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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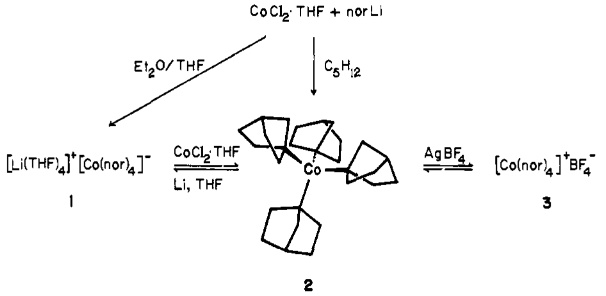
We are probing the chemistry of cobalt alkyls in unusually high oxidation states. Herein we report on the mechanism of formation and redox chemistry of tetrakis(1-norbornyl)cobalt (**2**). This compound was first prepared by Bower and Tennent[1] in 1972 and to this day remains the only isolable Co(IV) 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 ^1H 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



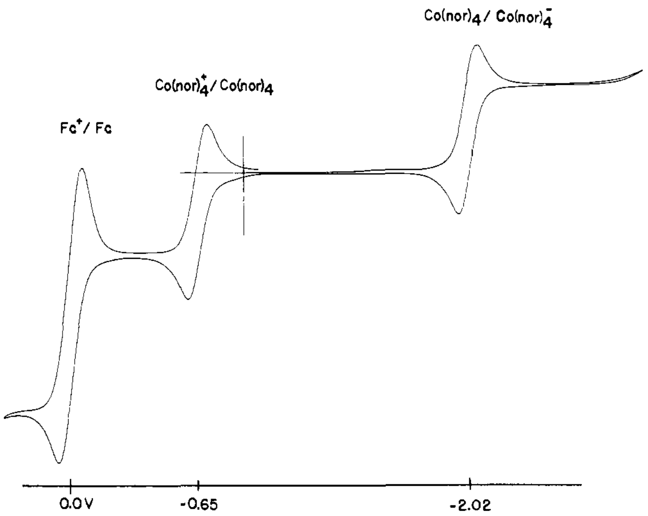


Figure 1. Cyclic voltammogram of **2** in THF with ferrocene as internal reference (platinum disk electrode, 0.1 M $N(n\text{-}Bu)_4BF_4$ supporting electrolyte, 20 mV/s scan rate).

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 ± 0.1 electrons/mol). Very little change in color

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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}; ^1H 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, θ = 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.

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was associated with this reaction, which may also be effected with chemical oxidants. Addition of 1 equiv of $AgBF_4$ to a solution of **2** in THF resulted in immediate precipitation of a black solid (Ag), and from the brown solution crystalline $[Co(1\text{-norbornyl})_4]^+BF_4^-$ (**3**) could be isolated in 84% yield (Scheme I).[9] *3 contains Co in the formal oxidation state V.* It is expected to be a low spin tetrahedral complex like its precursor **2**.[3] With a d^4 electronic configuration, it should be diamagnetic, and in accord with this prediction, the ^1H NMR and ^{13}C NMR spectra of **3** are those of a normal closed-shell compound containing norbornyl groups.

Some speculation on the origin of the stability of unusually high oxidation states of cobalt in this system seems appropriate. We believe that the tetrahedral geometry, in concert with the four strong field ligands, destabilizes **3** of the **5** metal d-orbitals (the σ-antibonding t_2 set) sufficiently to make their occupation energetically unfavorable. In other words, Co(V) in a tetrahedral environment is stable for the same reason that makes Co(III) the preferred oxidation state in a strong octahedral ligand field.

Given the rapid and reversible nature of the interconversions between **1**, **2**, and **3**, we decided to examine these electron-transfer reactions more closely. The room temperature ^1H NMR spectrum of a 1:1 mixture of **1** and **2** (0.014 M in **1** and 0.016 M in **2**, THF-d_8) is an averaged spectrum rather than the sum of the two individual spectra.[10] At this temperature the electron self-exchange reaction (eq 1), which equilibrates the two species, is

$$^{*}\mathrm{Co(nor)_4} + [\mathrm{Co(nor)_4}]^- \overset{k}{\rightleftharpoons} [^{*}\mathrm{Co(nor)_4}]^- + \mathrm{Co(nor)_4} \qquad (1)$$

apparently fast on the time scale of the NMR experiment. Upon cooling the sample, the resonances first broaden and finally separate into two sets assignable to **1** and **2**. This phenomenon is reversible and the coalescence temperature was determined to be 279 ± 2 K. From this and the independently measured temperature-dependent chemical shifts of the two reactants, the rate constant of the self-exchange reaction at the temperature of coalescence could be determined ($k = 4.1\ (\pm 1.0) \times 10^4\ M^{-1}\ s^{-1}$).[11] A decrease in concentration of **1** and **2** (0.0062 M in **1**, 0.0071 M in **2**) increased the coalescence temperature to 292 ± 2 K, consistent with the bimolecular nature of the reaction. The rate of the exchange was not affected significantly by substitution of the $[Na(18\text{-crown-}6)]^+$ salt of **1**. This lack of involvement of the counterion in the reaction is consistent with a simple outer-sphere electron transfer. Preliminary ^1H NMR experiments with mixtures of **2** and **3** show that this self-exchange is also fast on the NMR time scale. Our attempts to freeze out this reaction as observed by ^1H NMR have been unsuccessful and work is in progress to determine the exchange rate by other techniques.

The above electron transfers are very fast in comparison with the more standard Co(II)/Co(III) couples.[12] In both cases described herein the transfered electron occupies a σ-antibonding molecular orbital, leading us to expect a sizable reorganizational barrier and thus a slow exchange rate. However, there is little experimental precedent for the present situation, making a comparison of rate constants difficult.[13]

The chemistry of high valent alkyl complexes of the late transition metals is proving fascinating. These compounds and their interconversions via electron-transfer reactions are of particular interest as models for metal-catalyzed oxidations of hydrocarbons. We are now extending our experiments to other ligands and metals.

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(9) **3**: IR (Nujol) 1053 cm^{-1}; ^1H NMR (CD_2Cl_2) 2.37 (s, 4 H), 1.98 (m, 8 H), 1.80 (m, 16 H), 1.66 (s, 8 H), 1.47 (m, 8 H) ppm; ^{13}C NMR (CD_2Cl_2) 91.6, 44.3, 35.8, 32.5, 32.1 ppm. Anal. Calcd for $C_{28}H_{44}BCoF_4$: C, 63.89; H, 8.43; Co, 11.2. Found: C, 63.77; H, 8.53; Co, 12.2.

(10) **2**: ^1H NMR (THF-d_8) 10.4 (br s, 4 H), 7.2 (br s, 16 H), 4.3 (br s, 16 H), –3.4 (br s, 8 H) ppm. See ref 5 for data on **1**.

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Membrane-Enclosed Enzymatic Catalysis (MEEC): A Useful, Practical New Method for the Manipulation of Enzymes in Organic Synthesis[1]

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We wish to describe a useful technique for the efficient manipulation of enzymes in organic synthesis,[3] in which the enzyme in soluble form is enclosed in commercially available dialysis membranes. We have tested this technique (membrane-enclosed enzymatic catalysis, MEEC) in a number of representative enzyme-catalyzed reactions (Scheme I)[4-12] and have found that it combines the simplicity of use of soluble enzymes with certain of the advantages of immobilized enzymes. This technique may not be applicable to all enzymes, but it provides the simplest and most effective methods of using many of them in organic synthetic applications.

Enzyme-catalyzed reactions can use either soluble or immobilized enzymes.[13,14] Procedures based on soluble enzymes are, in general, more convenient than those using immobilized enzymes, but the enzymes are not easily recovered for reuse, and their lifetime may be shortened by shear or interfacial deactivation. Immobilization allows the separation and reuse of enzymes and often protects them from deactivation by organic cosolvents, shear, interfacial adsorption, and proteases,[15,16] but it is experimentally inconvenient and even under ideal conditions can cause significant deactivation of sensitive proteins.

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