constant for the initial step.[4] Thus, the observed rate constant for reaction 1 is anticipated to be twice the rate constant for the reduction of *P*FeOOFe*P* by triphenylphosphine if the latter reaction occurs via eq 7 and 8.

$$P\mathrm{Fe}^{III}\mathrm{OOFe}^{III}P \rightarrow 2P\mathrm{Fe}^{IV}\mathrm{O} \qquad (7)$$

$$P\mathrm{Fe}^{IV}\mathrm{O} + \mathrm{Ph_3P} \rightarrow P\mathrm{Fe}^{II} + \mathrm{Ph_3PO} \qquad (8)$$

Scheme I



These data allow us to propose Scheme I as the mechanism of oxidation of triphenylphosphine to triphenylphosphine oxide by dioxygen. The reactivity of *P*FeO is such that it can attack either triphenylphosphine to complete the catalytic cycle or it could react with iron porphyrins in reactions 5 and 6 to form *P*FeOFe*P*. These latter possibilities lead to termination of the catalytic activity.

The mechanism shown in Scheme I offers a new route for oxygen activation. It differs substantially from the $(\mathrm{Ph_3P})_3\mathrm{Pt}$-catalyzed oxidiation of triphenylphosphine in polar media which involves the formation of uncoordinated peroxide.[14] The behavior of the ferryl complexes reported here parallels that of their ruthenium congeners, which also are capable of oxygen-atom transfer to oxidize triphenylphosphine to triphenylphosphine oxide.[15] In related work, iron(III) and chromium(III) porphyrins have been shown to catalyze oxygen-atom transfer from iodosylbenzene to olefins, and high-valent metal-oxo complexes have been implicated as intermediates.[16,17] The results reported here also demonstrate

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(10) Throughout this work, iron porphyrin complexes have been quantitatively detected via their characteristic electronic and ^{1}H NMR spectra. Triphenylphosphine and triphenylphosphine oxide have been detected via ^{31}P NMR spectra.

(11) Other substances which reduce B*P*FeO include triphenylarsine, triphenylstilbine, and nitrosodurene. We presume that triphenylarsine oxide, triphenylstilbine oxide, and nitrodurene are products, and we are at work on their quantitative detection. Neither triphenylbismuth, which does not oxidize to form triphenylbismuth oxide, an unknown compound, nor triphenylamine reduce B*P*FeO. The failure of triphenylamine to reduce B*P*FeO is consistent with the fact the B*P*FeO is stable in the presence of other amines, including pyridine, *N*-MeIm, and piperidine.

(12) In this case, in order to detect triphenylphosphine and triphenylphosphine oxide by ^{31}P NMR spectroscopy, it is necessary to add a base (pyridine or *N*-MeIm) *after reduction* in order to convert the iron(II) porphyrin into a diamagnetic species. Otherwise, the presence of a paramagnetic species, five-coordinate $P\mathrm{FeOPPh_3}$ in particular, causes line broadening which vitiates the experiment.

(13) In the presence of varying amounts of dioxygen, the rate of reduction slows due to the re-formation of *P*FeOOFe*P*.

(14) Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1977**, *99*, 8337-8339.

(15) Moyer, B. A.; Meyer, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3601-3603.

(16) Groves, J. T.; Nemo, T. E.; Myers, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 1032-1033.

(17) Chang, C. K.; Kuo, M.-S. *J. Am. Chem. Soc.* **1979**, *101*, 3413-3415.

that the peroxo-bridged dimer *P*FeOOFe*P* forms in the presence of potential axial ligands. Further studies of oxygenation transfer by iron porphyrin complexes are in progress.

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(18) Groves, J. T.; Kruper, W. J., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 7613-7615.

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Macrocyclic Hexacarboxylic Acid. A Highly Selective Host for Uranyl Ion

Sir:

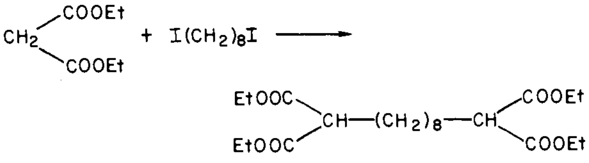
Macrocyclic polydentates have attracted enormous attention from chemists because of their unique and significant characterisitic of the strong and selective binding of a variety of metal ions.[1,2] The metal binding is governed mostly by the size of the macroring and the nature of heteroatoms involved. The most important role of the macrocyclic structure is, in general, the so-called "macrocyclic effect"[3] —to increase (making less negative) a large negative entropy change involved in the polydentate chelation.

Basic strategy then is to design a ligand of very strong metal binding to take advantage of this macrocyclic effect as well as the enthalpy effect (negative enthalpy change) associated with the chelation under consideration. For the latter purpose, a negatively charged ligand should be chosen as a strong candidate although only a few examples[4] are known in which anions are appropriately arranged in a macroring host.[5]

We have currently been interested in the highly selective binding of a family of metal ions of pseudoplanar hexacoordination,[6] to which uranyl (UO_2^{2+}) belongs as an important member from a practical viewpoint. As an application of the basic strategy described above to the solution of this rather difficult problem, we have prepared a macrocyclic hexaketone which bound uranyl ion effectively.[4e,7]

Now we report that selective members of the family, **3** and **4**, were newly designed. These ligands were prepared by symmetrically arranging six carboxylates on a macrocyclic skeleton in which the ring size was adjusted to give a cavity to accommodate uranyl ion comfortably. Three of the six carboxylates seem to compose a binding site. One of the three additional carboxylic acid units in either **3b** and **4** is amenable to attachment to a suitable polymer support. The other two probably act to make the microscopic environment around the metal binding site more hydrophilic as well as to decrease the entropy loss involved in the complexation. Compared with the previous hexaketone, the new macrocycle hexacarboxylic acids are capable of much more facile preparation in reasonable overall yields and are more effective and selective for the binding of the uranyl ion.

Preparation is straightforward and is described by eq 1–3.



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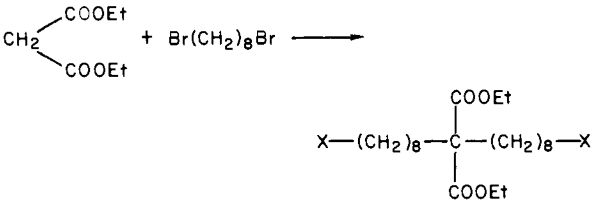
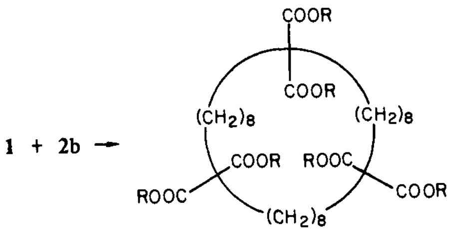
(1)



(2)

2a, X = Br
b, X = I



(3)

3a, R = Et
b, R = H

Tetraethyl *n*-decane-1,1,10,10-tetracarboxylate, **1**, and diethyl α,α-bis(8-iodooctyl)malonate, **2b**, were prepared according to the conventional method for the malonate synthesis and were obtained in 67% and 54% yields, respectively. The final cyclization was achieved under high-dilution conditions. For example, to a mixture of 1.7 g (3.9 mmol) of **1** and 2.5 g (3.9 mmol) of **2b** in 800 mL of THF was added 0.56 g (12 mmol) of sodium hydride dispersion (50%). After 20 h of refluxing followed by usual workup, the hexaethyl ester of macrocyclic hexacarboxylic acid, **3a**, was isolated through silica gel column chromotagraphy. The yield of colorless crystals obtained from *n*-hexane was 1.47 g (46%): mp 82–84 °C; IR (KBr) 1723 cm^{-1}; NMR ($CDCl_3$) δ 1.23 (t, 18 H), 1.0–1.4 (br, 36 H), 1.4–2.0 (br, 12 H), 4.10 (q, 12 H); mass spectrum (hexamethyl ester), *m/e* 726 (M^+), 694 (base), 662, 634. Anal. Calcd: C, 66.64; H, 9.69. Found C, 66.63; H, 9.61. Alkaline hydrolysis of 1.52 g of **1a** yielded 1.11 g (92%) of hexacarboxylic acid **1b**: mp 200–205 °C; IR (KBr) 1697 cm^{-1}; NMR (Me_2SO-d_6) δ 1.0–1.5 (br, 36 H), 1.5–2.0 (br, 12 H), FD mass spectrum *m/e* 643 ($M^+ + 1$). Anal. Calcd: C, 61.66; H, 8.47. Found: C, 61.63; H, 8.49. Similar procedures gave a hexacarboxylic acid of type **4**, containing an ether bridge, in an overall yield of 17.5%. All of the spectral and analytical data are satisfactory.

Uranyl ion is known to form a stable complex with carbonate (CO_3^{2-}). The stability constant (log K_f) ranges from 20.7 to 23.0, depending on the conditions.[8] The addition of hexacarboxylic acid **3b** (1.0×10^{-3} M) to a uranyl tricarbonate solution (5.0×10^{-4} M in 1.0×10^{-2} M Na_2CO_3, pH 10.4) gave a change of visible

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(1) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017-7036.

(2) For reviews, see: (a) Cram, D. J.; Cram, J. M. *Science (Washington, D. C.)* **1974**, *183*, 803-809. (b) Lehn, J. M. *Struct. Bonding (Berlin)* **1973**, *16*, 1-69; (c) Christensen, J. J.; Eatough, D. J.; Izatt, R. M. *Chem. Rev.* **1974**, *74*, 351-384. (d) Gokel, G. W.; Durst, H. D. *Synthesis* **1976**, 168-184.

(3) Cabbiness, D. K.; Margerum, D. W. *J. Am. Chem. Soc.* **1969**, *91*, 6540-6541; **1970**, *92*, 2151-2153.

(4) (a) Alberts, A. H.; Cram, D. J. *J. Chem. Soc., Chem. Commun.* **1976**, 958-959. (b) *J. Am. Chem. Soc.* **1977**, *99*, 3880-3882. (c) *Ibid.* **1979**, *101*, 3545-3553. (d) Ito, Y.; Sugaya, T.; Nakatsuka, M.; Saegusa, T. *Ibid.* **1977**, *99*, 8366-8367. (e) Tabushi, I.; Kobuke, Y.; Nishiya, T. *Tetrahedron Lett.* **1979**, 3515-3518.

(5) The first introduction of carboxyl groups as counterions of crown complexes is reported: (a) Helgeson, R. C.; Timko, J. M.; Cram, D. J. *J. Am. Chem. Soc.* **1973**, *95*, 3023-3025. (b) Cram, D. J.; Helgeson, R. C.; Koga, K.; Kyba, E. P.; Madan, K.; Sousa, L. R.; Siegel, M. G.; Moreau, P.; Gokel, G. W.; Timko, J. M.; Sogah, G. D. Y. *J. Org. Chem.* **1978**, *43*, 2758-2772. (c) Newcomb, M.; Cram, D. J. *J. Am. Chem. Soc.* **1975**, *97*, 1257-1259. (d) Newcomb, M.; Moore, S. S.; Cram, D. J. *Ibid.* **1977**, *99*, 6405-6410.

(6) (a) Fankuchen, I. *Z. Kristallogr.* **1935**, *91*, 473-479; **1935**, *94*, 212-221. (b) Zachariasen, W. H. *Acta Crystallogr.* **1948**, *1*, 277-287. (c) Graziani, R.; Bombieri, G.; Forsellini, E. *J. Chem. Soc., Dalton Trans.* **1972**, 2059-2061.

(7) Tabushi, I.; Kobuke, Y.; Nishiya, T. *Nature (London)* **1979**, *280*, 665-666.

(8) (a) Babko, A. K.; Kodenskaya, V. S. *Zh. Neorg. Khim.* **1960**, *5*, 2568-2574. (b) Klygin, A. E.; Smirnova, I. D. *Ibid.* **1959**, *4*, 42-45. (c) Paramonova, V. I.; Nikolaeva, N. M. *Radiokhimiya* **1961**, *4*, 84-89. (d) Cinnēide, S. Ó.; Scanlan, J. P.; Hynes, M. J. *J. Inorg. Nucl. Chem.* **1975**, *37*, 1013-1018.

0002-7863/80/1502-5947$01.00/0