Table I. Effect of Catalyst and Reaction Medium on Benzoylation of *p*-Toluate Ion–Isobutyrate Ion Mixtures[a]

equivalent of catalyst	reaction medium	anhydride[b] total yield, %	products, mole fraction[c]		
			p-MePhCOOCOPh	$Me_2CHCOOCOPh$	PhCOOCOPh
		Catalysis by PNO[d]			
1.0	H_2O	79	0.50	0.50	0.00
1.0[e]	H_2O	73	0.66	0.34	0.00
1.0[f]	H_2O	81	0.33	0.67	0.00
0.1	H_2O/CH_2Cl_2	69	0.68	0.32	0.00
1.0	H_2O/CH_2Cl_2	84	0.58	0.42	0.00
		Catalysis by DMAP[d]			
1.0	H_2O	52	0.85	0.15	0.00
0.1	H_2O/CH_2Cl_2	64	0.92	0.08	0.00
1.0	H_2O/CH_2Cl_2	35	1.00	0.00	0.00
1.0[g]	H_2O/CH_2Cl_2	50	0.88	0.12	0.00
		Catalysts by TEA[d]			
1.0	H_2O	60	0.52	0.00	0.48
0.1	H_2O/CH_2Cl_2	65	0.67	0.00	0.33
1.0	H_2O/CH_2Cl_2	69	0.63	0.00	0.37

[a] Reaction conditions and workup procedure are described in ref 11 and 16. [b] Reaction mixtures also contained mixtures of carboxylic acids (excess reactants and hydrolysis products). [c] Composition of product mixtures was estimated by integration of ^1H NMR spectra of isolated materials. Signals used for anslysis: δ 2.4, s (Me–Ph); 1.3, d (Me_2CH-). Repeatability based on three or more experiments: ±2%. [d] PNO = pyridine 1-oxide; DMAP = 4-(dimethylamino)pyridine; TEA = triethylamine. [e] Reactants included 2.0 equiv of sodium *p*-toluate and 1.0 equiv of sodium isobutyrate. [f] Reactants included 1.0 equiv of sodium *p*-toluate and 2.0 equiv of sodium isobutyrate. [g] Reaction time was 10 s.

sodium isobutyrate in aqueous solution.[16] The results summarized in Table I show that product ratios correspond closely to ratios of reactant carboxylate ion concentrations.

Similar experiments[11] carried out in two-phase mixtures of dichloromethane–water furnished contrasting and especially revealing results, Table I. Reaction mixtures containing equimolar quantities of benzoyl chloride, sodium *p*-toluate, and sodium isobutyrate gave anhydride mixtures that contained somewhat more benzoic *p*-toluic anhydride than benzoic isobutyric anhydride when PNO was used as catalyst. Product composition was found to depend on catalyst concentration. A catalytic amount of PNO (0.10 equiv) gave a higher ratio of benzoic p-toluic anhydride to benzoic isobutyric anhydride than a stoichiometric amount of catalyst.[17] Similar reactions catalyzed by DMAP gave somewhat smaller yields of benzoic *p*-toluic anhydride but little or no benzoic isobutyric anhydride. Surprisingly, catalysis by triethylamine (TEA) led to product mixtures that included benzoic anhydride as well as the expected benzoic *p*-toluic anhydride. However, the second expected product, benzoic isobutyric anhydride, could not be detected.

The results obtained under two-phase conditions are consistent with reaction between either **1** or **2** and carboxylate ion both in the bulk aqueous phase and at the water–organic solvent interface where concentrations of the more lipophilic *p*-toluate ion are expected to be greater than those of the smaller, more hydrophilic isobutyrate ion. DMAP appears to function in much the same fashion as PNO, except **2** is either much more selective with carboxylate ions than **1** or anhydride products, particularly benzoic isobutyric anhydride, are unstable in the reaction mixtures that contain DMAP. In control experiments, DMAP has been shown to catalyze rapid hydrolysis of benzoic isobutyric anhydride, but hydrolysis of benzoic *p*-toluic anhydride occurs much more slowly.[18] Reactions catalyzed by TEA appear to be more typical of PTC processes with reaction occurring in the organic phase. TEA is believed to function as a general base to accelerate hydrolysis of benzoyl chloride, and the benzoate ion so formed remains in the organic phase to produce symmetrical anhydride by reaction with benzoyl chloride, Scheme II.[19,20] The mixed anhydride, benzoic *p*-toluic anhydride, is believed to form at the interface or in the organic layer after phase transfer of the more lipophilic *p*-toluate ion. Apparently, the more hydrophilic isobutyrate ion remains isolated in the aqueous layer.

From the above results, we conclude that inverse phase-transfer catalysis like phase-transfer catalysis includes an interphase component as evidenced by selective transport of the more lipophilic p-toluate ion at the dichloromethane–water interface. The results from more extensive studies currently in progress will be reported fully in due course.

Acknowledgment. We gratefully acknowledge financial support for this project from the Reilly Tar & Chemical Corp. and from the Research Corp. We thank Professors E. T. Harper and M. J. O'Donnell for helpful discussions.

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(16) Reactive intermediates, **1** and **2**, were produced with PNO or DMAP and 1.0 equiv of benzoyl chloride in dichloromethane. For reactions run in water, the dichloromethane was removed by evaporation, and the residues were treated, unless otherwise noted, with aqueous solutions containing 1.0 equiv of sodium *p*-toluate and 1.0 equiv of sodium isobutyrate for 1.0 min at ~22.0 °C.

(17) The experiments that used 1.0 equiv of catalyst (Table I) represent an extreme case scenario in which formation of 1.0 equiv of acylating ion, **1** or **2**, is expected to maximize the possibility for reaction in the bulk aqueous phase.

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Unexpected Diversity in the Coordination Chemistry of Tartrate Esters with Titanium(IV)

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Our interest in the structural[2] and mechanistic[3] aspects of the titanium-catalyzed asymmetric epoxidation reaction has led us to undertake a more general investigation of the solution and solid-state properties of titanium tartrate ester complexes. One of the most intriguing features of titanium tartrate reaction chemistry, beyond the standard asymmetric epoxidation system, is the number of other asymmetric oxidation reactions that have

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(1) (a) Massachusetts Institute of Technology. (b) Exxon Chemical Co.

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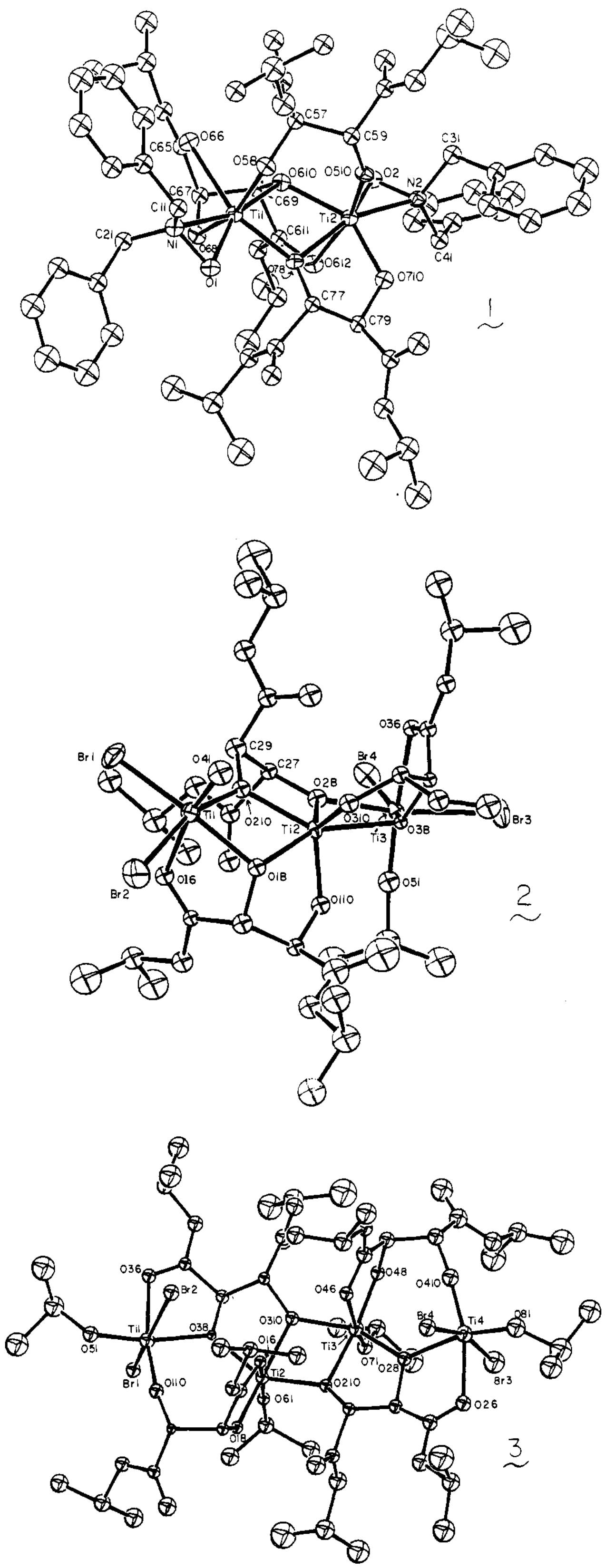
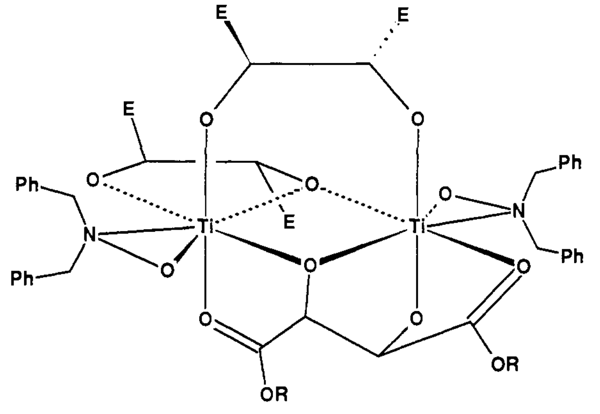


Figure 1. ORTEP diagrams of **1**, **2**, and **3**. Atoms O313, C314, C315, C316, C42, C43, and C44 have been omitted from **2** for clarity.

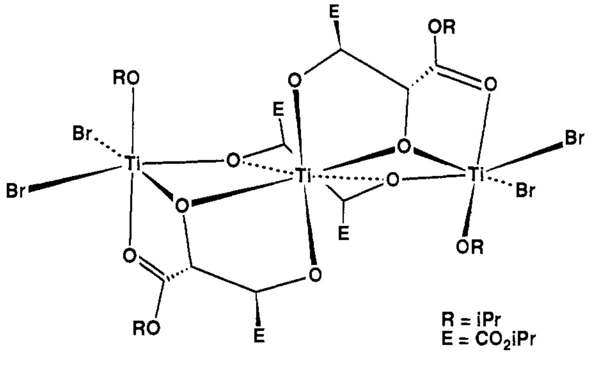
arisen from simple variations in the titanium tartrate ratio and/or ligand changes.[4] Since tartrate ester is the common ligand in all these reactions, it seems reasonable that, in addition to establishing a chiral environment, it must play a crucial role in the in situ assembly of these rather elaborate metal alkoxides. Defining ways in which tartrate binds to metal alkoxides is an important problem if one wishes to take a rational approach toward designing new asymmetric reagents (e.g., chiral Lewis acids) based on titanium tartrate ester systems. Our previous structural studies[2] on two asymmetric epoxidation catalysts suggested that titanium tartrate complexes might prefer dimeric structures to other more elaborate frameworks. Here we present the structures of **1**, **2**, and **3** (a dimer, trimer, and tetramer, Figure 1), showing this assumption to be incorrect. The structures also show that a tartrate ester can display a remarkably wide range of binding modes.



R = iPr
E = CO_2iPr

1

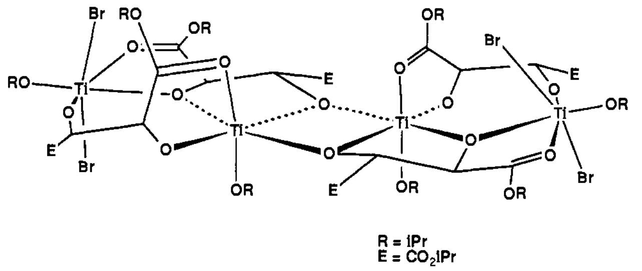
$Ti_2(DIPT)_3(ONBn_2)_2$



R = iPr
E = CO_2iPr

2

$Ti_3(DIPT)_3(OiPr)_2Br_4$



R = iPr
E = CO_2iPr

3

$[Ti(DIPT)(OiPr)Br]_4$

The dimeric asymmetric epoxidation catalyst is prepared by reaction of $Ti(O\text{-}i\text{-}Pr)_4$ and DIPT in a 1:1 ratio [DIPT = (*R*,-

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[4] (a) Pitchen, P.; Dunach, E.; Desmukh, M. N.; Kagan, H. B. *J. Am. Chem. Soc.* **1985**, *106*, 8188. (b) Lu, L. D.-L.; Johnson, R. A.; Finn, M. G.; Sharpless, K. B. *J. Org. Chem.* **1984**, *49*, 728. (c) Miyano, S.; Lu, L. D.-L.; Viti, S. M.; Sharpless, K. B. *J. Org. Chem.* **1983**, *48*, 3608.

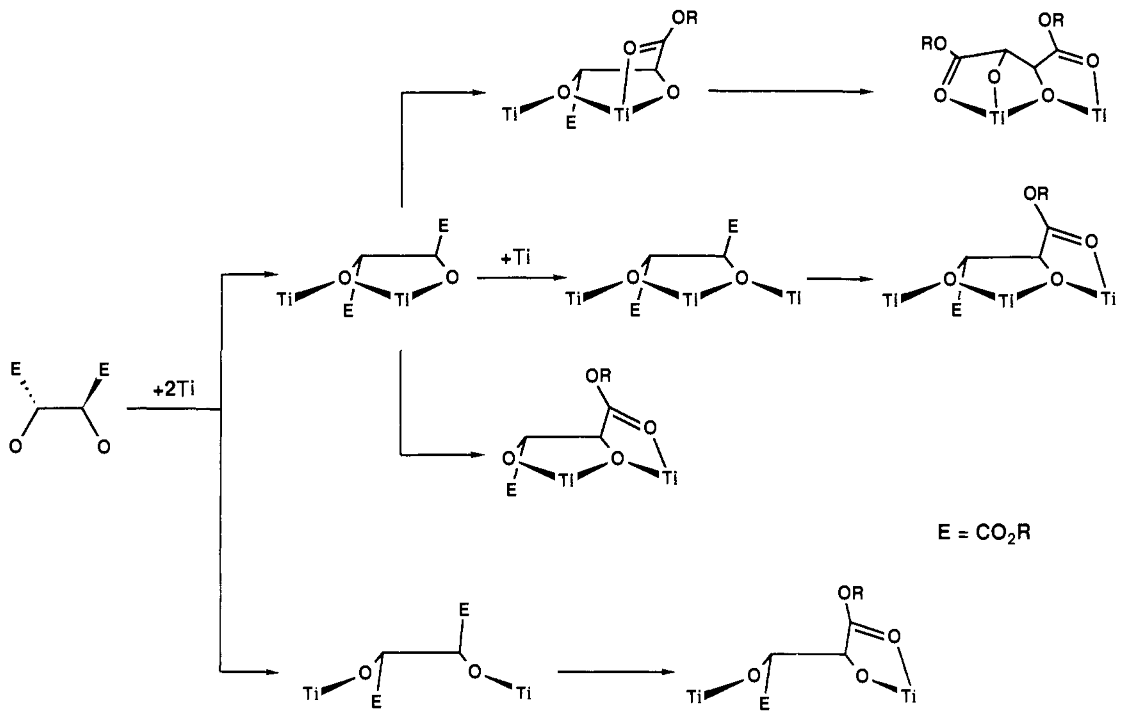

Figure 2. Range of binding modes that have been observed between tartrate ester ligands and titanium.

R)-diisopropyl tartrate]. Attempts to prepare analogues of reaction intermediates by adding these components, and HON$(CH_2Ph)_2$, in a ratio of 1:1:1 as described previously for PhC(O)N(OH)Ph,[2] led to the crystallization of **1** having the unexpected 2:3:2 stoichiometry. Compound **1** can now be prepared in high yield as shown in eq 1. The syntheses of **2** and **3** are outlined in equations 2 and 3.

$$2Ti(O\text{-}i\text{-}Pr)_4 + 3DIPT + 2HON(CH_2Ph)_2 \rightarrow \underset{\mathbf{1}}{Ti_2(DIPT)_3[ON(CH_2Ph)_2]_2} \quad (1)$$

$$2Ti(O\text{-}i\text{-}Pr)_4 + 3DIPT + TiBr_4 \rightarrow \underset{\mathbf{2}}{Ti_3(DIPT)_3(O\text{-}i\text{-}Pr)_2Br_4} \quad (2)$$

$$4Ti(O\text{-}i\text{-}Pr)_3Br + 4DIPT \rightarrow \underset{\mathbf{3}}{[Ti(DIPT)(O\text{-}i\text{-}Pr)Br]_4} \quad (3)$$

The dimer, **1**, consists of two distorted pentagonal-bipyramidal titanium centers joined by two bridging diolate oxygens (O610, O78). The three DIPT ligands all bind differently between the two titanium centers. The *N*,*N*-dibenzylhydroxylamino(1–) ligands bind in a manner similar to that reported for similar ligands bound to vanadium[5] and molybdenum.[6] Pentagonal-bipyramidal geometry is prevalent in early-transition-metal complexes containing bidentate ligands similar to R_2NO^- that have a short donor atom–donor atom distance (e.g., O_2^{2-},[7] ROO^-,[8] and RNO^{2-}[9]).

The three titanium atoms in the trinuclear **2** are each six-coordinate, with the geometry around the central titanium being highly distorted, and two types of DIPT ligand are found. One of these uses its diolate oxygens (O28, O210) to bridge all three titanium atoms while the other two serve as tridentate ligands consisting of one bridging (O18, O38) and one terminal diolate oxygen (O110, O310) and one bound carbonyl group (O16, O36).

The tetramer, **3**, contains an approximate C_2 axis of symmetry and the four DIPT ligands are of two types. One set functions as tridentate ligands using both diolate oxygens (O28, O210, and O38, O310) to bridge a total of three titanium atoms. The other set is also tridentate and spans two titanium atoms without using a bridging diolate oxygen. The diolate oxygens (O110, O410) function as very efficient π-donors as is evident in the short bond lengths [Ti1–O110 = 1.75 (2) Å; Ti4–O410 = 1.81 (2) Å] and angles [Ti1–O110–C19 = 168 (2)°; Ti4–O410–C49 = 174 (2)°]. These appear to be some of the most obtuse angles observed for any d-block metal alkoxide.[10] The overall structure of **3** is slightly concave. In **1**–**3** the O-*i*-Pr ligand is always terminal.

The above results are graphically summarized in Figure 2. Compounds **1**, **2**, and **3** contain bi-, tri-, and tetradentate tartrate ester ligands that represent *seven* different ways that tartrate esters can bind to two or three titanium centers. Including two previous titanium tartrate structures,[2] the number of observed binding modes is now *eight*, which establishes that the tartrate ligand can assemble and stabilize a variety of structural types. Titanium is almost always six-coordinate, being surrounded by six oxygen atoms. In this sense the structures all bear some resemblance to the lattices of the inorganic oxide TiO_2.[11] The oxygen-containing cores appear to be sections carved out of the TiO_2 lattice and decorated with organic substituents. Upon closer scrutiny of these structures one notices some severe departures from the ideal coordination geometries of the TiO_2 lattices, and many of these nonideal geometries no doubt contribute to the unusual reactivity of these compounds in applications such as asymmetric oxidation reactions.[4]

High-resolution magic-angle solid-state ^{13}C NMR techniques, in a controlled helium atmosphere, have been applied to **1**–**3**.[12] This technique can complement X-ray structure analysis and may eventually serve as an alternative or primary source of solid-state structural data, particularly in cases where suitable crystals cannot be obtained. Comparison of solid-state and solution ^{13}C NMR spectra reveals that the solid-state and solution structures of **1**, **2**, and **3** are very similar, if not identical,[13] and allows us to check

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the relevance of the X-ray structures to the solution chemistry. Further characterization of coordination compounds of tartrate esters with titanium(IV) is in progress.

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Supplementary Material Available: Solid-state ^{13}C NMR spectra, analytical and crystallographic details, and tables of atomic positional and thermal parameters for **1**–**3** (14 pages); table of structure factors for **1**–**3** (48 pages). Ordering information is given on any current masthead page.

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(13) The solution molecular weights of these species (see supplementary material) are all as expected from their solid-state structures. However, with such fluxional/dynamic molecules one cannot rely on mere molecular weight identity to establish structural correspondence between the solid state and solution.

Redox Chemistry of Tetrakis(1-norbornyl)cobalt. Synthesis and Characterization of a Cobalt(V) Alkyl and Self-Exchange Rate of a Co(III)/Co(IV) Couple

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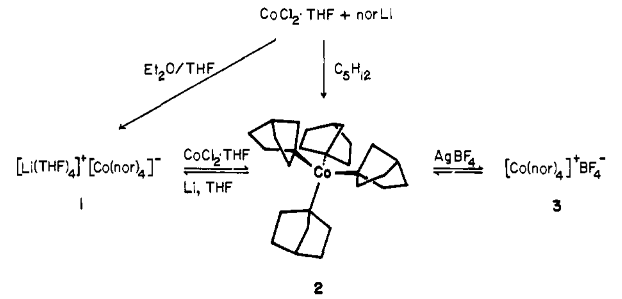
We are probing the chemistry of cobalt alkyls in unusually high oxidation states. Herein we report on the mechanism of formation and redox chemistry of tetrakis(1-norbornyl)cobalt (**2**). This compound was first prepared by Bower and Tennent[1] in 1972 and to this day remains the only isolable Co(IV) alkyl.[2] We have recently characterized **2** structurally and shown it to be the first unambiguous example of a low-spin tetrahedral complex of a first-row transition metal.[3]

The published procedure[1] for the preparation of **2** calls for the reaction of $CoCl_2 \cdot 1.5THF$ with 1-norbornyllithium in pentane. Such a reaction mixture rapidly assumes the red-brown color of **2**. However, when solid $CoCl_2 \cdot THF$[4] was added to a stirred solution of 4 equiv of norbornyllithium in Et_2O/THF (30:1 by volume), the solution immediately turned green. Removal of the solvent and recrystallization of the residue from Et_2O gave $[Li(THF)_4]^+[Co(1\text{-norbornyl})_4]^-$ (**1**, Scheme I) in 27% yield (based on $CoCl_2 \cdot THF$) as an air-sensitive crystalline solid.[5] **1** is paramagnetic and at 300 K exhibits an effective magnetic moment of 3.18 μ_B.[6] Its ^{1}H NMR spectrum (in THF-d_8) features isotropically shifted, yet reasonably sharp, resonances for the norbornyl ligands. The chemical shifts assigned to the norbornyl groups were not changed by substitution of $[Na(18\text{-crown-}6)]^+$ or Et_4N^+ for the $[Li(THF)_4]^+$ counterion, militating against a covalent interaction between the lithium atom and either the cobalt or its norbornyl ligands. Besides being a rare example of a four-coordinate Co(III) complex,[7] **1** is intermediate in oxidation state between the starting material ($CoCl_2 \cdot THF$) and **2**. We have found that it is easily oxidized to **2** by a variety of reagents. For example, reaction of **1** with 1 equiv of $CoCl_2 \cdot THF$ produced **2** in 44% isolated yield along with a black ferromagnetic powder (presumably elemental Co).

Scheme I



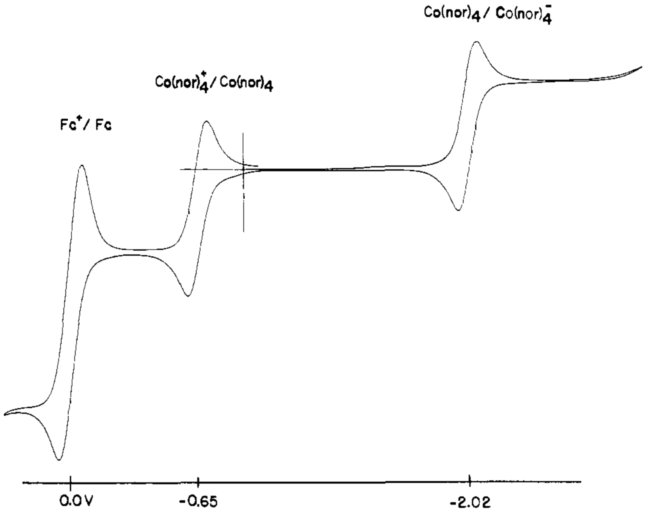


Figure 1. Cyclic voltammogram of **2** in THF with ferrocene as internal reference (platinum disk electrode, 0.1 M $N(n\text{-}Bu)_4BF_4$ supporting electrolyte, 20 mV/s scan rate).

The cyclic voltammogram of **2** in THF (Figure 1) exhibits two reversible electron-transfer waves at −0.65 and −2.02 V (vs. Fc^+/Fc).[8] When a THF solution of **2** was electrolyzed with an applied potential of −2.89 V, 1.03 ± 0.1 electrons were passed per mole of **2**, and at the same time the solution assumed the intense green color characteristic of **1**. The wave at −2.02 V thus corresponds to the Co(IV)/Co(III) couple. The second wave at −0.65 V must therefore represent an accessible oxidation of **2**. Indeed, controlled potential electrolysis of a THF solution of **2** at an applied potential of +0.26 V showed this to be a 1-electron oxidation ($n = 1.24 \pm 0.1$ electrons/mol). Very little change in color

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[1] Bower, B. K.; Tennent, H. G. *J. Am. Chem. Soc.* **1972**, *94*, 2512.

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[4] Bower and Tennent reported the use of $CoCl_2 \cdot 1.5THF$. We have found that Soxhlet extraction of anhydrous $CoCl_2$ with THF yields crystalline materials with THF contents varying from batch to batch between 0.94 and 1.23 mol of THF per mol of $CoCl_2$.

[5] **1**: IR (Nujol) 1042, 887 cm^{-1}; ^{1}H NMR (THF-d_8, 299 K) 52.2 (br s, 8 H), 14.1 (s, 4 H), 10.4 (br s, 8 H), 7.7 (s, 8 H), 4.0 (s, 8 H), −1.4 (br s, 8 H) ppm and resonances of free THF-d_0; mp 156–157 °C. Anal. Calcd for $C_{44}H_{76}CoLiO_4$: C, 71.91; H, 10.42. Found: C, 71.04; H, 10.13.

[6] The magnetic susceptibility of **1** in the temperature interval 3–300 K was measured with a Faraday balance. The data from 25 to 300 K was fitted with a Curie–Weiss expression ($\chi_m = C/[T - \theta] + TIP$). $C = 1.35$ emu K/mol, $\theta = 8.0$ K, TIP = 7.1×10^{-4} emu/mol.

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[8] Potentials throughout this paper are given vs. ferrocene/ferricinium (Fc/Fc^+) in THF. In all electrochemistry experiments a Ag/AgCl,AgCl(THF) reference electrode was used. The Fc^+/Fc potential vs. this reference was +0.89 V.

0002-7863/87/1509-1282$01.50/0