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Synthesis, Characterization, and Electron-Transfer Reactivity of Norbornyl Complexes of Cobalt in Unusually High Oxidation States

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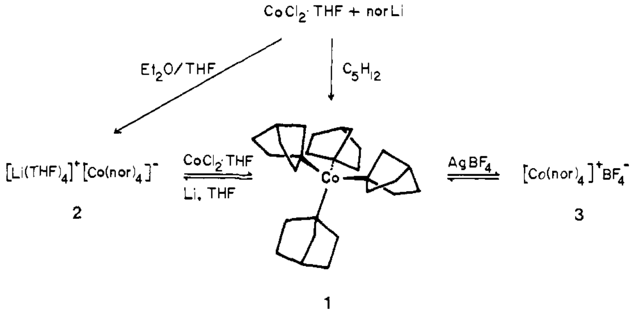
Abstract: Reaction of cobaltous chloride with 1-norbornyllithium in THF afforded the anionic alkyl complex $[\mathrm{Li(THF)_4}]^+[\mathrm{Co^{III}(1\text{-}nor)_4}]^-$ (**2**), where nor = norbornyl, while the same reaction in pentane yielded the previously reported $\mathrm{Co^{IV}(1\text{-}nor)_4}$ (**1**). The latter complex was oxidized to the cationic cobalt(V) alkyl $[\mathrm{Co^V(1\text{-}nor)_4}]^+\mathrm{BF_4}^-$ (**3**). The crystal structure of **1** has been determined. It crystallizes in the orthorhombic space group $Pmn2_1$ with a = 11.948 (3) Å, b = 10.104 (2) Å, and c = 9.805 (3) Å with Z = 2. The norbornyl groups exhibit rotational disorder, but the coordination geometry about cobalt is clearly tetrahedral and features very short cobalt–carbon bonds (1.92 Å). Magnetic susceptibility measurements show that all three complexes have low-spin configurations. Values of the tetrahedral ligand field splitting Δ_t were determined from the electronic absorption spectra and range from 15 000 to 22 000 $\mathrm{cm^{-1}}$. The cyclic voltammogram of **1** in THF exhibits two reversible waves at −2.02 V (**1**/**2**) and −0.65 V (**3**/**2**) vs $\mathrm{Cp_2Fe^+/Cp_2Fe}$. The self-exchange rate constants for the degenerate electron transfers were measured by ^{1}H NMR and ^{59}Co NMR techniques. The activation parameters are $\Delta H^\ddagger$ = 12.0 (9) kcal/mol and $\Delta S^\ddagger$ = +8 (3) cal/mol·K for the **1**/**2** couple and $\Delta H^\ddagger$ = 8.5 (3) kcal/mol and $\Delta S^\ddagger$ = −6 (1) cal/mol·K for the **3**/**2** couple. Diamagnetic **3** exhibited several resonances in the low-temperature ^{59}Co NMR spectra, which were attributed to rotational isomers. The rate of interconversion of two isomers was measured by a ^{59}Co NOESY experiment.

One of the significant achievements of organometallic chemistry is the stabilization of unusual oxidation states of the transition elements in compounds with metal–carbon bonds. While the common oxidation states of cobalt in traditional coordination compounds are +II and +III,[1] Mond's discovery of metal carbonyls a century ago[2] eventually led to cobalt complexes in very low oxidation states (e.g. $\mathrm{HCo(CO)_4}$, Co(I); $\mathrm{Co_2(CO)_8}$, Co(0); $[\mathrm{Co(CO)_4}]^-$, Co(−I)). More recently this emphasis on low-valent compounds has begun to shift to metal alkyls in high formal oxidation states.[3] This development coincides with the rise of a new challenge, namely oxidation catalysis.[4] Alkyl ligands are among the strongest σ-donors known and are thus ideally suited to stabilize metals in high oxidation states.

At the outset of this research stood the question whether cobalt alkyls in oxidation states higher than +III can be prepared and what the reactivity of such molecules would be. Very few compounds of cobalt in the +IV oxidation state are known. Most are extended solids, with highly electronegative oxide or fluoride ligands supporting the hard Co(IV) center. $\mathrm{Ba_2CoO_4}$,[5] $\mathrm{Na_4CoO_4}$,[6] and $\mathrm{Cs_2CoF_6}$[7] are representative examples thereof. More recently, Anson et al. have reported a neutral coordination complex containing Co(IV) surrounded by a tetraanionic chelating ligand.[8] The organometallic chemistry of Co(IV) has recently been reviewed.[9] It largely consists of transient species generated by oxidation of octahedral cobalt(III) alkyl precursors. In general, the resulting complexes are stable only at low temperature. They have been characterized by ESR spectroscopy, electrochemical measurements, and identification of their decomposition products. Metal–carbon bond homolysis and nucleophilic attack at the cobalt-bound carbon appear to be the prevalent reaction pathways exhibited by these compounds. To our knowledge, the only stable cobalt(IV) alkyl is the remarkable tetrakis(1-norbornyl)cobalt (**1**). This complex was reported in 1972 by Bower and Tennent as one member of a series of homoleptic transition-metal alkyls (M(1-nor)$_4$, M = Ti, V, Cr, Mn, Fe, Co, Zr, Hf, nor = norbornyl).[10] We and others[11] reasoned that it should be possible to prepare other similar compounds. However, the mechanism of formation of **1** was ill understood. Thus, we began with a reinvestigation of the reaction of cobalt chloride with 1-norbornyllithium. Some of our results have been published in preliminary form.[12]

Scheme I



Results and Discussion

Synthesis. The published procedure for the preparation of **1** calls for the reaction of $\mathrm{CoCl_2{\cdot}1.5THF}$ with 1-norbornyllithium in pentane, followed by filtration through a column of alumina and recrystallization from pentane.[10] In our hands this method reliably afforded **1** in reasonable yield. The importance of the filtration step is attested to by the following observations. When $\mathrm{CoCl_2{\cdot}THF}$[13] was added to a stirred solution of 4.0 equiv of 1-norbornyllithium in pentane, the solution slowly assumed the characteristic red-brown color of **1**. Evaporation of the solvent and extraction of the residue with pentane followed by recrystallization from the same solvent yielded a brown solid, apparently the cobalt(IV) alkyl. However, dissolution of this solid in THF resulted in a dark green solution, from which green crystals of

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

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a new compound could be isolated. Similarly, when $CoCl_2 \cdot THF$ was added to a solution of 4.0 equiv of 1-norbornyllithium in Et_2O containing some THF, the solution immediately assumed a dark green color. Filtration, evaporation of the solvent, and recrystallization of the residue from Et_2O afforded crystals of the same green product. Analytical data and spectroscopic characterization of this material are consistent with the formula $[Li(THF)_4]^+[Co(nor)_4]^-$ (**2**, see Scheme I), a four-coordinate Co(III) complex.[14] The formation of **2** is accompanied by the deposition of a small amount of a black powder, which adheres to the magnetic stir bar (elemental cobalt, see the Experimental Section). Thus, the reaction is a disproportionation (eq 1). **2** is isolated in 27% yield on the basis of eq 1. It forms dark green cubes, and solutions of it are extremely sensitive to air and water.

$$3CoCl_2 \cdot THF + 8norLi + 5THF \xrightarrow{Et_2O} 2[Li(THF)_4]^+[Co(nor)_4]^- + Co + 6LiCl \quad (1)$$

Our interpretation of these results is as follows. Apparently, the reaction of cobaltous chloride with 1-norbornyllithium is solvent dependent. Multiple ligand substitution of norbornyl groups for chloride probably gives $[Co(nor)_4]^{2-}$ in each case. Several compounds of the type $[CoR_4]^{2-}$ have been isolated (R = Me, CH_2SiMe_3, Ph) and serve as precedent for this species.[15] However, in THF the subsequent oxidation of the cobalt(II) alkyl complex with $CoCl_2$ stops at the Co(III) stage, while it rapidly proceeds to Co(IV) (i.e. **1**) in pentane. Given the 4:1 stoichiometry of the experiments described, the pentane reaction is expected to yield a mixture of **1** and 1-norbornyllithium (eq 2). Upon addition

$$CoCl_2 \cdot THF + 4norLi \xrightarrow{C_5H_{12}} \tfrac{1}{2}Co(nor)_4 + \tfrac{1}{2}Co + 2LiCl + 2norLi + THF \quad (2)$$

of the ether solvent THF to this mixture, **1** is reduced by the alkyllithium reagent to **2**. Alternatively, the excess 1-norbornyllithium may be removed by filtration through alumina. Several experiments were carried out to test these notions. The feasibility of the disproportionation was demonstrated by the observation that **2** was slowly oxidized to **1** by $CoCl_2 \cdot THF$ in pentane suspension (44% isolated yield). Furthermore, pure **1** was not reduced to **2** by 1-norbornyllithium in pentane. In contrast, addition of the alkyllithium reagent to a THF solution of **1** resulted in a rapid color change from red-brown to green and workup afforded **2** in 70% isolated yield.

Electrochemical experiments (see below) indicated an accessible oxidation of **1**. When 1.0 equiv of $AgBF_4$ was added to a solution of **1** in THF, a black solid (Ag) precipitated immediately and the solution turned yellow-brown. Filtration, removal of solvent, and recrystallization of the residue from CH_2Cl_2/Et_2O yielded brown crystals of a new material. Its analytical data and spectroscopic properties were consistent with the formula $[Co(nor)_4]^+BF_4^-$ (**3**, see Scheme I). **3** features four-coordinate cobalt in the oxidation state +V.

Structure Determination. Despite several attempts,[10,16] none of the tetrakis(norbornyl) complexes had been structurally characterized. This situation was unfortunate for several reasons. Not only is **1** the only stable cobalt(IV) alkyl but it also exhibits only one unpaired electron. The splitting of the five degenerate d orbitals of a transition-metal ion in a tetrahedral ligand field is not generally big enough to enforce pairing of its electrons. Thus, no low-spin tetrahedral complex of a first-row transition metal has been shown to exist prior to this work. The lack of structural information on tetrakis(1-norbornyl)metal complexes is the result of a more general problem. The norbornyl group is notorious for exhibiting disorder in crystal structure determinations. This problem arises due to the near 3-fold symmetry with respect to rotation about an axis connecting the two bridgehead carbons. In the faint hope of overcoming the disorder by engaging the norbornyl ligands in a close interaction with a counterion, we attempted to grow crystals of the anionic complex $[Co(nor)_4]^-$ for an X-ray diffraction study. Several crystals were isolated from a solution of $PPN^+[Co(nor)_4]^-$ (PPN = bis(triphenylphosphine)iminium), which had been kept at −30 °C for ca. 1 month. X-ray diffraction data were collected, and during the refinement of the structure, we realized that the particular crystal used in this experiment consisted of neutral **1**. Apparently, a small fraction of the sample had been oxidized by adventitious traces of oxygen or water. In our preliminary communication of this work,[12a] we speculated that the slow generation and crystallization of **1** had been responsible for minimizing the disorder problem. In light of more recent experiments on conformational dynamics of the tetrakis(1-norbornyl)cobalt fragment (see below), we no longer believe this to be true. In any case, the refinemement of the structure converged to a final *R* factor of 0.071 using standard procedures (see the Experimental Section). Inspection of the structure revealed some unrealistic bond distances and angles within the norbornyl ligands. We attributed this to the abovementioned 3-fold rotational disorder. As there is little doubt about the actual structural features of the norbornyl skeleton and because one of the disordered conformations seemingly predominated, we decided to impose a corresponding constraint on the refinement. Using experimentally determined structural parameters of the bicyclo[2.2.1]heptane fragment,[17] we refined the structure according to a method described by Waser.[18] This procedure resulted in a slightly higher *R* factor (0.089) because less of the overall electron density has been assigned. On the other hand, the model makes more sense chemically. In any case, the structural information of interest concerns the immediate surroundings of the cobalt atom. These parameters were not affected significantly by the method of refinement and are quite well determined. Table I gives the interatomic distances and angles of interest for both refinements. We do not consider the remainder of the structural parameters meaningful and have thus omitted them from the table. The tables of atomic positions and thermal parameters as well as complete tables of interatomic distances and angles resulting from both refinements have been included as supplementary material.

Table I. Interatomic Distances (Å) and Angles (deg) of the Coordination Environment of Cobalt in Co(1-nor)$_4$ (**1**)

	refinement	
	constrained	unconstrained
Co–C1	1.910 (21)	1.930 (21)
Co–C6	1.911 (23)	1.929 (19)
Co–C11(C11A)	1.930 (27)	1.912 (23)
C1–Co–C6	113.4 (15)	114.4 (12)
C1–Co–C11	106.9 (12)	106.5 (11)
C6–Co–C11	109.0 (13)	108.4 (12)
C11–Co–C11A	111.6 (15)	112.7 (8)

The molecular structure of **1** (see Figure 1) features a slightly distorted tetrahedron as the coordination environment of cobalt. The molecule has crystallographic C_s symmetry only (the Co atom and carbon atoms C1, C2, C3, C6, C7, and C8 lie on the mirror plane), but the four cobalt-bonded carbon atoms approximate the pseudo D_{2d} symmetry of a tetragonally compressed tetrahedron.

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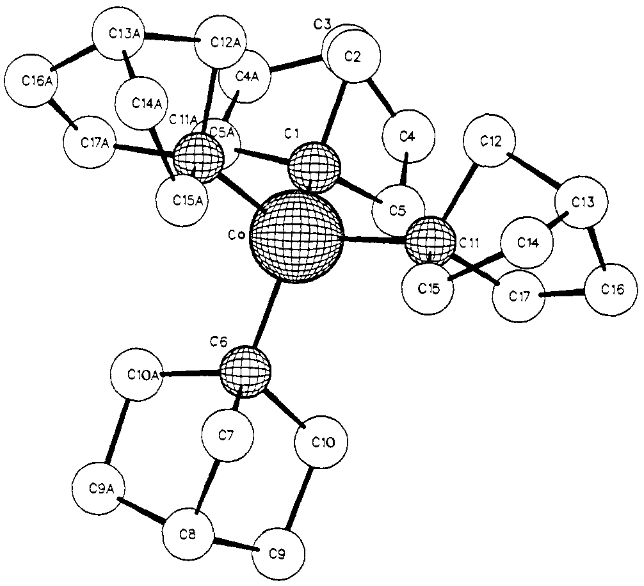

Figure 1. Molecular structure of tetrakis(1-norbornyl)cobalt (**1**), looking down the crystallographic mirror plane (result of constrained refinement is shown). The shaded atoms constitute the tetrahedral inner coordination sphere of the complex. These atoms are not affected by the rotational disorder of the norbornyl groups.

Table II. Vibrational Frequencies (in cm^{-1}) Observed in the Far-Infrared Spectra of **1**–**3** and Some Representative Tetrahedral and Square-Planar Molecules

$[Co(1\text{-}nor)_4]^-$	272	168	
$Co(1\text{-}nor)_4$	297	171	
$[Co(1\text{-}nor)_4]^+$	303	187	
$[GaBr_4]^-$	278	102	
$GeBr_4$	332	111	
GeI_4	273	77	
$[PdBr_4]^{2-}$	243	114	104
$[PdCl_4]^{2-}$	321	161	150

The Co–C bond distances are equal within the error of the measurement and average 1.92 Å. For comparison, cobalt–carbon distances range between 1.93 and 2.22 Å in six-coordinate cobalt(III) alkyl complexes, many of which have been structurally characterized.[19] The short metal–carbon bond distance in **1** probably reflects the lesser steric demand of the four-coordinate molecule as well as the high formal oxidation state of the cobalt atom.

Having established tetrahedral geometry for **1**, there remains the question of the structures of its derivatives **2** and **3**. Several lines of reasoning lead us to suggest that these compounds also adopt tetrahedral coordination. Inspection of molecular models shows that the bulky nature of the norbornyl groups would not allow a square-planar arrangement of these ligands around cobalt without considerable lengthening of the cobalt–carbon bonds. Degenerate electron transfers between **1** and **2** and between **1** and **3** are very facile processes (see below), consistent with little reorganization of the inner coordination sphere upon reduction or oxidation. Finally, vibrational spectroscopy supports the similarity of structure of all three compounds. Simple tetrahedral molecules have four vibrational normal modes, two of which are infrared active. Square-planar molecules exhibit seven normal modes of vibration, three of which are observable in the infrared spectrum.[20] Table II lists vibrational frequencies observed in the far-infrared spectra (500–20 cm^{-1}) of **1**–**3** along with some data for representative tetrahedral and square-planar molecules. Two bands are observed in the expected area. The progression of the bands is consistent with a modest strengthening of the metal–ligand bonds upon oxidation. We believe that the similarity of the spectra both among the three alkyl complexes and in comparison to other tetrahedral molecules strongly supports our structural assignment.

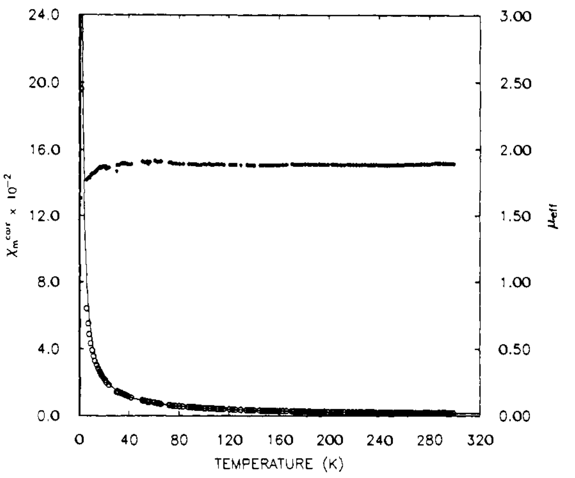

Figure 2. Molar magnetic susceptibility (χ_m, open circles) and effective magnetic moment (μ_{eff}, filled circles) of $Co(1\text{-}nor)_4$ (**1**).

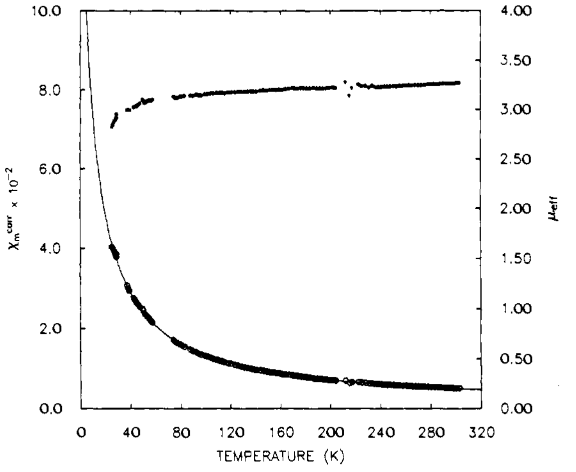

Figure 3. Molar magnetic susceptibility (χ_m, open circles) and effective magnetic moment (μ_{eff}, filled circles) of $[Li(THF)_4]^+[Co(1\text{-}nor)_4]^-$ (**2**).

Magnetism. The effective magnetic moment of **1** had been measured by a solution NMR method by Bower and Tennent.[10] Their numerical result (μ_{eff} = 2.00 μ_B) in combination with our determination of the crystal structure of **1** makes this compound a low-spin tetrahedral complex. Because of the unusual nature of this result and as a check of the solution measurement, we have measured the magnetic susceptibility of solid **1** in the temperature interval 1.7–299 K using a Faraday balance (Figure 2). The complex is paramagnetic, and the data were fitted with a Curie–Weiss expression.[21] The effective magnetic moment of **1** at 299 K is 1.89 μ_B (corrected for diamagnetism and TIP). This result is close to the expected spin-only moment for one unpaired electron (1.73 μ_B). Thus, **1** is a rare example of a tetrahedral compound in which the tetrahedral ligand field splitting is strong enough to enforce pairing of the d electrons, giving the cobalt an $e^4t_2^1$ electronic configuration.

It was then of some interest to find out what effect reduction or oxidation of **1** would have on the magnetic behavior. Three-valent cobalt (as in **2**) has a d^6 configuration, which should result in two unpaired electrons in a low-spin tetrahedral complex and four unpaired electrons in a high-spin situation. The temperature dependence of the molar magnetic susceptibility and the effective magnetic moment of **2** are shown in Figure 3. The complex is

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(21) Carlin, R. L. *Magnetochemistry*; Springer-Verlag: Berlin, 1986; pp 5–12. The data were fit with the expression $\chi_M = C/(T - \Theta) + TIP$. C = 0.447 emu·K/mol, Θ = 0.7 K, and TIP = 1.35 × 10^{-4} emu/mol.

Table III. Electronic Absorption Spectra of **1**–**3**

λ, nm	E, cm^{-1}	ε, M^{-1} cm^{-1}	transition
	$[Co(1\text{-}nor)_4]^+BF_4^-$		
276	36 200	36 000	
344	29 100	7 300	
440	22 700	560	$^1A_1 \rightarrow {}^1T_2$
609	16 400	170	$^1A_1 \rightarrow {}^1T_1$
	$Co(1\text{-}nor)_4$		
269	37 200	20 000	
328	30 500	11 600	
458	21 800	1 400	$^2T_2 \rightarrow {}^2E$
511	19 600	1 250	$^2T_2 \rightarrow {}^2T_1, {}^2A_2$
	$[Li(THF)_4]^+[Co(1\text{-}nor)_4]^-$		
264	37 900	21 300	
313	31 900	12 800	
428	23 400	2 600	$^3T_1 \rightarrow$?
738	13 550	1 620	$^3T_1 \rightarrow {}^3T_2$

paramagnetic and $\mu_{eff} = 3.18\ \mu_B$ at 300 K (corrected for diamagnetism and TIP). This result is only slightly higher than the expected spin-only value of 2.83 μ_B, consistent with a small orbital contribution to the total moment. Thus, $[Co(nor)_4]^-$ is a low-spin complex also, with an $e^4t_2^2$ configuration of the cobalt ion. Finally, the cobalt(V) alkyl **3** with its d^4 configuration should be a diamagnetic closed-shell molecule in a low-spin configuration, while a high-spin form should exhibit four unpaired electrons. The diamagnetic nature of **3** manifests itself clearly in our ability to record ^1H, ^{13}C, and ^{59}Co NMR spectra of the compound, which exhibit sharp resonances not shifted from the normal positions. In addition, the magnetic susceptibility of **3** was measured by the Faraday method, and the compound was found to be diagmagnetic (χ_m (284 K) = -1.92×10^{-4} emu/mol).

To summarize, all three compounds formed by coordinating four norbornyl ligands to cobalt in a tetrahedral fashion feature low-spin electronic configurations, irrespective of the oxidation state of cobalt (III, IV, or V). We attribute this effect to the high valence states of the cobalt and the covalent nature of the metal–carbon bond.

Electronic Absorption Spectra. The splitting of the cobalt d orbitals in the tetrahedral field of the four norbornyl ligands (Δ_t or 10 Dq) must be unusually large. To determine numerical values of Δ_t, we have recorded the UV–vis spectra of compounds **1**–**3** in hydrocarbon solutions (see the supplementary material and Table III). They were interpreted using extensions of the strong field regions of the appropriate d^{10-n} Tanabe–Sugano diagrams[22] for octahedral coordination (n is the number of d electrons of cobalt in the tetrahedral complexes). In each case the lines in these diagrams were assumed to be linear in the region of interest. Analytical expressions (see eq 3) for the lines corresponding to

$$E/B = m(Dq/B) + b \tag{3}$$

the lowest energy ligand field transitions were derived. Ratios of the energies of the observed absorption bands were used in conjunction with the analytical expressions to determine Dq/B for each compound. The energies of individual absorption bands were then used to calculate the Racah parameter B and finally 10 Dq (i.e. Δ_t). We note that Abrahamson et al. have reported an investigation of the spectroscopy and photochemistry of $Ti(nor)_4$ and $Cr(nor)_4$.[16] In order to account for the full complexity of the spectrum of the chromium complex, these authors assumed a symmetry reduction from T_d to D_{2d}. On the basis of the crystal structure of 1 and on striving for conceptual simplicity, we have assumed tetrahedral symmetry for the purposes of the following analysis.

Table III lists the absorption frequencies, extinction coefficients, and transition assignments for all three complexes. The spectrum of **3** exhibited four bands, of which two (440, 609 nm) were assigned as ligand field transitions. On the basis of this assignment, Dq/B was calculated as 3.72, yielding approximate values of 470 cm^{-1} for B and 17 400 cm^{-1} for Δ_t. For this closed-shell system the transition of lowest energy corresponds to Δ_t in the the limit of infinitely strong ligand field. As the ligand field strength decreases, it assumes a slightly lower energy. Thus, our assignment of Δ_t = 17 400 cm^{-1} is consistent with the observation of the lowest energy transition at 16 420 cm^{-1}. Four bands were also found in the spectrum of **1**, and two of these (458, 511 nm) were assigned as ligand field transitions on the basis of their extinction coefficients. Dq/B was calculated as 5.05, yielding approximate values for B and Δ_t of 435 and 22 000 cm^{-1}, respectively. Finally, the spectrum of **2** also exhibits four absorptions. Once again, two of these may be assigned as d–d transitions on the basis of their extinction (738, 428 nm). The Tanabe–Sugano diagram for this case shows five triplet states lying very close in energy. These probably give rise to the very broad band centered at 738 nm. Unfortunately, no higher lying triplet states are shown in the diagram, which would correspond to the 428-nm transition. In order to get a rough estimate of Δ_t, in this case we have assumed a B parameter of 400 cm^{-1} for **2**. This value was arrived at by extrapolation of the B values of **3** and **1**. On the basis of this assumption Dt was estimated using only one transition, yielding a value of 15 000 cm^{-1}.

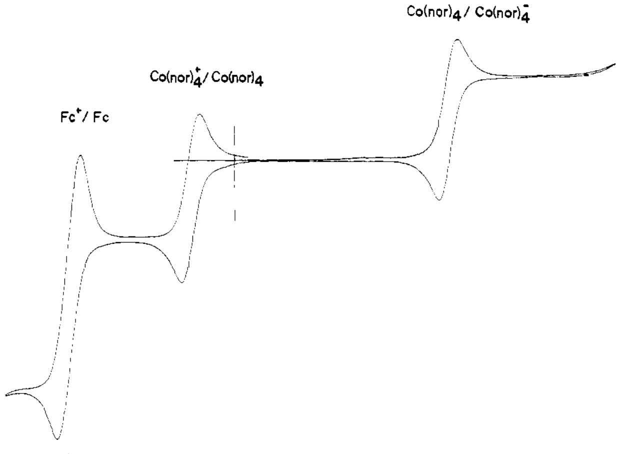

Figure 4. Cyclic voltammogram of $Co(1\text{-}nor)_4$ (**1**) in THF with ferrocene as internal reference (platinum disk electrode, 0.1 M $N(^nBu)_4BF_4$ supporting electrolyte, 20 mV/s scan rate).

The ligand field splittings determined from the spectra fall in the range 15 000–22 000 cm^{-1}, in contrast to Δ_t values below 10 000 cm^{-1} exhibited by more typical tetrahedral coordination compounds. They do not follow the expected trend (i.e. Δ_t[Co(III)] < Δ_t[Co(IV)] < Δ_t[Co(V)]). As a possible explanation we suggest that the cobalt–carbon bond distances of **2** may decrease significantly upon oxidation to **1**, thereby increasing the ligand field splitting. However, further oxidation of **1** to **3** may be ineffectual in shortening these bonds beyond the 1.92 Å found in **1**, due to ligand–ligand repulsion. The concomitant contraction of the cobalt valence orbitals may then result in a decrease in overlap and covalency, thus reducing Δ_t. The pairing energy for the free Co(III) ion has been calculated as 21 000 cm^{-1}.[23] However, this value is expected to be greatly reduced in the complexed ion due to the nephelauxetic effect. We suggest, on the basis of our magnetic measurements, that Δ_t exceeds the pairing energy for every one of these complexes.

Electron Transfer. The synthesis and characterization of alkyl complexes in extremely high formal oxidation states of cobalt raises the question of the physical meaning of such numbers. How electron poor or oxidizing is a Co(V) complex? This question may be answered by electrochemical experiments. Figure 4 depicts the cyclic voltammogram of **1** in THF. It exhibits two reversible electron-transfer waves at −0.65 and −2.02 V vs the ferriceni-

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(22) Tanabe, Y.; Sugano, S. *J. Phys. Soc. Jpn.* **1954**, *9*, 753.

(23) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; p 646.

um/ferrocene couple (Fc^+/Fc). The currents passed, and the differences in peak potentials were consistent with two one-electron-transfer processes. This was confirmed by coulometric experiments. When a THF solution of **1** was electrolyzed with an applied potential of −2.83 V, 1.03 ± 0.1 e/mol of **1** were passed, and at the same time the solution assumed the intense green color characteristic of **2**. The wave at −2.02 V thus corresponds to the Co(IV)/Co(III) couple. Cobalt(III) complex **2** turns out to be an extremely strong reducing agent, and its sensitivity to air and water is not surprising. The second wave at −0.65 V was therefore assigned to the oxidation of **1** to **3**. Indeed, controlled potential electrolysis of a THF solution of **1** with an applied potential of +0.26 V showed this to be a 1-e oxidation ($n = 1.24 \pm 0.1$ e/mol). Very little change in color was associated with this reaction. The potential of the ferricenium/ferrocene couple in water is +0.400 V vs the normal hydrogen electrode (NHE).[24] Thus we are faced with the unlikely—yet inescapable—conclusion that Co(IV) complex **1** is a better reducing agent than hydrogen. This conclusion is supported by the possible use of strong acid as a reagent for the conversion of **1** to **3**.

Given the reversibility of the redox chemistry of the tetrakis(norbornyl)cobalt system on both the electrochemical and chemical time scales, we decided to measure the self-exchange rates of the two couples. Electron transfers are among the most basic reactions in chemistry, yet nearly all available data on self-exchange rates of inorganic complexes concern octahedral coordination compounds with nitrogen- or oxygen-based ligands. This is certainly true for cobalt complexes, as there exists a number of studies of $CoL_6^{3+/2+}$ couples (where L is typically a nitrogen base).[25] Other coordination environments and oxidation states of cobalt have received much less attention with regard to electron transfer. For both couples under consideration (i.e. **1**/**2** and **1**/**3**) the electron is transferred from a t_2 orbital into a t_2 orbital. These are metal–ligand antibonding MOs, and the measured rate might reflect a large inner sphere reorganizational barrier. However, we also note that both couples involve the neutral molecule **1**, eliminating a work term contribution to the activation barrier to electron transfer. In any case, the unusual oxidation states and the low-spin nature of the reactants at hand preclude comparison with other similar systems.

The room-temperature ^1H NMR spectrum of a 1:1 mixture of **1** and **2** (0.016 M in **1** and 0.014 M in **2**, THF-d_8) was an averaged spectrum rather than the sum of the two individual spectra. This was quite evident, as the spectrum of **2** in THF-d_8 exhibits the expected six resonances for a norbornyl group, while that of **1** is broader, exhibiting only four resonances (the exo and endo protons are not resolved). At this temperature the degenerate self-exchange (eq 4), which equilibrates the two species, is apparently fast on the time scale of the NMR experiment. Four resonances were observed, none of which exhibited the chemical shifts expected for pure **1**. Upon cooling the sample in the probe of the spectrometer, the resonances first broadened and finally separated into two sets assignable to **1** and **2**. This phenomenon was reversible and the coalescence temperature of the resonances assigned to the bridgehead protons of the two complexes (10.4 ppm in **1** and 14.1 ppm in **2** at room temperature) has been determined as 279 ± 2 K (at 300 MHz). From this and the independently measured temperature-dependent chemical shifts of the two reactants (the chemical shifts of paramagnetic molecules exhibit a $1/T$ dependence, caused by the temperature dependence of the magnetic susceptibility), the rate constant for the degenerate self-exchange at the coalescence temperature could be determined.[26] The second-order rate constant was calculated from the first-order rate constant obtained from the coalescence expression by dividing by the sum of the concentrations in solution. That value was $k_{34}(279\ K) = 4.1 \pm 1.0 \times 10^4\ M^{-1}\ s^{-1}$. A decrease in the concentrations of **1** (to 0.007 M) and **2** (to 0.006 M) increased the coalescence temperature to 292 ± 2 K, consistent with the bimolecular nature of the reaction. The rate of electron transfer was not affected significantly by substitution of $[Na(18\text{-crown-}6)]^+[Co(nor)_4]^-$ for **2**. This lack of involvement of the counterion as well as the aliphatic nature of the ligands was consistent with a simple outer-sphere mechanism for electron transfer.

$$^*Co(nor)_4 + [Co(nor)_4]^- \overset{k_{34}}{\rightleftharpoons} [^*Co(nor)_4]^- + Co(nor)_4 \tag{4}$$

In principle, we could have used coalescence measurements on samples of varying concentrations of **1** and **2** to extract activation parameters for the Co(III)/Co(IV) self-exchange reaction. In practice, however, this method was hampered by limitations in temperature range and large errors associated with the weighing of very small samples of highly sensitive compounds. We have found that ^1H NMR line broadening in the fast-exchange limit provided a solution to these problems. Typically, this technique has been applied to electron-transfer couples consisting of one diamagnetic and one paramagnetic complex, although that is not a requirement.[27] The experiment consists of adding a small amount of the paramagnetic reactant to a solution of the diamagnet, which leads to a broadening and shifting of the NMR resonances of the diamagnet due to chemical exchange. The linewidth of a particular resonance is given by eq 5. In this

$$W_{DP} = (1 - f_P)W_D + f_P W_P + 4\pi f_P(1 - f_P)(\delta\nu)^2/kc \tag{5}$$

equation W_{DP}, W_D, and W_P are the linewidths (full-width at half-maximum) measured for the mixture, the pure diamagnet, and the pure paramagnet, respectively. The constant f_P is the mole fraction of paramagnet in solution, c is the total concentration of both species, $\delta\nu$ is the frequency separation between the diamagnet and the paramagnet in the absence of exchange, and k is the desired rate constant. For a sample of given f_P and c, measurement of W_{DP} at various temperatures, coupled with information about W_D and W_P, allows the calculation of activation parameters. Furthermore, the calculated f_P may be checked against a measured value. The chemical shift of an averaged resonance in the fast-exchange limit is the concentration-weighted average of the shifts of the exchanging species in the absence of exchange. Thus f_P may be determined by dividing the frequency difference between the resonance of the pure diamagnet and the averaged resonance by $\delta\nu$ (see above). If a large amount of the diamagnetic reactant is used f_P and c may be determined very accurately.

We have applied this method to a mixture of two paramagnetic compounds (i.e. **1** and **2**). **2** exhibits smaller linewidth in the ^1H NMR and was therefore assigned the role of the "diamagnet" in the experiment described above. A sample containing 16 mg of **2** and a small amount of **1** ($f_P = 0.207$, determined by NMR, see above) in THF-d_8 was prepared, and ^1H NMR spectra were taken at 30.1, 40.1, 50.1, and 60.1 °C. In addition, room-temperature spectra (25 °C) were taken of the samples originally used in the coalescence experiments. Values of f_P for these samples were determined from the spectra and used to recalculate the concentration of **1** in the samples. The corrected concentrations (deemed more accurate than those determined by weighing out very small amounts of **1**) were also used to reevaluate the rates at the coalescence temperatures. Another adjustment was made to all concentrations to correct for the large thermal expansion of the THF solvent.[28] The resulting rate constants for the degenerate electron transfer between **1** and **2** are listed in Table IV. The Arrhenius plot of the data is shown in Figure 5, and the activation parameters derived therefrom were $\Delta H^{\ddagger} = 12.0\ (9)$ kcal/mol and $\Delta S^{\ddagger} = +8\ (3)$ cal/mol·K.

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[24] (a) Koepp, H.-M.; Wendt, H.; Strehlow, H. *Z. Elektochem.* **1960**, *64*, 483. (b) Gagne, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2855.

[25] Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*; Wiley: New York, 1967; pp 475–6.

[26] $k_{34} = \pi\Delta\nu/(2)^{1/2}$ at the coalescence temperature. From: Sandstroem, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1982; pp 28, 79.

[27] (a) Dietrich, M. W.; Wahl, A. C. *J. Chem. Phys.* **1963**, *38*, 1591. (b) Larsen, D. W.; Wahl, A. C. *J. Chem. Phys.* **1964**, *41*, 908. (c) Larsen, D. W.; Wahl, A. C. *J. Chem. Phys.* **1965**, *43*, 3765. (d) Chan, M. S.; DeRoos, J. B.; Wahl, A. C. *J. Phys. Chem.* **1973**, *77*, 2163. (e) Chan, M. S.; Wahl, A. C. *J. Phys. Chem.* **1978**, *82*, 2542.

[28] Borisov, G. K.; Chugunova, S. G. *Zh. Fiz. Khim.* **1976**, *50*, 3004.

Table IV. Self-Exchange Rate Constants of the Degenerate Electron Transfer between **1** and **2** in THF-d_8 at Various Temperatures

temp, °C	k_{34}, M^{-1} s^{-1}	method
5.6	1.0 (2) × 10^5	coalescence
12.6	1.9 (3) × 10^5	coalescence
18.6	2.5 (4) × 10^5	coalescence
24.1	7 (2) × 10^5	line broadening
24.1	8 (2) × 10^5	line broadening
30.1	7.9 (5) × 10^5	line broadening
40.1	1.3 (1) × 10^6	line broadening
50.1	2.8 (2) × 10^6	line broadening
60.1	4.3 (3) × 10^6	line broadening

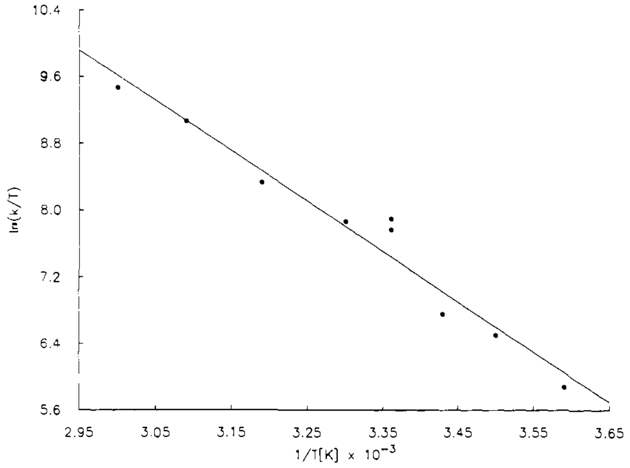

Figure 5. Arrhenius plot for the degenerate self-exchange reaction of **1** and **2** (eq 4).

Attempts to measure the rate of electron transfer for the Co(IV)/Co(V) couple (eq 6) by the coalescence technique were not successful. It was clear from the ^{1}H NMR spectra, however,

$$^*\text{Co(nor)}_4 + [\text{Co(nor)}_4]^+ \overset{k_{45}}{\rightleftharpoons} [^*\text{Co(nor)}_4]^+ + \text{Co(nor)}_4 \quad (6)$$

that mixtures of **1** and **3** having concentrations of approximately 0.01 M in CD_2Cl_2 were exchanging fast on the NMR time scale at room temperature. Since **3** is diamagnetic, NMR spectra of nuclei other than ^{1}H in this compound are easily observed. Specifically, the ^{59}Co NMR spectrum of **3** at 40 °C exhibited a single relatively sharp resonance at +5146 ppm relative to the reference compound $K_3Co(CN)_6$. Addition of the paramagnetic **1** resulted in observable broadening of that line, attributed to exchange by electron transfer. Under the condition that the frequency difference (in the absence of exchange) between two exchanging species is very large compared to the rate of exchange, eq 7 may be used to calculate the rate of electron transfer between

$$k = (\pi/[\text{P}])(W_{\text{DP}} - W_{\text{D}}) \quad (7)$$

a diamagnet (D) and a paramagnet (P).[29] This condition is presumed to be met in this case, as a ^{59}Co NMR resonance of **1** has never been located; it is probably shifted isotropically out of the already huge range of chemical shifts of diamagnetic cobalt compounds. A control experiment was carried out to establish that the line broadening was not simply caused by the presence of a paramagnet in solution. A solution containing **3** (0.081 M) and $Cp_2Fe^+PF_6^-$ (0.017 M), a paramagnetic compound that does not react with **3**, showed no increase in linewidth over that of pure **3**. Three solutions of **3** in CD_2Cl_2 containing various amounts of added **1** were prepared and their ^{59}Co NMR spectra measured (Figure 6). The rate constants determined from these three independent experiments agreed rather well and averaged to $k_{45}(313\ \text{K}) = 2.0\ (5) \times 10^6\ M^{-1}\ s^{-1}$.

The activation parameters for the Co(IV)/Co(V) exchange were determined for solutions of **1** and **3** in pyridine, using the same method for determining the electron-transfer rates. Table V lists the results of measurements between 30 and 60 °C. Above 60 °C **1** begins to decompose, and below 30 °C the spectra are complicated by an unrelated phenomenon (see below). Interestingly, the rate of electron transfer in pyridine at 40 °C is slower than in CD_2Cl_2 by a factor of 5. This change is opposite to what might be expected for the substitution of a solvent of higher dielectric constant (pyridine, $D = 12.3$) for a medium of lesser dielectric constant (CH_2Cl_2, $D = 9.1$).[30] An Arrhenius plot of the rates in pyridine (Figure 7) yielded activation parameters of $\Delta H^{\ddagger} = 8.5\ (3)$ kcal/mol and $\Delta S^{\ddagger} = -6\ (1)$ cal/mol·K.

As expected the rates and activation parameters for the two electron-transfer reactions are similar. Unfortunately, the cobalt–carbon bond distances of **2** and **3** are not available, thus making a Marcus-type calculation of the barrier to electron transfer impossible. We note that it is unlikely that the Co–C bond of **3** is significantly shorter than the already extremely short distance featured by **1** (1.92 Å). The reduction of **1** to **2**, however,

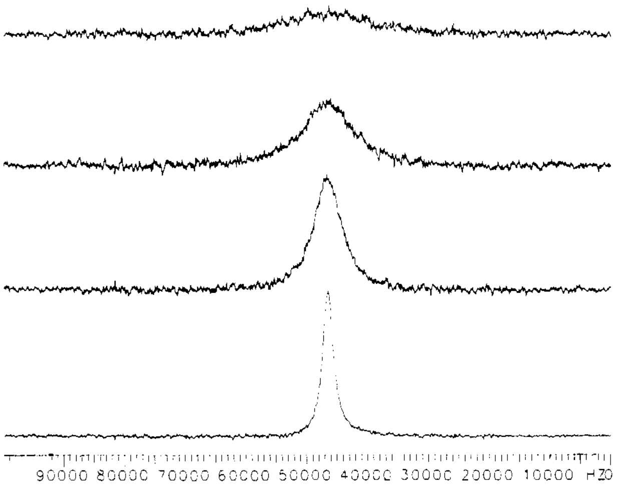

Figure 6. ^{59}Co NMR spectra of $[\text{Co(1-nor)}_4]^+BF_4^-$ (**3**) with various added amounts of paramagnetic Co(1-nor)_4 (**1**). The concentrations of **1** are (from bottom to top): 0, 6.8, 16.0, and 28.8 mM; at 40 °C in CD_2Cl_2.

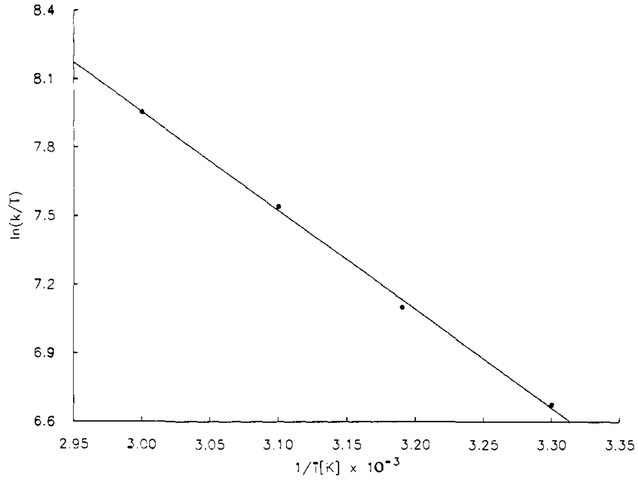

Figure 7. Arrhenius plot for the degenerate self-exchange reaction of **1** and **3** (eq 5).

Table V. Self-Exchange Rate Constants of the Degenerate Electron Transfer between **1** and **3** in Pyridine-d_5 at Various Temperatures

temp, °C	k_{45} × 10^{-5} M^{-1} s^{-1}	temp, °C	k_{45} × 10^{-5} M^{-1} s^{-1}
29.8	2.4 (5)	49.9	6.1 (6)
39.9	3.8 (5)	60.0	9.5 (7)

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[29] Koval, C. A.; Margerum, D. W. *Inorg. Chem.* **1981**, *20*, 2311.

[30] *CRC Handbook of Chemistry and Physics*, 55th ed.; CRC Press: Cleveland, OH, 1974; p E56.

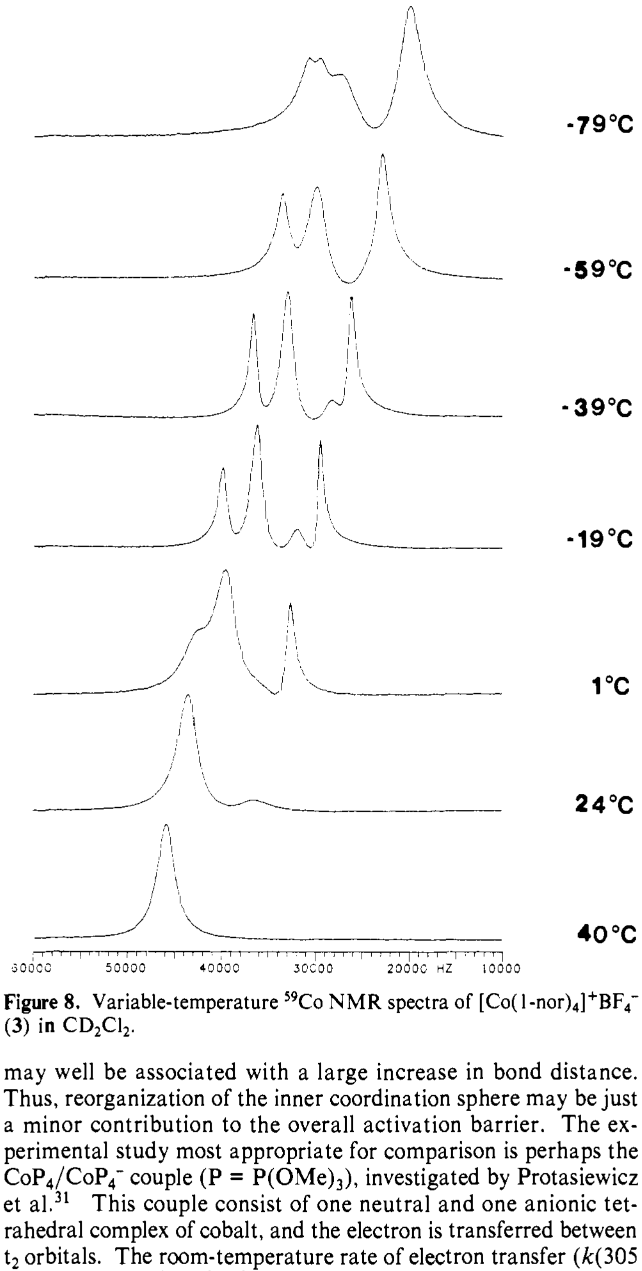

Figure 8. Variable-temperature ^{59}Co NMR spectra of $[Co(1\text{-nor})_4]^+BF_4^-$ (**3**) in CD_2Cl_2.

may well be associated with a large increase in bond distance. Thus, reorganization of the inner coordination sphere may be just a minor contribution to the overall activation barrier. The experimental study most appropriate for comparison is perhaps the CoP_4/CoP_4^- couple ($P = P(OMe)_3$), investigated by Protasiewicz et al.[31] This couple consist of one neutral and one anionic tetrahedral complex of cobalt, and the electron is transferred between t_2 orbitals. The room-temperature rate of electron transfer ($k(305\ K) = 1.4 \times 10^4\ M^{-1}\ s^{-1}$) is comparable to the values reported herein.

Conformational Dynamics. Figure 8 depicts the ^{59}Co NMR spectra of **3** in CD_2Cl_2 in the temperature range +40 to −80 °C. Several resonances in varying intensities were observed. This phenomenon was reversible, and the spectra were independent of the concentration of **3**. At 40 °C the chemical shift of **3** was +5146 ppm relative to $K_3Co(CN)_6$, but the entire manifold of resonances exhibited a large temperature dependence of the shifts. This is a common feature of ^{59}Co NMR spectra, as the paramagnetic contribution to the chemical shift is large for this nucleus.[32] In the case of **3**, it resulted in a temperature dependence of 1.6 ppm/deg. Care must be taken to maintain a constant temperature during acquisition of spectra.

We attribute the multiple resonances observed at low temperatures to the presence of various isomers of **3**. Rotation of a given norbornyl ligand about the cobalt–carbon bond is thought to describe a potential surface with three minima. The number of possible isomers was evaluated by beginning with an arbitrary arrangement of all four norbornyl groups and systematically generating other isomers by 120° rotations.[33] Following this procedure, we have found six unique isomers of the tetrakis(norbornyl)cobalt fragment, belonging to the point groups S_4, D_{2d}, C_2, C_s, C_1, and C_1. Of these, three (C_2, C_1, C_1) are pairs of enantiomers. Experimentally, only four resonances were ever observed at any one temperature, and a total of five may be discerned over the whole temperature range. Efforts to further resolve the observed spectra using a shift reagent (Resolve-Al) were unsuccessful, as were attempts to split the resonances associated with pairs of enantiomers by addition of a chiral shift reagent (tris[3-(((heptafluoropropyl)hydroxy)methylene)-(−)-camphorato]ytterbium(III)).

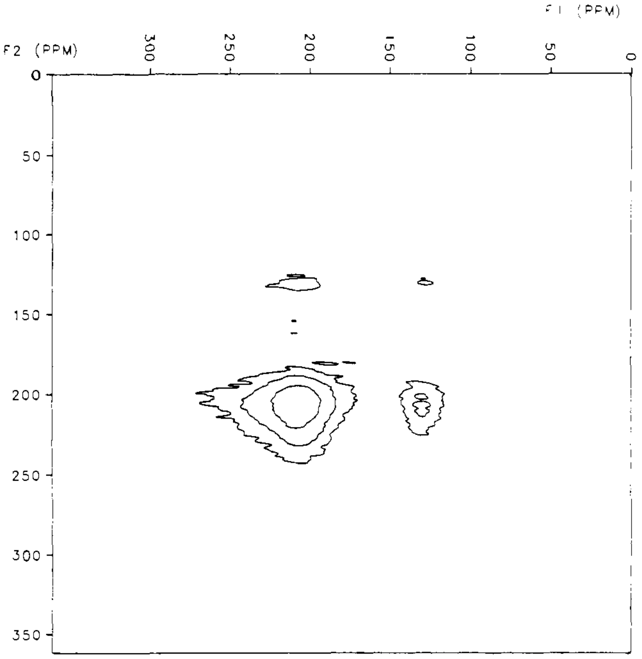

Figure 9. Contour plot resulting from ^{59}Co NOESY experiment on $[Co(1\text{-nor})_4]^+BF_4^-$ (**3**) at 11.6 °C. Diagonal from left bottom to right top represents the 1D spectrum of **3**, which exhibits two peaks of unequal intensity. Off-diagonal peaks indicate exchange on the time scale of the experiment (mixing time 0.5 ms).

In support of our explanation for the observation of several isomers of **3**, we note that the low-temperature ESR spectrum of **1** (at 77 K in a cyclohexane glass) has been interpreted as being due to three different conformers of the neutral molecule.[34] In addition, the presence of various rotamers in the solid state is exactly what gave rise to the disorder problem in the determination of the crystal structure of **1**. In this context it was of some interest to determine the rate of interconversion of the various isomers of **3**. This process presumably involves a hindered rotation around a cobalt–carbon single bond. It was not obvious to us whether the observation of only one ^{59}Co resonance above 40 °C was the result of a coalescence phenomenon or whether it reflected the shift of a temperature-dependent equilibrium predominantly to one side. Thus, we sought an independent way of measuring the rate of interconversion of the isomers of **3**. We have found that the 2D NMR experiment NOESY (nuclear Overhauser and exchange spectroscopy),[35] as applied to the ^{59}Co NMR of **3** at low temperature, provided a solution to this problem. The NOESY technique provides the equivalent of several spin saturation transfer experiments in one. In order to simplify the quantitative analysis, a NOESY experiment was performed at

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[31] Protasiewicz, J. D.; Theopold, K. H.; Schulte, G. *Inorg. Chem.* **1988**, *27*, 1133.

[32] (a) Brevard, C.; Granger, P. *Handbook of High Resolution Multinuclear NMR*; Wiley: New York, 1981; p 125. (b) Mason, J. *Multinuclear NMR*; Plenum Press: New York, 1987.

[33] In all isomers the plane through the norbornyl group defined by the two bridgehead carbons and the methylene bridge was constrained to coincide with one of the mirror planes of the CoC_4 tetrahedron.

[34] Bower, B. K.; Findlay, M.; Chien, J. C. W. *Inorg. Chem.* **1974**, *13*, 759.

[35] Jeener, J.; Meier, B. H.; Bachmann, P., Ernst, R. R. *J. Chem. Phys.* **1979**, *71*, 4546.

11.6 °C (Figure 9). At that temperature the one-dimensional ^{59}Co NMR spectrum exhibited only two resonances of unequal intensity (isomers A and B, $K_{eq} = 0.22$). The observation of cross peaks in the 2D spectrum indicated transfer of magnetization between the two sites on the time scale of the experiment (mixing time $t_m = 5 \times 10^{-4}$ s). The rate of interconversion between the two isomers was calculated using a modification of the method of Jeener et al.[35] The microscopic rate constants thus derived were $k_{A-B} = 6\ (1) \times 10^2$ s^{-1} and $k_{B-A} = 3.0\ (5) \times 10^3$ s^{-1} at 11.6 °C in CD_2Cl_2. We note that these numbers are smaller than the frequency separation between the two resonances (ca. 7000 Hz), as they must be to allow the observation of two resolvable signals. However, an increase in temperature to 40 °C may well increase the rate of interconversion to the point where it becomes fast on the NMR time scale, resulting in coalescence of the resonances. Thus we believe that the observation of a single resonance for **3** above 40 °C is the result of isomerizations that proceed fast on the ^{59}Co NMR time scale. Nevertheless, the trends in signal intensities observed at lower temperatures seem to indicate the presence of one predominant species near room temperature. This notion lends some support to our earlier assertion that one of the disordered rotamers predominated in crystals of **1**.

Conclusions. A group of closely related homoleptic alkyl complexes of cobalt in unusually high formal oxidation states has been fully characterized. The reaction of 1-norbornyllithium with cobaltous chloride yields Co^{IV}(1-nor)$_4$ (**1**) or $[Li(THF)_4]^+[Co^{III}(1\text{-nor})_4]^-$ (**2**), depending on the solvent. **1** may be oxidized to afford the stable $[Co^{V}(1\text{-nor})_4]^+BF_4^-$ (**3**). The crystal structure of **1** has been determined. It exhibited disorder of the norbornyl ligands but established the tetrahedral geometry of the Co(IV) complex. This structure is probably retained in all oxidation states. Magnetic measurements showed that **1** has one unpaired electron, **2** exhibits two unpaired electrons, and **3** is diamagnetic. Thus all three complexes are rare examples of low-spin tetrahedral complexes of a first-row transition metal. The electronic absorption spectra of **1**–**3** have been recorded and the tetrahedral ligand field splittings extracted. Δ_t ranges from 15 000 to 22 000 cm^{-1}, consistent with the low-spin nature of the complexes. The redox potentials of the **1**/**2** and **3**/**1** couples have been measured by cyclic voltammetry. They are very low, despite the high formal oxidation states involved. The rates and activation parameters of the degenerate electron-transfer reactions have been measured by a combination of ^{1}H and ^{59}Co NMR. The latter technique has also revealed the presence and rapid interconversion of rotational isomers of **3**.

It is remarkable how much the properties of an element can be influenced by its chemical environment. Cobalt(III) in the form of the hexaaquo ion oxidizes water to O_2,[36] yet cobalt(IV) in the form of **1** reduces protons to dihydrogen. The $[Co(NH_3)_6]^{3+/2+}$ couple exchanges electrons at the rate of 1×10^{-6} M^{-1} s^{-1},[37] yet the cobalt alkyls described herein exhibit self-exchange rates 11 orders of magnitude faster. Such flexibility is an invaluable asset for the purposeful designer of molecules. We look forward to applying the lessons learned in the study of these fascinating compounds to the synthesis of other high-valent cobalt compounds.

Experimental Section

General Techniques. ^{1}H NMR spectra were recorded primarily on a Bruker WM-300 spectrometer; a Varian XL-200 spectrometer was also employed. ^{13}C (100-MHz) and ^{59}Co (95-MHz) spectra were recorded on a Varian XL-400 spectrometer. Temperatures were measured on the Bruker instrument using a copper/constantan thermocouple and Fluke digital thermometer. The thermocouple wire was placed into an NMR tube containing the solvent of choice and allowed to equilibrate for ca. 10 min, after which the temperature was recorded. Temperatures on the Varian instruments were measured using a built-in methanol thermometer. IR spectra were obtained on a Perkin-Elmer Model 337 spectrophotometer or on a Mattson Alpha Centauri FTIR spectrophotometer. Melting points were measured using a Mel-Temp apparatus and are uncorrected. Far-IR spectra were recorded on an IBM IR 98 2A spectrophotometer.

All manipulations involving air-sensitive compounds were carried out using a Vacuum Atmospheres inert-atmosphere box under N_2 or standard Schlenk and high-vacuum techniques. Hydrocarbon solvents, diethyl ether, and THF were purified by distillation from purple sodium benzophenone ketyl. CH_2Cl_2, CD_2Cl_2, and C_5D_5N were purified by distillation from CaH_2. C_6D_6 and THF-d_8 were predried over potassium and stored over Na/K alloy.

Electrochemical measurements were performed in the glovebox using a Soltec Model VP-6423S X-Y recorder and BAS Model CV-27 potentiostat. A reference electrode consisting of a cracked-glass bead outer shell (Fisher) containing a silver wire in a saturated $AgCl/Me_4N^+Cl^-$. THF solution was used in all cases. The potential of the Cp_2Fe/Cp_2Fe^+ couple vs this reference was +0.89 V. Cyclic voltammograms were recorded in a single-compartment cell using either a 0.02- or 0.03-in. Pt-disk working electrode; a 0.03-in. Pt wire served as the auxiliary electrode. Coulometry measurements were made using a three-compartment cell. The central compartment contained the solution to be electrolyzed, a stir bar, and the reference and working electrodes. The outer compartments containing only electrolyte solution, and the auxiliary electrode was placed in one of them. Both the working and auxiliary electrodes for the coulometric experiments consisted of a piece of Pt gauze (about 2 cm^2) attached to a 0.07-in. Pt wire.

Microanalyses were performed by the University of California at Berkeley microanalytical laboratory or by Analytische Laboratorien, Elbach, FRG. Magnetic measurements were performed using a Faraday balance.

Co(1-nor)$_4$[10] and 1-chloronorbornane[38] were prepared according to published procedures. A literature preparation of 1-norbornyllithium[16] was modified: 1-norbornyllithium was prepared by the addition of 1-chloronorbornane to a stirred solution of excess Li sand (1% Na) in cyclohexane, followed by reflux for 3 h under Ar. 1-norLi was then isolated as a white solid and titrated after each preparation using anhydrous methanol. The titration was performed in ether to a colorless end point using 1,10-phenanthroline as indicator. $CoCl_2$·THF was prepared via Soxhlet extraction of anhydrous $CoCl_2$ in THF and analyzed after each preparation. Various batches ranged in THF content from $CoCl_2$·0.94THF to $CoCl_2$·1.225THF.

Tetrakis(tetrahydrofuran)lithium Tetrakis(1-norbornyl)cobaltate(III), $[Li(THF)_4]^+[Co(1\text{-nor})_4]^-$ (2). A solution of 0.347 g (1.75 mmol) of $CoCl_2$·THF was added all at once to a stirred solution of 1.072 g (7.01 mmol at 66.7%) of 1-norbornyllithium in 15 mL of Et_2O/0.5 mL of THF. The solution immediately took on an intense dark green color and precipitated a black solid (Co, see below). The solution was stirred at room temperature for 5 min, after which the insolubles were filtered off and the solvent was evaporated to dryness. The resulting solid was crystallized from Et_2O at −30 °C to yield 0.231 g (0.315 mmol) of **2** as dark green crystals. The yield was 18% based on Co and 27% of theoretical (see eq 1). ^{1}H NMR (THF-d_8, 299 K): δ 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) and resonances of free THF-d_0. Mp: 156–157 °C. IR (Nujol): 1130 (w), 1082 (w), 1042 (s), 971 (w), 917 (w), 887 (m), 742 (w), 668 (w) cm^{-1}. Far-IR (polyethylene pellet): 407 (s), 309 (s), 272 (s), 168 (w) cm^{-1}. By comparison with $[Li(THF)_4]^+[Co(Mes)_3]^-$,[39] the stretches at 1042 and 887 cm^{-1} are due to THF, and those at 407 and 309 cm^{-1} in the far-IR are due to the $Li(THF)_4^+$ counterion. Magnetic moment (300 K) = 3.18 μ_B. Anal. Calcd for $C_{44}H_{76}CoLiO_4$: C, 71.91; H, 10.42. Found: C, 71.04; H, 10.13. The insoluble black powder was attracted by a magnet (ferromagnetic). It dissolved in aqua regia and tested positive for cobalt according to the standard tests of qualitative inorganic analysis.[40]

Sodium(18-crown-6) Tetrakis(1-norbornyl)cobaltate(III), $[Na(18\text{-crown-}6)]^+[Co(1\text{-nor})_4]^-$. Co(1-nor)$_4$ (0.070 g, 0.159 mmol) was dissolved in about 8 mL of THF. Na metal (0.010 g, 0.435 mmol, 2.7-fold excess) was added with stirring. The mixture was stirred at room temperature for about 30 min, during which time the color changed from red-brown to deep green. The excess Na was then filtered away, and 0.084 g (0.319 mmol, 2-fold excess) of 18-crown-6 was added. This solution was stirred at room temperature for 3 h. It was then filtered, the solvent evaporated to dryness, and the resulting green solid recrystallized from Et_2O at −30 °C. Long green needles formed quickly; the yield was 0.071 g (0.098 mmol, 61%). ^{1}H NMR (THF-d_8, 299 K): δ 52.2 (br s, 8 H), 14.1 (s,

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4 H), 10.4 (br s, 8 H), 7.7 (s, 8 H), 4.0 (s, 8 H), 3.4 (s, 24 H), −1.3 (br s, 8 H). IR (Nujol): 1352 (m), 1241 (m), 1114 (s), 1055 (m), 967 (m), 840 (w), 741 (w) cm^{-1}.

Tetraethylammonium Tetrakis(1-norbornyl)cobaltate(III), $[Et_4N]^+[Co(1\text{-nor})_4]^-$. A solution of 0.459 g (0.624 mmol) of **2** in 4 mL of THF was added to a suspension of 0.205 g (1.24 mmol, 2-fold excess) of $Et_4N^+Cl^-$ in 8 mL of THF. The $Et_4N^+Cl^-$ had been previously recrystallized from MeCN and washed with THF. The mixture was stirred at room temperature overnight. Excess $Et_4N^+Cl^-/LiCl$ was filtered away and the solvent evaporated. The green product was triturated a few times with Et_2O, evaporated to dryness, and recrystallized at −30 °C from THF/Et_2O (1:2). The yield of green crystals = 0.069 g (0.121 mmol, 19%). ^1H NMR (THF-d_8, 299 K): δ 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), 3.2 (s, 8 H), 1.2 (s, 12 H), −1.3 (br s, 8 H). IR (Nujol): 1234 (m), 1169 (m), 1131 (m), 1081 (m), 995 (s), 782 (m), 742 (m) cm^{-1}.

Tetrakis(1-norbornyl)cobalt(V) Tetrafluoroborate, $[Co(1\text{-nor})_4]^+[BF_4]^-$ (3). To a stirred solution of 0.219 g (0.499 mmol) of $Co(1\text{-nor})_4$ in 18 mL of THF was added 0.097 g (0.499 mmol) of $Ag^+BF_4^-$. Immediate reaction occurred, yielding a precipitate of silver, which was filtered off after 10 min. The solvent was then evaporated and the resulting solid recrystallized at −30 °C from CH_2Cl_2/Et_2O. Yellow-brown crystals (0.220 g, 0.418 mmol) were obtained in 84% yield. ^1H NMR (CD_2Cl_2, 300 K): δ 2.37 (s, 4 H), 1.98 (m, 8 H), 1.66 (s, 8 H), 1.47 (m, 8 H). ^{13}C NMR (CD_2Cl_2, 300 K): δ 91.6, 44.3, 35.8, 32.5, 32.1. ^{59}Co NMR (CD_2Cl_2, 40 °C): δ +5146 (relative to $K_3Co(CN)_6$ in D_2O). Mp: 98–103 °C. IR (Nujol): 1303 (w), 1282 (m), 1238 (m), 1213 (m), 1143 (m), 1091 (s), 1053 (s), 1034 (s), 957 (m), 926 (w), 822 (m), 795 (m), 741 (s) cm^{-1}. Far-IR (polyethylene pellet): 303 (s), 187 (w) cm^{-1}. 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.

Crystal Structure of $Co(1\text{-nor})_4$ (1). A suitable crystal of $Co(1\text{-nor})_4$ was isolated from a diethyl ether solution of its anion $PPN^+[Co(1\text{-nor})_4]^-$ ($PPN^+ = (Ph_3P)_2N^+$), which had been cooled to −30 °C for 1 month. The crystal, which measured 0.35 × 0.35 × 0.40 mm, was sealed in a 0.5-mm Lindemann capillary. Preliminary X-ray diffraction photographs displayed orthorhombic symmetry. Precise lattice constants, determined from a least-squares fit of 15 diffractometer-measured 2θ values at 25 °C, were a = 11.948 (3) Å, b = 10.104 (2) Å, and c = 9.805 (3) Å. The cell volume was 1183.75 (50) Å^3, with a calculated density of 1.233 g/cm^3. The space group was determined to be $Pmn2_1$, and the asymmetric unit consisted of half of a $Co(nor)_4$ molecule (Z = 2). The other half was generated by a mirror plane, and those atoms were labeled with "A" in Figure 1. All unique diffraction maxima (h,k,l) with $2\theta < 114°$ were measured on a four-circle computer-controlled Syntex $P2_1$ diffractometer with variable-speed, 1° ω scans. Cu Kα (λ = 1.54178 Å) radiation was used, and the scan method was θ–2θ. A total of 681 (37%) of the 1820 reflections was judged observed ($|F_o| \geq 3\sigma(F_o)$). The structure was solved routinely by the heavy-atom method.[41] The Co atom was located via a Patterson synthesis, and the other C atoms were revealed in successive difference Fourier syntheses. Block-diagonal least-squares refinements (minimization of $\sum w(|F_o| - |F_c|)^2$, where w is based on counting statistics modified by an ignorance factor of $\beta = 0.03$) with 17 anisotropic non-hydrogen atoms, and all hydrogens included in calculated positions converged to a final R factor of 0.071. Inspection of the resulting structure revealed some unrealistic bond distances and angles within the ligands. A constraint was then imposed on the refinement (see text). Starting with the bond distances and angles of 1,1′-binorbornyl[17] as constraints, the program CRYSTALS[42] was used to refine the structure of the major contributor to the disordered structure according to the method of Waser.[18] This procedure resulted in a chemically sensible model for the ligands upon which the discussion is based. The final constrained R factor was 0.089, R_w = 0.107. Crystal data and data collection parameters are listed in Table VI.

Table VI. Parameters of Crystal Structure Determination of **1**

formula	$C_{28}H_{44}Co$
formula wt	439.59
cryst syst	orthorhombic
space gp	$Pmn2_1$
Z	2
a, Å	11.948 (3)
b, Å	10.104 (2)
c, Å	9.805 (3)
$\alpha = \beta = \gamma$, deg	90.00
V, Å^3	1183.8 (5)
d_{calc}, g/cm^3	1.233
cryst dimens, mm	0.35 × 0.35 × 0.40
diffractometer	syntex $P2_1$
radiatn	Cu Kα (λ = 1.54178 Å)
temp, °C	25
scan method	θ–2θ
2θ range, deg	0–114
scan rate, deg/min	variable (1° ω scans)
no. of data colld	1820
no. of unique data > 3σ	681
no. of variables	146
linear abs coeff, cm^{-1}	56.1

Chemical Oxidation of $[Li(THF)_4]^+[Co(1\text{-nor})_4]^-$. $[Li(THF)_4]^+[Co(1\text{-nor})_4]^-$ (0.138 g, 0.188 mmol) was suspended in 10 mL of C_5H_{12}. $CoCl_2\cdot THF$ (0.037 g, 0.186 mmol) was added. The mixture was stirred at room temperature for 14 h, while the color changed from green to red-brown. The insoluble products were then filtered off, the solvent was evaporated, and the product was recrystallized at −30 °C from C_5H_{12}. The total recrystallized yield of **1** was 0.036 g (0.082 mmol, 44%, four crops). The product was identified by IR.

Chemical Reduction of $Co(1\text{-nor})_4$. (a) With 1-Norbornyllithium. $Co(1\text{-nor})_4$ (0.204 g, 0.465 mmol) was dissolved in 12 mL of THF, and 1-norbornyllithium (0.176 g, 0.929 mmol at 54%, 2-fold excess) was added with stirring. The solution color changed from red-brown to green within 1 min. After 5 min at room temperature, the solution was filtered and the solvent evaporated to dryness. The green product was triturated once with Et_2O and then recrystrallized from Et_2O at −30 °C. The yield of $[Li(THF)_4]^+[Co(1\text{-nor})_4]^-$ (**2**) was 0.241 g (0.328 mmol, 70%). The product was identified by IR.

(b) With Li. $Co(1\text{-nor})_4$ (0.204 g, 0.465 mmol) was dissolved in 10 mL of THF, and 0.100 g (0.014 mol, excess) of Li sand was added with stirring. The Li had been previously washed with C_5H_{12} to remove mineral oil from the dispersion. The reaction proceeded for 20 min while the color changed from red-brown to green. The excess Li was then filtered away, the solvent evaporated, and the product $[Li(THF)_4]^+[Co(1\text{-nor})_4]^-$ recrystallized at −30 °C from Et_2O. Yield of **5**: 0.162 g (0.220 mmol, 47%) in three crops. The product was identified by IR.

Electronic Spectra of $Co(1\text{-nor})_4^{-,0,+}$. UV–visible spectra were recorded at 25 °C using a Hewlett-Packard Model 8450A spectrophotometer capable of measuring absorbances from 0 to 4 and wavelengths from 200 to 800 nm. In each case a 1-mm quartz cell was used in order to allow the use of relatively concentrated solutions. The cell was fitted with a 14/20 ground glass joint through the use of a graded quartz to Pyrex seal. Samples were prepared under nitrogen in the glovebox. The instrument was balanced using air vs air, since the region of interest was the visible light region and no solvent absorbances interfered. A background spectrum of each solvent was recorded, however, and the minimal absorbances of the solvent were subtracted from those of the compounds in calculating extinction coefficients for the ligand field bands.

Cyclic Voltammogram of $Co(1\text{-nor})_4$. $NBu_4^+BF_4^-$ was purchased from Aldrich and recrystallized from hot ethyl acetate. It was then thoroughly dried on the high-vacuum line and taken into the drybox. A total of 25 mL of a 10^{-3} M THF solution of **1** was prepared. $NBu_4^+BF_4^-$ (0.327 g, 1.0 mmol) was added to 10 mL of this solution to make the concentration 0.1 M in that reagent. A 0.03-in. Pt disk served as the working electrode, with the rest of the conditions as described in the general section. The voltammogram was first recorded at 20 mV/s in the absence of ferrocene. Cp_2Fe did not affect the potentials of the two couples; it was added (in 1 mM concentration) as an additional potential reference. The following reversible one-electron waves were observed: $Cp_2Fe^{+/0}$, $E_{1/2}$ = +0.00 V, ΔE_p = 0.111 V; $Co(nor)_4^{+/0}$, $E_{1/2}$ = −0.65 V, ΔE_p = 0.083 V; $Co(nor)_4^{0/-}$: $E_{1/2}$ = −2.02 V, ΔE_p = 0.092 V. All potentials quoted here are versus the $Cp_2Fe^{+/0}$ potential reference.

Electrochemical Reduction of $Co(1\text{-nor})_4$. Controlled-potential electrolysis (using the coulometry technique described in General Techniques) of 10 mL of a THF solution containing 1.09×10^{-5} mol of **1** and 1.00×10^{-3} mol of $NBu_4^+BF_4^-$ was performed at a potential of −2.89 V vs $Cp_2Fe^{+/0}$. Current was passed for 70 min, during which time the solution color changed from red-brown to green. After 70 min, 1.123 C

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(41) All crystallographic calculations were done on a Prime 850 computer operated by the Cornell Chemistry Computing Facility. Principal programs employed were as follows: REDUCE and UNIQUE, data reduction programs by M. E. Lewonowicz, Cornell University, 1978; MULTAN 78, a system of computer programs for the automatic solutions of crystal structures from X-ray diffraction data (locally modified to perform all Fourier calculations including Patterson syntheses), written by P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, University of York, England, 1978; BLS78A, an anisotropic block-diagonal least-squares refinement written by K. Hirotsu and E. Arnold, Cornell University, 1980; PLIPLOT, by G. VanDuyne, Cornell University, 1984; TABLES, by G. VanDuyne, Cornell University, 1986.

(42) CRYSTALS is a crystallographic program written by D. J. Watkin and J. R. Carruthers, Chemical Crystallography Laboratory, University of Oxford, 1981.

had been passed. A control experiment to measure background charge from the solvent/electrolyte system yielded 0.041 C after 70 min at −2.89 V. Subtraction of this value from 1.123 C gave 1.082 C for the reduction of 1.09×10^{-5} mol of Co(nor)$_4$. The expected charge for a single electron per molecule was 1.052 C, yielding a value for *n* of 1.03 e/molecule.

Electrochemical Oxidation of Co(1-nor)$_4$. Controlled-potential electrolysis of 10 mL of a THF solution containing 1.05×10^{-5} mol of **1** and 1.00×10^{-3} mol of $NBu_4^+BF_4^-$ was performed at a potential of +0.26 V vs $Cp_2Fe^{+/0}$. Current was passed for 83 min, during which time the solution color changed from red-brown to yellow-brown. After 83 min, 1.454 C had been passed. A control experiment to measure background charge from the solvent/electrolyte system yielded 0.199 C after 82 min at +0.26 V. Subtraction of this value from 1.454 C gave 1.255 C for the oxidation of 1.05×10^{-5} mol of Co(nor)$_4$. The expected charge for a single electron per molecule was 1.013 C, yielding a value for *n* of 1.24 e/molecule.

Coalescence Measurement of Rate Constants for Electron Transfer between 1 and 2. In the glovebox, an NMR tube, which had been previously sealed to a 14/20 ground glass joint, was charged with 0.004 g (9.1×10^{-6} mol) of **1** and 0.006 g (8.1×10^{-6} mol) of **2**. A needle valve was attached, the system evacuated to 10^{-5} Torr on a high-vacuum line, and THF-d_8 condensed into the tube. It was then flame-sealed under vacuum, and variable tempertaure ^{1}H NMR spectra were recorded at 300 MHz. Coalescence was observed for the bridgehead protons of the two compounds at 279 K, below which both components are distinguishable. The cooling and warming process was repeated to establish the reversibility of the coalescence behavior. The volume of solvent in the tube (0.057 mL) was calculated by measuring the mass of CCl$_4$ required to attain the level of the solution in an NMR tube of the same type. The coalescence expression, $k = (\pi^2/2)^{1/2}\Delta\nu$,[26] was used to calculate a first-order rate constant at the coalescence temperature. The difference in frequency in the absence of exchange, $\Delta\nu$, was obtained by recording variable-temperature spectra in THF-d_8 of **1** and **2** individually. The chemical shift of all resonances was plotted vs $1/T$ to yield straight lines, from which the chemical shift of any proton at a given temperature may be calculated. The second-order rate constant for the electron transfer was obtained by dividing the first-order rate constant *k* obtained from coalescence by the total concentration of the two species in solution. Evidence for the bimolecular nature of the reaction was obtained by performing a similar experiment using 0.002 g (4.5×10^{-6} mol) of **1** and 0.003 g (4.0×10^{-6} mol) of **2** in 0.63 mL of THF-d_8. The coalescence temperature rose to 292 K. This rise is predicted on the basis that smaller concentrations should require a higher temperature to achieve coalescence at about the same $\Delta\nu$. An analogous experiment using 0.0053 g (7.2×10^{-6} mol) of [Na(18-crown-6)]$^+$[Co(1-nor)$_4$]$^-$ and 0.0023 g (5.2×10^{-6} mol) of **1** in 0.69 mL of THF-d_8 exhibited a coalescence temperature of 286 K.

^{1}H NMR Line-Broadening Measurement of Rate Constants for Electron Transfer between 1 and 2. Calculation of Activation Parameters. In the glovebox, an NMR tube, which had been previously sealed to a 14/20 ground glass joint, was charged with 0.016 g (2.2×10^{-5} mol) of **2** and approximately 0.004 g (9.1×10^{-6} mol, $f_{p,calc} = 0.293$) of **1**. A needle valve was attached, the system evacuated to 10^{-5} Torr on the high-vacuum line, and THF-d_8 condensed into the tube. The volume of THF-d_8 was measured by the height of the solution in the tube, which was multiplied by the factor of 0.01377 mL/mm to obtain the volume at 22 °C (0.530 mL). This volume was adjusted for THF contraction or expansion at the temperature of interest by calculating a new density according to the formula $d_T = 0.9097\ (1{-}0.001212T\ (°C))$.[28] The tube was flame-sealed under 500 Torr prepurified N$_2$, which had been passed through a liquid N$_2$ trap. Variable-temperature ^{1}H NMR spectra were recorded between 30 and 60 °C at 200 MHz. Samples of pure **1** and **2** were prepared in an analogous fashion and also observed at those temperatures. The linewidths of the bridgehead protons were recorded in each case, along with their chemical shifts. An accurate measure of the actual amount of **1** in solution was made by calculating f_p from those chemical shifts ($f_{p,obs} = 0.207$). The total concentration *c* for eq 5 was adjusted using the measured f_p. Equation 5 was then applied to calculate a rate constant for each temperature. In addition, the three tubes measured earlier by coalescence were observed at 24.1 °C. Two rate constants (for the tubes containing **2**) were obtained at that temperature using eq 5 with a measured f_p and adjusted *c*. Finally, the measured f_p and new *c* were factored back into the coalescence measurements to obtain more accurate rate constants at the coalescence temperatures. A total of 9 points (Table IV) were used in the Eyring plot to calculate activation parameters (see text).

^{59}Co NMR Line-Broadening Measurement of Rate Constants for Electron Transfer between 1 and 3. Calculation of Activation Parameters. **(a) In CD$_2$Cl$_2$.** In the glovebox, four NMR tubes sealed to 14/20 joints were charged with approximately 21 mg of **3** each. Various known amounts of **1** (2.4, 4.3, and 7.0 mg) were added to three of these tubes, which were then evacuated on the high-vacuum line and CD$_2$Cl$_2$ condensed into them. The tubes were flame-sealed under vacuum and observed by ^{59}Co NMR (95.368 MHz) at +40.0 °C. The linewidth of **3** alone was minimized to 2125 Hz at that temperature. All linewidths were measured by adding a 1000-Hz line broadening, creating smoother lines, before the Fourier transform of the data. Subtraction of 1000 Hz from the computer-measured linewidths then gave the vinal values. Volumes of the solutions were determined by measuring the mass of CCl$_4$ required to attain the level of the solution in question in an NMR tube of the same type. The linewidths of the ^{59}Co resonances of **3** broadened by exchange with **1** were used in eq 7 to calculate a rate constant for electron transfer. Three values were obtained (k_{45}([**1**]): 2.2 (4) $\times 10^6$ M^{-1} s^{-1} (0.0288 M), 1.9 (4) $\times 10^6$ M^{-1} s^{-1} (0.0160 M), and 1.8 (6) $\times 10^6$ M^{-1} s^{-1} (0.0068 M)) and averaged to give k_{45} (CD$_2$Cl$_2$, +40.0 °C) = 2.0 (5) $\times 10^6$ M^{-1} s^{-1}. A control experiment showed that a sample containing 0.0811 M **3** and 0.0172 M $Cp_2Fe^+PF_6^-$ exhibited the same linewidth (to ±20 Hz) as the sample of pure **3**.

(b) In C$_5$D$_5$N. In the glovebox, two NMR tubes sealed to 14/20 joints were prepared. One was charged with approximately 12 mg of **3**. The other contained 15.0 mg of **3** and 2.7 mg of **1**. Both were evacuated on the high-vacuum line, and C$_5$D$_5$N was condensed into them. The tubes were flame-sealed under 500 Torr prepurified N$_2$, which had been passed through a liquid N$_2$ trap. Variable-temperature ^{59}Co spectra were recorded between 30 and 60 °C at 95.4 MHz. The volume of the solution containing **1** was measured by the height of the solution in the tube, which was multiplied by the factor of 0.01377 mL/mm to obtain the volume at 22 °C. This volume was not adjusted for temperature changes. The concentration of **3** in the tube with the mixture was 0.062 M, and that of **1** was 0.0133 M. The linewidths of the mixture and **3** alone were recorded at each temperature, from which rate constants were extracted using eq 7.

^{59}Co NOESY Spectra of [Co(1-nor)$_4$]$^+$[BF$_4$]$^-$. Spectra were recorded at 95.368 MHz using a Varian XL-400 spectrometer. The temperature was maintained at 11.6 °C. The spectral width was 30.5 kHz, and the 90° pulses were 18 ms in length. Spectra were collected in the phase-sensitive mode,[43] and no symmetrization routines were used. A 100-Hz line broadening was employed. The 1024×1024 data matrix was generated using the pulse sequence 90°-t_1-90°-T_m-90°-t_2 (acquisition), with 512 scans per t_1 value. A total of 16 increments of t_1 were collected. The T_1's for the two resonances at +11.6 °C were measured by the standard inversion–recovery technique and were both about 1 ms. Four experiments were performed at this temperature using four different mixing times, 1×10^{-4} s $< T_m < 1 \times 10^{-3}$ s. Magnetization exchange was observed in all four cases and was maximized at 5×10^{-4} s.

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Supplementary Material Available: Tables of fractional coordinates and thermal parameters, anisotropic thermal parameters, interatomic distances and angles, and hydrogen atom positions and figures of absorption spectra of **1–3** (16 pages). Ordering information is given on any current masthead page.

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