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Unimolecular and Bimolecular Homolytic Reactions of Organochromium and Organocobalt Complexes. Kinetics and Equilibria

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Abstract: The rates of the reversible alkyl group transfer between Cr^{2+} and $Co^{II}(dmgBF_2)_2(H_2O)_n$ in H_2O, pH 1–3, show a strong dependence on steric effects of the alkyl group, consistent with an S_H2 mechanism. The equilibrium constants for the alkylchromium formation $[Cr^{2+} + RCo(dmgBF_2)_2OH_2 = RCr^{2+} + Co(dmgBF_2)_2]$ are 6.43×10^{-2}, 3.70×10^{-3}, 2.80×10^{-3}, and $\leq 10^{-5}$ for R = CH_3, C_2H_5, $C_6H_5CH_2$, and CH_2OCH_3, respectively. The latter reaction yields the previously unknown $CH_3OCH_2Co(dmgBF_2)_2$. The benzyl complex undergoes unimolecular homolysis ($k = 7.6 \times 10^{-6}$ s^{-1} at 25 °C); the bond dissociation enthalpy of its Co–C bond is 24 ± 3 kcal/mol. The rate constant for the reverse reaction is 8.8×10^7 M^{-1} s^{-1}.

Homolytic metal–carbon bond cleavage occurs by both unimolecular[1-13] and bimolecular[14-22] homolytic reactions. Both mechanisms, but especially the former, are important in determing metal–alkyl bond dissociation enthalpies (BDE).[2,3,7,8,16,23] The approach is based on the assumption that the BDE can be approximated as ΔH^{*} for the unimolecular homolysis (eq 1) since the recombination reaction (the reverse of eq 1) has a negligibly small activation enthalpy.

$$M\text{–}R \rightleftarrows M + R \qquad (1)$$

The latter point has been confirmed for a number of reactions between carbon-centered radicals and transition metal complexes[24-26] all of which have rate constants in excess of 10^7 M^{-1} s^{-1}. Applied to organochromium cations $(H_2O)_5CrR^{2+}$ (R = alkyl, aralkyl, substituted alkyl), kinetic studies of the forward[2] and reverse[25] reactions have yielded equilibrium constants for the indicated homolytic equilibrium. On the basis of the kinetics, products, substituent effects, and activation parameters the mechanism for dissociation has been characterized as unimolecular homolytic dissociation (S_H1 mechanism).

Methyl exchange reactions between a series of cobalt macrocycles[16] (eq 2) follow a second-order rate equation and occur by

$$R(Co) + [Co] \rightleftarrows R[Co] + (Co) \qquad (2)$$

direct displacement. The same S_H2 mechanism has been assigned to the reactions between carbon-centered radicals and some organocobalt complexes (eq 3).[27,28]

$$R' + R(Co) \rightarrow RR' + (Co) \qquad (3)$$

In this paper we report on certain reactions of $RCo(dmgBF_2)_2H_2O$. The "BF_2-capped" macrocyclic ligand offers a considerable advantage over the $(dmgH)_2$ pseudomacrocycle in terms of kinetic stability. The Co(II) complex of the former is stable toward H_3O^+ whereas the parent cobalt(II) cobaloxime $Co(dmgH)_2(H_2O)_n$ decomposes almost instantaneously[6] to $Co(aq)^{2+}$. Thus a complete kinetic and thermodynamic description of reversible alkyl transfer between Cr^{2+} and $RCo(dmgBF_2)_2H_2O$ was possible. In addition the unimolecular thermal homolysis of $PhCH_2Co(dmgBF_2)_2H_2O$ was studied by using several scavenging reagents.

Experimental Section

Materials. $Co(dmgBF_2)_2(H_2O)_2$ was prepared by a procedure similar to that used in the preparation of the analogous diphenylglyoximato complex.[29] The suspension resulting from addition of 10 mL of $BF_3\cdot Et_2O$ to 2 g of $Co(OAc)_2\cdot 4H_2O$ and 1.9 g of $dmgH_2$ in 150 mL of diethyl ether was stirred at room temperature for 6 h and filtered. The solid $Co(dmgBF_2)_2(H_2O)_2$ was washed with ice-cold water and recrystallized from methanol; yield 2 g. Analytical and spectroscopic data are given in Table I. The presence of the two axial water molecules in the solid state is assumed, and in solution the complex may either be penta-

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Table I. Characterization of $RCo(dmgBF_2)_2(H_2O)$ Complexes

	elemental analysis							
	calcd				exptl			
	Co	C	H	N	Co	C	H	N
R								
H_2O	14.0	22.8	3.80	13.3	14.0	23.1	3.78	13.1
CH_3	14.1	25.9	4.07	13.4	13.9	26.1	4.19	13.1
C_2H_5	13.6	27.8	4.40	13.0	13.5	28.7	4.76	12.8
$C_6H_5CH_2$	11.9	36.5	4.25	11.3	12.0	36.7	4.42	11.3
CH_2OCH_3	13.2	26.8	4.24	12.5	13.2	26.4	4.36	12.0
CH_2OCH_3[a]	14.3				14.4			
	^1H NMR (acetone-d_6), δ							
CH_3	1.07 (3 H), 2.40 (12 H)							
C_2H_5	0.04 (3 H), ~2,[b] 2.36 (12 H)							
$C_6H_5CH_2$	2.26 (12 H), 3.15 (2 H), 7.12 (5 H)							
CH_2OCH_3	2.38 (12 H), 3.07 (3 H), 4.42 (2 H)							
CH_2OCH_3[a]	2.19 (12 H), 3.30 (3 H), 4.45 (2 H)							
	UV–visible, λ(max)/nm (ϵ/M^{-1} cm^{-1})							
H_2O[c]	456 (4.06×10^3), 328 (1.92×10^3), 260 (5.82×10^3)							
CH_3[d]	432 (1.78×10^3), 398 (1.74×10^3)							
C_2H_5[e]	448 (2.03×10^3), 412 sh (1.59×10^3)							
$C_6H_5CH_2$[f]	456 (1.54×10^3), 380 (4.80×10^3)							
CH_2OCH_3[c]	446 (2.18×10^3), 350 (2.60×10^3)							
CH_2OCH_3[a,c,g]	438 (1.42×10^3), 380 sh (2.39×10^3)							

[a] The compound is $CH_3OCH_2Co(dmgH)_2py$. [b] The signal coincides with the acetone signal. [c] In H_2O. [d] In 1.0 M aqueous Acetone. [e] In 2 M aqueous Acetone. [f] In 3 M aqueous acetone. [g] Pyridine is partly dissociated under these conditions.

coordinate or hexacoordinate with a highly labile axial water molecule.

Organocobaloximes, prepared according to the published procedures,[30] were converted to the aquo derivatives by addition of 5 M aqueous perchloric acid to a solution in CH_2Cl_2. After filtration of $HpyClO_4$ and addition of some ice-cold water, the precipitated $RCo(dmgH)_2H_2O$ was washed with hexanes and dried in a desiccator overnight.

$RCo(dmgBF_2)_2H_2O$ complexes (except for R = CH_2OCH_3) were prepared from $RCo(dmgH)_2H_2O$ and BF_3·etherate.[30] The purity of all the complexes was checked by elemental analysis and ^1H NMR spectra (Table I).

Alkylchromium complexes $(H_2O)_5CrR^{2+}$ (R = CH_3, C_2H_5 and $PhCH_2$) were prepared in solution according to the published procedures.[31-33] The benzylpentaaquochromium(2+) ion was purified by ion exchange. Owing to the more rapid decomposition of $CrCH_3^{2+}$ and $CrC_2H_5^{2+}$, solutions of these complexes were used without purification, and thus contained approximately equimolar concentrations of Cr^{3+} and CrR^{2+}. In addition, solutions of $CrCH_3^{2+}$ used for kinetics experiments contained low concentrations of Me_2SO used in its preparation.[31]

$CH_3Co(14\text{-}aneN_4)^{2+}$[34] was prepared photochemically from $CH_3Co(dmgH)_2H_2O$ and $Co(14\text{-}aneN_4)^{2+}$. Typically 100 mL of an ice-cold, air-free solution containing 1 mM $Co(14\text{-}ane)^{2+}$, 1 mM $CH_3Co(dmgH)_2H_2O$, and 0.05 M $HClO_4$ was photolyzed with a 275-W sunlamp until the intense yellow of $CH_3Co(dmgH)_2H_2O$ disappeared (~10 min). The pale orange-yellow solution was ion exchanged, yielding 30 mL of 2 mM $CH_3Co(14\text{-}aneN_4)^{2+}$.

Owing to the low water solubility of $RCo(dmgBF_2)_2H_2O$ complexes, stock solutions were prepared in 1 M aqueous acetone, so that the actual experimental solutions contained ≤0.32 M acetone. Blank experiments showed that even much higher concentrations of acetone (0.5 M) had no effect on the equilibrium constants.

Measurements. The kinetics of the pyridine dissociation from $CH_3OCH_2Co(dmgH)_2py$ were studied by monitoring the absorbance when aqueous $CH_3OCH_2Co(dmgH)_2py$ was mixed with dilute perchloric acid (0.020 and 0.10 M). These measurements, made by the stopped-flow technique, yielded $k_{trans} = 37.4 \pm 4.8$ s^{-1}.

The kinetic and equilibrium data for R = CH_3 and $PhCH_2$ were measured at 0.10 M ionic strength. Because high concentrations of reagents were necessary for R = C_2H_5, the ionic strength was adjusted to 0.50 M, but experiments for R = CH_3 showed that this change had no effect (≤4% difference in k_{obsd}) on the kinetics, as expected from the charge types involved.

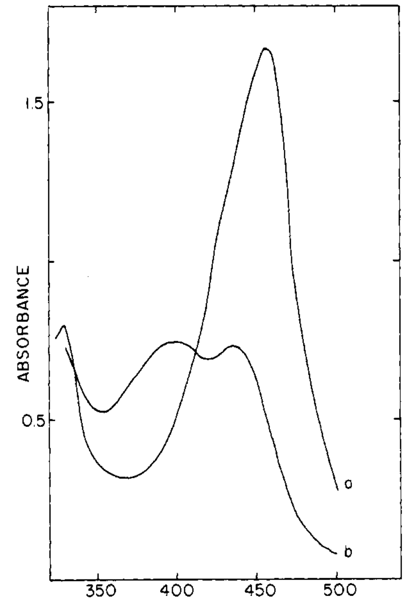

Figure 1. Spectral changes (1 cm cell) accompanying the reaction of $Co(dmgBF_2)_2$ with $CrCH_3^{2+}$: (a) 4×10^{-4} M $Co(dmgBF_2)_2$; (b) $CH_3Co(dmgBF_2)_2H_2O$ formed quantitatively on addition of 7×10^{-4} M CH_3Cr^{2+} to a.

Results

The $Co(dmgBF_2)_2(H_2O)_n$ Complex. Unlike the parent cobaloxime, the BF_2-capped derivative is quite unreactive toward acid and oxygen. At 0.10–0.50 M $HClO_4$ the rate constant for the reaction with H^+ is $k = 6.9 \times 10^{-4}$ M^{-1} s^{-1},[6b] approximately 9 orders of magnitude lower than the (extrapolated) rate for the parent complex in the same acidity range.[6a] No reaction with oxygen occurs in short periods of time (~30 min), although higher concentrations of oxygen or longer reaction times, immaterial for our purpose, were not used.

Equilibrium Constants for Alkyl Transfer Reactions. Addition of a moderate (3–5-fold) excess of Cr^{2+} to a solution of

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Table II. Kinetic and Equilibrium Data for the Alkyl Exchange Reactions[a]

R	k_4/M^{-1} s^{-1}	k_{-4}/M^{-1} s^{-1}	K[b]	K_k[c]
Me	50.8 ± 1.6	(8.46 ± 0.06) × 10^2	(6.43 ± 0.11) × 10^{-2}	(6.00 ± 0.22) × 10^{-2}
Et	(2.62 ± 0.15) × 10^{-2}	7.08 ± 0.12		(3.70 ± 0.27) × 10^{-3}
$PhCH_2$	16.3 ± 0.6	(7.10 ± 0.65) × 10^3	(2.80 ± 0.09) × 10^{-3}	(2.29 ± 0.29) × 10^{-3}
CH_2OCH_3	$\lesssim 10^{-4}$	~10		$\lesssim 10^{-5}$

[a] 25 °C; μ = 0.10 M (R = Me, $PhCH_2$) or 0.50 M (R = Et). No ionic strength adjustment was made in the case of R = CH_2OCH_3. [b] Determined from the equilibrium data. [c] Determined from the kinetic data as a ratio k_4/k_{-4}.

$CH_3Co(dmgBF_2)_2OH_2$ causes an absorbance increase at $\lambda > 400$ nm and a decrease at $\lambda < 400$ nm with each addition of Cr^{2+}. The constant spectrum finally attained at high $[Cr^{2+}]$ shows a single maximum at 456 nm, consistent with quantitative formation of $Co(dmgBF_2)_2$ and $CrCH_3^{2+}$. Conversely, independently prepared products form the methyl cobalt complex, as illustrated in Figure 1. The reversibility of the system (eq 4, R = CH_3, C_2H_5,

$$RCo(dmgBF_2)_2 + Cr^{2+} \rightleftharpoons RCr^{2+} + Co(dmgBF_2)_2 \quad (4)$$

CH_2Ph) can be further demonstrated by addition of reagents that selectively react with one of the four components. Since Hg^{2+} reacts very rapidly with RCr^{2+} [35] (eq 5) but negligibly slowly with

$$RCr^{2+} + Hg^{2+} \rightarrow RHg^+ + Cr^{3+} \quad (5)$$

$CH_3(Co)$, addition of a small amount of Hg^{2+} pulls eq 4 to the right and leads to quantitative formation of $Co(dmgBF_2)_2$ even with barely sufficient Cr^{2+}. Similarly, $Co(NH_3)_5F^{2+}$ pulls eq 4 to the left by rapidly removing Cr^{2+}.[36a] Qualitatively similar behavior is also observed for R = C_2H_5 and CH_2Ph.

Equilibrium constants for reaction 4 with R = CH_3 and $PhCH_2$ were determined spectrophotometrically at 456 nm. The data were fit to eq 6 by use of a nonlinear least-squares program. D_0 and

$$D_{obsd} - D_0 = -0.5bK[Cr^{2+}]\Delta\epsilon + 0.5b\Delta\epsilon\{K^2[Cr^{2+}]^2 + 4K[Cr^{2+}][R(Co)]_T\}^{1/2} \quad (6)$$

D_{obsd} represent the initial and final absorbances, $\Delta\epsilon$ is the difference between the molar absorptivities of products and reactants in eq 4, b is the optical pathlength, and K is the equilibrium constant for the reaction as written in eq 4. This treatment yields values of equilibrium constants K_{CH_3} = (6.43 ± 0.11) × 10^{-2} and K_{PhCH_2} = (2.80 ± 0.09) × 10^{-3} at 25.0 °C.

When R = C_2H_5, equilibrium is established so slowly that the formation of $C_2H_5Cr^{2+}$ and its decomposition[32] take place on the same time scale. The equilibrium constant was thus determined from the kinetic data only, as described in the next section. Good agreement between the two methods for the benzyl and methyl complexes justifies this approach.

Kinetics of the Alkyl Transfer Reactions. The transalkylation reactions follow mixed second-order rate laws. The rate constants in the forward direction in eq 4 for R = CH_3 and $PhCH_2$ were determined by utilizing Hg^{2+} to block the reverse reaction. The concentrations of Hg^{2+} used were sufficient to remove CrR^{2+} but low enough to avoid a reaction[36b] between Cr^{2+} and Hg^{2+}. Figure 2 shows that the pseudo-first-order rate constant varies linearly with the average concentration of Cr^{2+}. The values of k_4 are independent of $[Hg^{2+}]$, as expected.

The rate constants k_{-4} were determined under pseudo-first-order (R = CH_3) or second-order conditions (R = $PhCH_2$). Since alkyl transfer occurs more rapidly in this direction, conditions are easily realized where the equilibrium lies sufficiently far to the left that no specific scavenger was needed. Under the conditions used k_4 contributed <1% to the overall reaction.

The determination of k_{-4} for R = Et was done as for R = Me and $PhCH_2$. With $CrC_2H_5^{2+}$, prepared in situ by mixing $C_2H_5C(CH_3)_2OOH$ with a small excess of Cr^{2+}, $k_{-4(Et)}$ = 7.08 ± 0.12 M^{-1} s^{-1}.

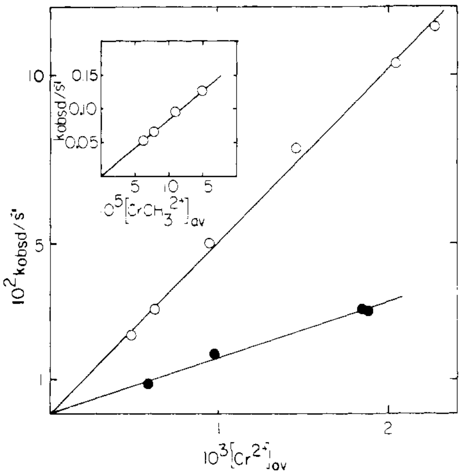

Figure 2. Plots of k_{obsd} vs. $[Cr^{2+}]_{av}$ for the reaction of Cr^{2+} with $RCo(dmgBF_2)_2H_2O$ in the presence of variable amounts of Hg^{2+} at 25 °C and 0.10 M $HClO_4$ for $[CH_3Co(dmgBF_2)_2H_2O]_0$ = (1.7–5.6) × 10^{-5} M, $[Hg^{2+}]_0$ = (0.50–3.4) × 10^{-4} M (○), and for $[PhCH_2Co(dmgBF_2)_2H_2O]_0$ = (0.8–1.2) × 10^{-5} M, $[Hg^{2+}]_0$ = (2.50–6.10) × 10^{-4} M (●). Inset: plot of k_{obsd} vs. $[CrCH_3^{2+}]_{av}$ for the reverse reaction.

The forward reaction for R = Et was studied with both Cr^{2+} and $C_2H_5Cr^{2+}$ present in large excess. The experimental rate constant was fitted to the expression

$$k_{obsd} = k_4[Cr^{2+}] + k_{-4}[CrC_2H_5^{2+}] \quad (7)$$

With $k_{-4(Et)}$ fixed at 7.08 M^{-1} s^{-1}, $k_{4(Et)}$ = (2.62 ± 0.15) × 10^{-2} M^{-1} s^{-1}. The ratio of the two gives K_{Et} = (3.70 ± 0.27) × 10^{-3}. The data for all systems are summarized in Table II.

Reactions of Related Complexes. Organochromium complexes with more sterically hindered organic groups such as $c\text{-}C_5H_9Cr^{2+}$ and $C_2H_5O(CH_3)CHCr^{2+}$ react too slowly to be observed in competition with their decomposition reactions.

The methoxymethyl complex $CrCH_2OCH_3^{2+}$ has $k_{-4} \simeq 10$ M^{-1} s^{-1}, yielding a product with the UV-visible spectrum of an organocobalt complex. The reaction is quantitative when a 1:1 ratio of the two reactants is used, implying a high equilibrium constant for the organocobalt formation ($k_4 << 1$). On a larger scale the reaction enabled the isolation of $CH_3OCH_2Co(dmgBF_2)_2OH_2$ as a brownish yellow solid. Its UV-visible spectrum, elemental analysis, and ^1H NMR data are given in Table I. This complex, when treated with a large excess of Cr^{2+} (>0.3 M), reacts very slowly to produce only a minute amount of $Co(dmgBF_2)_2$. Additional amounts of Cr^{2+} have a similar effect. On the basis of these data, $K_{CH_2OCH_3} < \sim 10^{-5}$.

The α-hydroxyalkyl complexes $CrCH_2OH^{2+}$ and $CrC(CH_3)_2OH^{2+}$ react in a complicated sequence of reactions, with some evidence for the transient formation of the hydrido complex $HCo(dmgBF_2)_2$ in the former case.[37] The organocobalt complexes possibly formed in these reactions could decompose by internal electron transfer (eq 8).[24e] This avenue was not pursued further.

$$HOCH_2Co(dmgBF_2)_2 \rightarrow HCo(dmgBF_2)_2 + CH_2O \quad (8)$$

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(36) (a) Candlin, J. P.; Halpern, J. *Inorg. Chem.* **1965**, *4*, 766. (b) Doyle, J.; Sykes, A. G. *J. Chem. Soc. A* **1968**, 215 (The rate constant between Hg^{2+} and Cr^{2+}, measured independently at 0.10 M H^+ and 0.10 M ionic strength, the conditions used in these experiments, is $2k$ = 9.9 M^{-1} s^{-1}).

(37) The reaction is accompanied by a large absorbance increase in the ~600-nm region as expected for the H(Co) or $(Co)^-$ formation (Chao, T.-H.; Espenson, J. H. *J. Am. Chem. Soc.* **1978**, *100*, 129. Schrauzer, G. N.; Weber, J. H.; Beckham, T. M. *J. Am. Chem. Soc.* **1970**, *92*, 7078). The evolution of large amounts of gas during the reaction was noted, but its chemical identity was not determined.

Table III. Kinetic Data for the Homolysis of $PhCH_2Co(dmgBF_2)_2H_2O$ Using O_2, H_2O_2, and HTMPO[a] as Scavengers

T/°C	$[H_2O_2]$/ M	$10^3[O_2]^c$/ M	10^3[HTMPO]/ M	$10^5k_H/s^{-1}$
23.5	0.50^b			0.690
25.0		1.25		0.758
34.2		1.10		3.47
42.2		1.04		12.2
42.2	0.14^d			10.5, 9.9^e
42.2	0.069^d			10.1
42.2			6.19	12.2
50.2			4.9	42.2

$\Delta H^{\ddagger} = 28.6 \pm 0.8$ kcal/mol
$\Delta S^{\ddagger} = 14.0 \pm 2.6$ cal/(mol K)
$k_{H,calcd} = 7.99 \times 10^{-6}\ s^{-1}$ (25 °C)

[a] Reactions were run in neutral aqueous solutions unless noted otherwise; λ 456 nm; $[PhCH_2Co(dmgBF_2)_2H_2O]_0 = (3–7) \times 10^{-5}$ M. [b] $[H^+] = 0.01$ M. [c] O_2-saturated solution, calculated from the data in: Linke, W. F. "Solubilities, Inorganic and Metal-Organic Compounds", 4th ed.; American Chemical Society: Washington, D.C., 1965. [d] $[H^+] = 0.1$ M, [t-BuOH] = 1 M. [e] λ 380 nm.

Table IV. Effect of Added (Co) on the Initial Rate of $PhCH_2Co(dmgBF_2)_2H_2O$ Decomposition in the Presence of HTMPO at 42.2 °C[a]

10^5-$[PhCH_2(Co)]^b$/ M	10^5-$[(Co)]^b$/ M	10^5-[HTMPO]/ M	$10^9R_i^c$	$10^5k^d/s^{-1}$
2.31	0.330	19.3	2.22	9.63
3.22	0.460	5.05	2.82	8.76
3.99	3.78	5.09	2.13	5.34
3.26	6.51	4.76	1.38	4.23

[a] All the concentrations were corrected by the average concentration change during the period of the initial rate measurement. [b] (Co) = $Co(dmgBF_2)_2$. [c] R_i = initial rate (mol L^{-1} s^{-1}). [d] Calculated by dividing the initial rate by the average $[PhCH_2Co(dmgBF_2)_2H_2O]$.

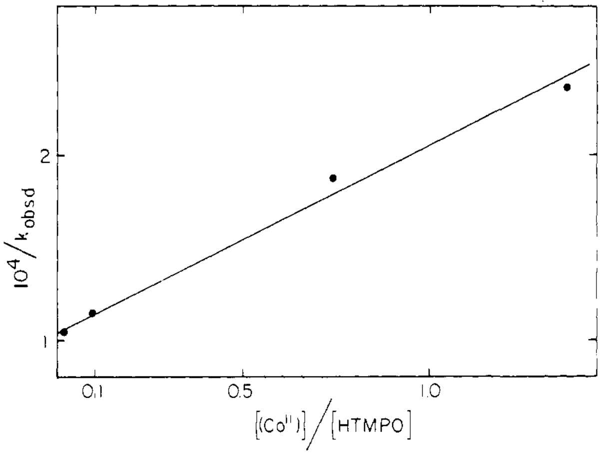

Figure 3. Plot of the reciprocal of k_{obsd} vs. the ratio $[Co(dmgBF_2)_2]$/[HTMPO] according to eq 13 to determine $k_H = 9.61 \times 10^{-5}\ s^{-1}$ and $k_{-H}/k_{HTMPO} = 1.18$.

Methyl transfer between $CH_3Co(14\text{-aneN}_4)^{2+}$ and Cr^{2+} was studied briefly. The reaction is slow (~0.2 M^{-1} s^{-1}), and some decomposition of $CrCH_3^{2+}$ always took place on the time scale of the overall reaction. No reaction between $CrCH_3^{2+}$ and $Co(14\text{-aneN}_4)^{2+}$ was observed.

Reaction of $PhCH_2Co(dmgBF_2)_2$ with Oxidants and HTMPO. Carefully deaerated neutral solutions of the benzyl complex are stable for days at room temperature in the absence of light. Acidified solutions decompose somewhat on the same time scale. Oxidants such as O_2 and H_2O_2 and radical scavengers (HTMPO[38] was used) in all cause a much faster, but still slow, decomposition of the compound. The kinetics of the reactions with O_2, H_2O_2, and HTMPO were studied at 23.5–50.2 °C. The first-order rate constants for the decomposition are shown in Table III. At a constant temperature the measured rate constant k_H is within the error independent of the nature and the concentration of these three reagents, consistent with unimolecular homolysis (eq 9),

$$PhCH_2Co(dmgBF_2)_2 \rightleftarrows Co(dmgBF_2)_2 + \cdot CH_2Ph \quad (k_H,\ k_{-H}) \tag{9}$$

$$Co(dmgBF_2)_2 \text{ and/or } \cdot PhCH_2 + S \xrightarrow{\text{fast}} \text{products } (k_S) \tag{10}$$

followed by radical scavenging (eq 10) where S stands for scavenger (O_2, H_2O_2, or HTMPO). With HTMPO as a radical scavenger, the formation of Co(II) was confirmed by its characteristic spectrum. Owing to the slow decomposition of $Co(dmgBF_2)_2$ under the reaction conditions, it was present at the end of the reaction in only ~85% yield. The kinetics were evaluated from the first 50–60% of the reaction. When O_2 or H_2O_2[39] were used, the absorbance at 456 nm decreased, implying that the Co(II) complex was subsequently oxidized in eq 10. This was expected for H_2O_2, which reacts quite rapidly ($2k \approx 12\ M^{-1}\ s^{-1}$) in a reaction which is accompanied by an absorbance decrease at 456 nm. Oxygen, on the other hand, although unreactive toward this Co(II) complex, scavenges benzyl radicals (eq 11). The

$$\cdot CH_2Ph + O_2 \rightarrow \cdot OOCH_2PH \tag{11}$$

benzylperoxy radical so formed is probably captured by cobalt(II) (eq 12).[24b,e,40] The activation parameters for the rate constant

$$Co(dmgBF_2)_2 + \cdot OOCH_2Ph \rightarrow PhCH_2OOCo(dmgBF_2)_2 \tag{12}$$

for homolysis, evaluated from the data in Table III, are $\Delta H^{\ddagger}$ = 28.6 ± 0.8 kcal/mol and $\Delta S^{\ddagger}$ = 14.0 ± 2.6 cal/(mol K).

Competition Kinetics. One of the more conclusive indications of homolysis would be a demonstration that its rate can be lowered by occurrence of the reverse reaction. The inhibitory effect of $Co(dmgBF_2)_2$ was examined by the initial rate method at 380 nm, where the molar absorptivity of the benzyl complex ($\epsilon = 4.8 \times 10^3\ M^{-1}\ cm^{-1}$) significantly exceeds that of Co(II) ($\epsilon = 7.0 \times 10^2\ M^{-1}\ cm^{-1}$), to permit such measurements. These experiments, with an excess of Co(II), used HTMPO as a radical scavenger. The reaction was monitored at 42.2 °C for 10–15 min (10–15% of the first half-life for homolysis). The rate constants evaluated from the initial rate measurements are listed in the last column of Table IV.

With cobalt(II) added to the reaction mixture and the reactions presumed to be those written in eq 9 and 10, k_{obsd} is defined[41] as

$$k_{obsd} = \frac{k_H k_S[S]}{k_{-H}[(Co^{II})] + k_S[S]} \tag{13}$$

A plot of $1/k_{obsd}$ vs. the ratio [Co(II)]/[S] is shown in Figure 3. The value of the homolysis rate constant so evaluated is $k_H = 9.6 \times 10^{-5}\ s^{-1}$ at 42.2 °C, in reasonable agreement with the directly measured value, $1.17 \times 10^{-4}\ s^{-1}$. The ratio of the rate constants for the reactions of benzyl radical with $Co(dmgBF_2)_2$ and HTMPO is $k_{-H}/k_{HTMPO} = 1.18$.

Discussion

Alkyl Group Exchange Reactions. The mixed second-order kinetics and the complete reversibility of the alkyl transfer are consistent with opposing bimolecular reactions. We conclude that they occur by an S_H2 mechanism, as previously assigned to several analogous alkyl exchanges.[14-22] The steric effects, considering that a bridging transition state involves a pentavalent carbon, are expected to be strong, as noted previously.[15,19,22] In this work the

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[38] HTMPO = 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy.

[39] 1 M *tert*-butyl alcohol was used in combination with H_2O_2 at 42.2 °C to scavenge any OH radicals possibly formed in the course of the $Co(dmgBF_2)_2$ oxidation by H_2O_2: $Co(dmgBF_2)_2 + H_2O_2 \rightarrow Co(dmgBF_2)_2 + \cdot OH$. The failure to use *tert*-butyl alcohol at 23.5 °C did not, however, adversely affect the reaction.

[40] Espenson, J. H.; Chen, J. T. *J. Am. Chem. Soc.* **1981**, *103*, 2036 and references therein.

[41] Espenson, J. H.; Shimura, M.; Bakac, A. *Inorg. Chem.* **1982**, *21*, 2537.

rate decreases by a factor of 10^2–10^3 $M^{-1}\,s^{-1}$ when methyl is replaced by ethyl, and even more so with more highly substituted alkyl groups, when the reactions became too slow to measure. The strong steric effects provide additional support for the S_H2 mechanism. Methyl and benzyl transfers occur at comparable rates, in agreement with similar systems.[15]

The equilibrium constants for the alkyl group exchange (eq 4) represent the first such measurements between different metals. They can be expressed as a ratio of the separate equilibrium constants for the homolysis of the organocobalt and organochromium complexes or in terms of rate constants:

$$K = \frac{K_{H(Co)}}{K_{H(Cr)}} = \frac{k_{H(Co)}/k_{-H(Co)}}{k_{H(Cr)}/k_{-H(Cr)}}$$

$$RCr^{2+} \rightleftarrows Cr^{2+} + R\cdot \quad K_{H(Cr)},\ k_{H(Cr)},\ k_{-H(Cr)} \tag{14}$$

$$RCo(dmgBF_2)_2 \rightleftarrows Co(dmgBF_2)_2 + R\cdot \quad K_{H(Co)},\ k_{H(Co)},\ k_{-H(Co)} \tag{15}$$

Since K_4 is less than unity, the thermodynamic stability of the cobalt–carbon bond is higher than that of the chromium-carbon bond. To develop this analysis further, we assume that the reverse of eq 14 and 15 occur with approximately equal rate constants, which seems reasonable considering the reactions of Cr^{2+} and cobalt(II) complexes with carbon-centered radicals.[2b,24,25] (We will show later that for R = CH_2Ph the ratio $k_{-H(Cr)}/k_{-H(Co)}$ indeed has a value of about unity.) Thus K_4 is approximately equal to the ratio of rate constants for the unimolecular homolysis of the Co–C and Cr–C bonds, $K \simeq k_{H(Co)}/k_{H(Cr)}$. Since $K_4 = 6.43 \times 10^{-2}$, 3.70×10^{-3}, and 2.80×10^{-3}, for R = Me, Et, and $PhCH_2$, respectively, the rates of Cr–C bond homolysis increase more rapidly along this series than do those for Co–C homolysis.

The increased homolysis rates for complexes with sterically crowded alkyl groups are caused by several factors, the most prominent of which is the steric interaction between the alkyl group and other ligands bound to the metal center. Other important contributions are the stability of the radical produced and the change in the polarization of the metal–carbon bond accompanying substitution on the alkyl group. For a given group R, one might anticipate that the latter two contributions have similar effects for both families. Thus the greater sensitivity of the homolysis rate for the organochromium complexes to the steric demand of the group R would seem to indicate that steric repulsion between the alkyl group and the four equatorial water molecules of the organochromium complex becomes relatively greater upon substitution of R than does the repulsion between the alkyl group and the macrocyclic ligand. Repulsion between R and the hydrogens of coordinated water molecules is quite substantial. In contrast, the peripheral methyl groups of the $(dmgBF_2)_2$ macrocycle are sufficiently removed from the vicinity of the cobalt–carbon bond as to have less pronounced interactions.

The kinetic and structural trans effect of the alkyl groups has been firmly established in organocobalt chemistry. The rates of the ligand substitution trans to the alkyl group in the series of $RCo(dmgH)_2L$ complexes (L = H_2O, py, etc.) increase[42] in the order Me < $PhCH_2$ < Et < *i*-Pr ≃ CH_2OCH_3 (Table V). The crystal structure data have revealed[43] that the Co–py bond trans to Me is shorter than the Co–py bond trans to *i*-Pr by 0.031 Å. The kinetic and structural trans effects thus closely parallel each other. We presume that the BF_2-capped derivatives follow the same qualitative pattern. The longer the Co–L bond trans to the alkyl ligand and the higher its dissociation rate, the more "pentacoordinate-like" the complex becomes in its ground state. This allows the C(R)–Co–N(dmgH) bond angle to increase so that the steric repulsion between the alkyl group and the macrocycle is reduced.[44] As a result the Co–C bond strength is increased and the homolysis is slower than in a (hypothetical) structurally rigid system. The absolute values of the homolysis rate constants for the organocobalt complexes still increase in the series Me < Et < *i*-Pr ≈ $PhCH_2$[45] but less than in the chromium case. Of course, the same consideration applies also to the latter class of compounds, but it tends to be offset by much more pronounced variations of the activation entropy.[46] The full impact of the steric effects, i.e., changes in the enthalpic contribution to $\Delta G^{\ddagger}$, is thus not observed for the CrR^{2+} complexes.

Table V. Rate Constants for the Pyridine Dissociation in $RCo(dmgH)_2py$ in Water

R	Co–N(py)/Å	k_{trans}/s^{-1}
CH_2OMe		37.4
2-Pr	2.099[a]	33.1[b]
Et		1.71[b]
CH_2Ph		(0.36)[c]
Me	2.068[a]	0.0552[b]

[a] Reference 43. [b] Reference 42b. [c] Estimated from the data in reference 42 assuming k_{Et}/k_{PhCH_2} for the dissociation of pyridine in H_2O[42b] is equal to k_{Et}/k_{PhCH_2} for the dissociation of 4-*t*-bu(py) in CH_2Cl_2.[42a]

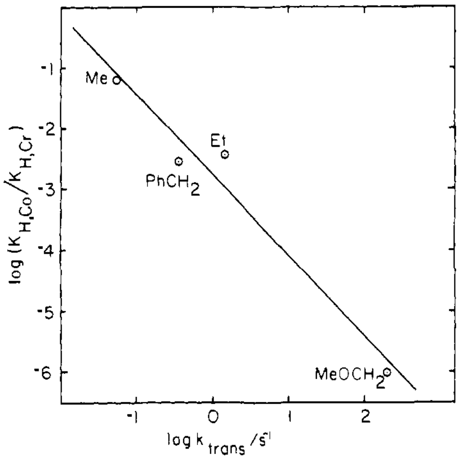

Figure 4. Plot of log $(K_{H(Co)}/K_{H(Cr)})$ against the rate constant for trans substitution in $RCo(dmgH)_2py$.

The explanation offered here seems to hold also for the methoxymethyl complex. The trans effect of this group (Table V) implies that a significant stabilization of $CH_3OCH_2Co(dmgBF_2)_2H_2O$ toward homolysis should be expected. The ratio $k_{H(Cr)}/k_{H(Co)} \gtrsim 10^5$ is in qualitative agreement with this prediction. More quantitatively, we note here the correlation of the trans substitution rates for organocobalt complexes with the ratio $k_{H(Co)}/k_{H(Cr)}$. The built-in assumption is that the change of the trans substitution rates in the organochromium series has an insignificant effect on $k_{H(Cr)}$, or a linear one, owing to the entropy effects mentioned earlier. A plot of log $K_{H(Co)}/K_{H(Cr)}$ ($\simeq k_{H(Co)}/k_{H(Cr)}$) against the logarithm of the trans substitution rate constants for $RCo(dmgH)_2py$ complexes,[47] k_{trans}, is shown in Figure 4. A reasonably good linear relationship for the four alkyl groups studied shows that homolysis of organocobalt complexes is indeed closely related to trans substitution. Thus the homolysis of the organochromium and organocobalt complexes

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[42] (a) Stewart, R. C.; Marzilli, L. G. *J. Am. Chem. Soc.* **1978**, *100*, 817. (b) Brown, K. L.; Lyles, D.; Pencovici, M.; Kallen, R. G. *Ibid.* **1975**, *97*, 7338.

[43] (a) Randaccio, L.; Bresciani-Pahor, N.; Toscano, P. J.; Marzilli, L. G. *J. Am. Chem. Soc.* **1981**, *103*, 6347. (b) The effect was not observed with the much longer Co–P bonds in $RCo(dmgH)_2PPh_3$ series (Randaccio, L.; Bresciani-Pahor, N.; Toscano, P. J.; Marzilli, L. G. *J. Am. Chem. Soc.* **1980**, *102*, 7372.)

[44] Although these considerations are meant to explain the *solution* behavior of the organocobalt complexes, the crystal structure data[43a] indicate that even in the *solid* state the C–Co–N(dmgH) angle in the $RCo(dmgH)_2py$ series increases upon replacing a methyl group by bulkier alkyls.

[45] Rate constants for the thermal homolysis of these complexes have not been measured. However, the photochemically induced Co–C bond homolysis follows this trend.

[46] The values of $\Delta S^{\ddagger}$ are substantially higher for the homolysis of the organochromium complexes,[1,2] reflecting mainly the greater changes in solvation between the ground and transition states.

[47] Values of k_{trans} are those for the cobaloximes, since data for $RCo(dmgBF_2)_2OH_2$ are not known. A close parallel between the two series is anticipated.[42]

is strongly influenced by both steric *and* electronic effects, in agreement with previous findings in related systems.[2a,7]

The Homolysis of $PhCH_2Co(dmgBF_2)_2H_2O$. The rate constant for the decomposition of $PhCH_2Co(dmgBF_2)_2H_2O$ in the presence of H_2O_2, O_2, and HTMPO is strongly indicative of a mechanism consisting of unimolecular homolysis (eq 9), followed by faster reactions (eq 16 and 17). Additional support for this mechanism

$$Co(dmgBF_2)_2 + H_2O_2 \xrightarrow{\text{fast}} \text{products} \qquad (16)$$

$$\cdot CH_2Ph + O_2 \text{ (or HTMPO)} \xrightarrow{\text{fast}} \text{products} \qquad (17)$$

comes from the formation of $Co(dmgBF_2)_2$ as a product, confirmed when HTMPO is used as a scavenger. The kinetic retarding effect of the Co(II) complex confirms the equilibrium nature of the initial homolysis reaction. Moreover, the homolysis rate constants calculated from both methods agree.

The activation parameters for the rate-limiting step are also strongly supportive of a homolytic process. The high enthalpy of activation (28.6 kcal/mol) is expected for an unassisted homolytic bond-breaking process. High positive entropies of activation have been observed before in the homolytic metal–carbon bond cleavage reactions in aqueous solvents,[2,4,6] in keeping with that $\Delta S^\ddagger = 14.0$ cal mol^{-1} K^{-1} in this reaction. It is interesting to note that $\Delta S^\ddagger$ values in nonaqueous solvents are much lower, typically close to 0,[48] suggesting at least two contributions to the $\Delta S^\ddagger$ term: the intrinsic contribution due to the radical dissociation and the effect of the release of the purely organic species on the structure of surrounding water. The latter effect appears to be quite substantial. The same conclusion has been reached independently by the group which has determined $\Delta V^\ddagger$ for the homolysis of $(H_2O)_5CrR^{2+}$ complexes.[49]

The rate constants are now known for the homolysis of $PhCH_2Co(dmgBF_2)_2$ ($k = 7.58 \times 10^{-6}$ s^{-1} at 25 °C) and $PhCH_2Cr^{2+}$ ($k = 2.63 \times 10^{-3}$ s^{-1}).[1] Combined with the equilibrium constant for the benzyl group transfer, $K = 2.80 \times 10^{-3}$, we calculate the ratio of the rate constants $k_{-H(Co)}/k_{-H(Cr)} = 1.03$. The measured value of $k_{-H(Cr)}$ is 8.5×10^7 M^{-1} s^{-1},[50] and thus $k_{-H(Co)} = 8.8 \times 10^7$ M^{-1} s^{-1}.[51] Both rate constants fall in the general range expected[24-26] for the recombination of metal complexes with carbon-centered radicals.

The calculated free energy of activation for the reactions of $Co(dmgBF_2)_2$ with $\cdot CH_2Ph$ at 25 °C is $\Delta G^\ddagger = 6.5$ kcal/mol. The high $\Delta S^\ddagger{}_{H(Co)}$ in the forward direction of reaction 9 implies $\Delta S^\ddagger{}_{-H(Co)} \lesssim 0$ for the reverse reaction. Taking $\Delta S^\ddagger{}_{-H(Co)} \simeq 0$ to -10 cal/(mol K), $\Delta H^\ddagger{}_{-H(Co)}$ for the reaction of $Co(dmgBF_2)_2$ with $\cdot CH_2Ph$ has a value of $\sim 5 \pm 2$ kcal/mol. The difference between the activation enthalpies for the forward and reverse reaction, $\Delta H^\ddagger{}_{H(Co)} - \Delta H^\ddagger{}_{-H(Co)}$, gives directly the Co–C bond energy, BDE = 24 ± 3 kcal/mol. This value is close to the previously published BDE's for similar organocobalt complexes.[3]

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(48) The only exception seems to be $RCo[C_2(DO)(DOH)_{pn}]I$[13] with $\Delta S^\ddagger = 8$ cal mol^{-1} K^{-1} ($R = PhCH_2$) and 18 cal mol^{-1} K^{-1} ($R = (CH_3)_3CCH_2$) in *o*-dichlorobenzene.

(49) Rindermann, W.; van Eldik, R.; Sisley, M. J.; Swaddle, T. W., unpublished observations (private communication).

(50) Blau, R. J.; Espenson, J. H.; Bakac, A. *Inorg. Chem.*, in press.

(51) k_S for the reaction of $Co(dmgBF_2)_2$ with HTMPO falls in the same range, $k = 7.5 \times 10^7$ M^{-1} s^{-1}, since $k_{-H}/k_S \simeq 1.18$.

Coordinative Interactions in Chelated Complexes of Silicon. 13.[1] Experimental Determination of the Electron Deformation Density of a Pentacoordinated Silicon Complex†

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Abstract: The electron deformation density in the pentacoordinated trigonal-bipyramidal 1-(trichlorosilyl)-1,2,3,4-tetrahydro-1,10-phenanthroline ($(C_{12}H_{11}N_2)SiCl_3$, monoclinic, $P2_1/m$, $a = 9.243$ (4) Å, $b = 7.076$ (2) Å, $c = 10.739$ (4) Å, $\beta = 114.97$ (3)°, $Z = 2$) was determined by combined X-ray and neutron diffraction. Neutron data (3356 measurements) were collected at $\lambda = 0.894$ Å (up to $(\sin\theta)/\lambda = 0.89$ Å^{-1}, 1617 unique observations) and 1.266 Å ($(\sin\theta)/\lambda_{max} = 0.63$ Å^{-1}, 1428 unique data) at 120 K; X-ray intensities were measured with Mo Kα radiation at 120 K up to $(\sin\theta)/\lambda = 0.81$ Å^{-1} (11 997 measurements, 3008 unique). The molecule contains two different Si–N bonds. The shorter one (1.746 (2) Å), located in the equatorial plane, is introduced by chemical substitution reaction. The X–N maps reveal a maximum of 0.4 e/Å^3 between Si and N in this equatorial bond, and maxima of the lone pair density, expected below and above the position of the trivalent nitrogen, are significantly displaced toward Si. This release of density into the Si–N bond might explain the "contraction" of the Si–N bond as compared with the sum of the covalent radii (1.87 Å). The axial Si–N bond (1.979 (2) Å) results from an intramolecular coordinative interaction. The lone pair of the coordinated "pyridine" nitrogen (centered 0.7 Å from N) is strongly polarized by silicon and the two equatorial chlorine atoms. The density distribution in the two topologically different Si–Cl bonds is rather low and diffuse.

In contrast to carbon, silicon is able to expand its valence shell from tetravalency to penta- and hexacoordination, forming well-defined stable compounds. These extracoordinated silicon derivatives can either be cations or anions or uncharged coordination complexes in which the valence shell expansion is achieved by Lewis acid–base interaction. For these coordinative interactions, interatomic distances in the range between "normal single" bonds and pure van der Waals contacts are observed.

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