Transition-Metal Complexes of Pyrrole Pigments. 16. Cobalt Complexes of 1,19-Dimethyldehydrocorrins as Vitamin B_{12} Models[1,2]

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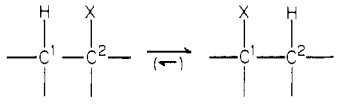
Abstract: The cobalt complexes of 1,19-dimethyl-*AD*-didehydrocorrin (BDHC) and its tetradehydro analogue (TDHC), both having additional double bonds at peripheral positions and an additional angular methyl group compared with the parent corrinoid, have been investigated from the viewpoint of vitamin B_{12} chemistry. The electronic effect of peripheral double bonds in TDHC is significant, and the TDHC complex is far from analogous to the corrinoid, while the BDHC complex is quite analogous to the corrinoid as far as the electronic properties are concerned on the basis of their spectroscopic, electrochemical, and axial coordination behaviors. The angular methyl groups in the BDHC complex exert an unusually large steric effect in the bimolecular reactions of Co^{I}(BDHC) with alkyl donors which result in the formation of an alkyl–cobalt bond. The steric interaction energies between an axial ligand and an angular methyl and between an axial alkyl ligand and the macrocyclic skeleton are estimated from the kinetic and thermodynamic data. The BDHC complex coordinated with a bulky alkyl ligand at its axial site undergoes a novel heterolytic carbon–cobalt bond cleavage in acidic media, giving Co(III) and a carbanionic intermediate under photolytic condition and even in the dark. In reference to the electrochemical data for the BDHC complex and the related cobalt complexes, the significant steric pressure provided by BDHC on the bulky axial ligand is responsible for the heterolytic carbon–cobalt cleavage. Significance of the steric pressure effect is briefly discussed in connection with the mechanism for 1,2-rearrangement of substituents placed in the alkyl ligand. A synthetic usage of the BDHC complex as a catalyst for the selective reduction of a primary alkyl bromide is also described.

Introduction

The coenzyme B_{12}-dependent enzymes catalyze the molecular rearrangements which can be formulated generally as an exchange of hydrogen for substituent X on the adjacent carbon (vicinal exchange, eq 1).[3] Among these are three carbon-skeleton re-



(1)

arrangements. They are the reversible interconversions: methylmalonyl-SCoA ⇌ succinyl-SCoA, β-methylaspartate ⇌ glutamate, and methylitaconate ⇌ α-methyleneglutarate. These conversions are without clear precedents in organic chemistry. However, recent nonenzymatic model studies have shown that the appropriate cobalamins and cobaloximes, which are coordinated with an alkyl moiety at the axial site of nuclear cobalt, induce similar carbon-skeleton rearrangements exercised by substituents (X) in the alkyl fragments.[4] The mechanisms of the enzyme actions are also subject to active speculations.[5]

Although the cobalt corrinoids have been studied rather extensively in the last two decades,[6] the significance of corrin as an equatorial ligand is not well understood. How does the corrin ligand affect the properties of the nuclear cobalt and the axial ligands, particularly alkyl ligands? A search for model cobalt complexes, which contain a carbon–cobalt bond axial to a planar equatorial ligand, has been stimulated in order to characterize coenzyme B_{12} as an organocobalt derivative. If we define a vitamin B_{12} model as a planar cobalt complex capable of forming a carbon–metal bond at its axial site, there are many model compounds.[7-13] In order to find out the structure–reactivity correlation, however, we carefully chose a set of model compounds so that the alteration in structure can be manipulated with minimal (ideally one) structural parameters, others being maintained constant, as has often been the case in physical organic chemistry. On this ground, we have taken up the cobalt complexes of the modified corrins 8,12-diethyl-1,2,3,7,13,17,18,19-octamethyl-*AD*-didehydrocorrin (BDHC)[14] and its tetradehydro analogue (TDHC).[14,15] The structural changes in these complexes relative to the parent cobalt corrinoid are distinct. Both BDHC and TDHC have additional double bonds at the peripheral positions which would give out electronic perturbations on the interior conjugation system existing in the corrinoid. Another important structural aspect of BDHC and TDHC is that these modified corrins possess the angular methyl groups at both C(1) and C(19) positions, while the corrinoid has only one at C(1). Thus, an axial ligand in the Co(BDHC) complex, irrespective of its location at

(1) Presented in part at the Symposium on Biomimetic Chemistry, ACS/CSJ Chemical Congress, Honolulu, Hawaii, April 1979.

(2) Preliminary accounts of this work: Murakami, Y.; Aoyama, Y.; Nakanishi, S. *Chem. Lett.* **1977**, 991-994. Murakami, Y.; Aoyama, Y.; Tokunaga, K. *Inorg. Nucl. Chem. Lett.* **1979**, *15*, 7-11.

(3) Hill, H. A. O. *Inorg. Biochem.* **1973**, *2*, Chapter 30.

(4) Models for methylmalonyl-SCoA → succinyl-SCoA conversion: (a) Dowd, P.; Shapiro, M. *J. Am. Chem. Soc.* **1976**, *98*, 3724-3725; (b) Scott, A. I.; Kang, K. *Ibid.* **1977**, *99*, 1997-1999; (c) Flohr, H.; Pannhorst, W.; Retey, J. *Angew. Chem.* **1976**, *88*, 613-614. A model for methylitaconate → α-methyleneglutarate conversion: (d) Dowd, P.; Shapiro, M.; Kang, K. *J. Am. Chem. Soc.* **1975**, *97*, 4754-4757; (e) Dowd, P.; Trivedi, B. K.; Shapiro, M.; Marwaha, L. K. *Ibid.* **1976**, *98*, 7875-7877. Other rearrangements: (f) Chemaly, S.; Pratt, J. M. *J. Chem. Soc., Chem. Commun.* **1976**, 988-989; (g) Bury, A.; Ashcroft, M. R.; Johnson, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 3217-3219.

(5) (a) Abeles, R. H.; Dolphin, D. *Acc. Chem. Res.* **1976**, *9*, 114-120. (b) Schrauzer, G. N. *Angew. Chem.* **1977**, *89*, 239-251. (c) Corey, E. J.; Cooper, N. J.; Green, M. L. H. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 811-815. (d) Golding, B. T.; Radom, L. *J. Am. Chem. Soc.* **1976**, *98*, 6331-6338. (e) Reference 4g. (f) Brown, K. L.; Ingraham, L. L. *J. Am. Chem. Soc.* **1974**, *96*, 7681-7686. (g) Silverman, R. B.; Dolphin, D. *Ibid.* **1976**, *98*, 4626-4633. (h) Brown, K. L.; Chu, M. M. L.; Ingraham, L. L. *Biochemistry* **1976**, *15*, 1402-1407.

(6) Pratt, J. M. "Inorganic Chemistry of Vitamin B_{12}"; Academic Press: London, 1972.

(7) Reviews: (a) Schrauzer, G. N. *Acc. Chem. Res.* **1968**, *1*, 97-103; (b) Costa, G. *Coord. Chem. Rev.* **1972**, *8*, 63-75; (c) Biggetto, A.; Costa, G.; Mestroni, G.; Pellizer, G.; Puxeddu, A.; Reisenhofer, E.; Stefani, L.; Tauzher, G. *Inorg. Chim. Acta Rev.* **1970**, *4*, 41-49; (d) Dodd, D.; Johnson, M. D. *Organomet. Chem. Rev.* **1973**, *52*, 1-232; (e) Schrauzer, G. N. *Angew. Chem.* **1976**, *88*, 465-474.

(8) Ochiai, E.; Long, K. M.; Sperati, C. R.; Busch, D. H. *J. Am. Chem. Soc.* **1969**, *91*, 3201-3206.

(9) Farmery, K.; Busch, D. H. *Inorg. Chem.* **1972**, *11*, 2901-2906.

(10) (a) Mok, C. Y.; Endicott, J. F. *J. Am. Chem. Soc.* **1977**, *99*, 1276-1277. (b) Mok, C. Y.; Endicott, J. F. *Ibid.* **1978**, *100*, 123-129.

(11) Esperson, J. H.; Martin, A. H. *J. Am. Chem. Soc.* **1977**, *99*, 5953-5957.

(12) Schaefer, W. P.; Waltzman, R.; Huie, B. T. *J. Am. Chem. Soc.* **1978**, *100*, 5063-5067.

(13) Elroi, H.; Meyerstein, D. *J. Am. Chem. Soc.* **1978**, *100*, 5540-5548.

(14) Dolphin, D.; Harris, R. L. N.; Huppatz, J. L.; Johnson, A. W.; Kay, I. T. *J. Chem. Soc. C* **1966**, 30-40. Preparation and properties of the dicyanocobalt(III) complex of BDHC were briefly described.

(15) Murakami, Y.; Aoyama, Y. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 683-688.

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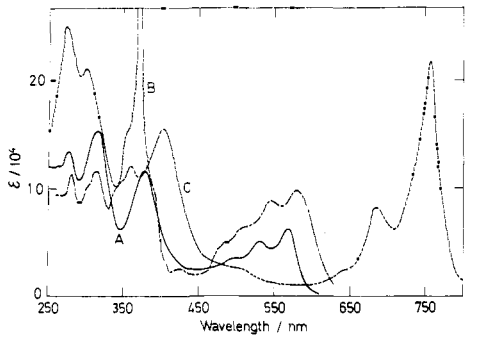


Figure 1. Electronic absorption spectra of cobalt(III) complexes at room temperature: A, $(CN)_2Co^{III}$(BDHC) in water; B, $(CN)_2Co^{III}$(cobinamide) in water; C, $(CN)_2Co^{III}$(TDHC) in methanol.

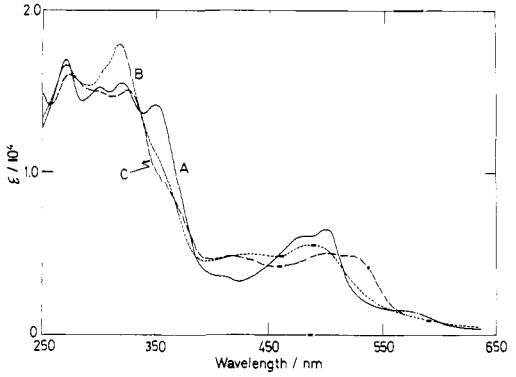
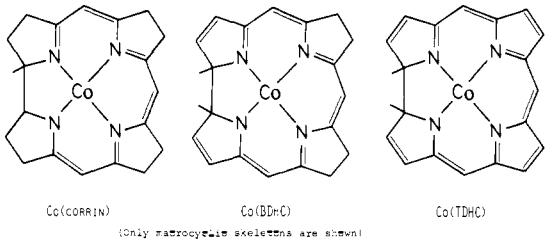


Figure 2. Electronic absorption spectra of cobalt(III) complexes in water at room temperature: A, $[(H_2O)_2Co^{III}(BDHC)]^{2+}$; B, $[(H_2O)(OH)Co^{III}(BDHC)]^{+}$; C, $(OH)_2Co^{III}(BDHC)$.

the upper or the lower side of the macrocycle, may be subjected to an inevitable steric interaction with one of the angular methyls. Aside from these differences in structure between corrinoid and the present analogues, the basic structures of BDHC, TDHC, and corrin complexes (cobinamide) are the same except for the identities of the peripheral substituents. Consequently, the differences which might be found in properties among the BDHC, TDHC, and corrinoid complexes can be interpreted in a more straightforward manner in this work.



Results

Spectroscopic, Electrochemical, and Axial Coordination Behaviors. Despite their apparently related structures, the BDHC and TDHC complexes behave mutually in quite different manners. As regards reactivity criteria, Co^{II}(BDHC) but not Co^{II}(TDHC) forms an oxygen adduct and the formation of a more or less stable carbon–cobalt bond is observed only for the BDHC system. The π-conjugation effects involved in corrin, didehydrocorrin, and tetradehydrocorrin rings are reflected on the electronic spectra of their dicyanocobalt(III) complexes as shown in Figure 1. The overall spectral feature for the BDHC complex involving vibrational fine structure with a spacing of 1.28×10^3 cm^{-1} bears a striking resemblance to that for the corrinoid complex[14,16,17] but far different from that for the TDHC complex. The spectra of BDHC complexes with various axial ligands [(X,Y)-Co^{III}-

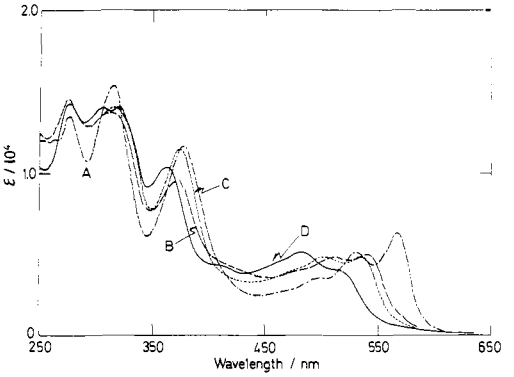


Figure 3. Electronic absorption spectra of cobalt(III) complexes in water at room temperature: A, $(CN)_2Co^{III}$(BDHC); B, (CN)(OH)Co^{III}(BDHC); C, $[(CN)(py)Co^{III}(BDHC)]^{+}$; D, $[(CN)(H_2O)Co^{III}(BDHC)]^{+}$.

Table I. α-, β-, and γ-Bands (in 10^3 cm^{-1}) for (X,Y)-Co^{III}(BDHC) and (X,Y)-Co^{III}(cobinamide)[a,b]

		γ		β		α	
X	Y	BDHC	cobinamide	BDHC	cobinamide	BDHC	cobinamide
H_2O	H_2O	28.41	28.65	21.10	20.41	20.04	19.23
H_2O	OH^-	27.8–28.6[c]	28.49	*d*	20.24	*d*	19.23
OH^-	OH^-	27.0–27.8[c]	28.09	20.16	19.80	ca. 19.05	18.76
CN^-	H_2O	27.62	28.25	20.79	20.16	19.38	19.01
CN^-	py	26.74		19.92		18.73	
CN^-	OH^-	26.88	27.70	19.61	19.23	18.52	18.12
CN^-	CN^-	26.46	27.10	18.90	18.35	17.61	17.06

[a] In water at room temperature. The data for cobinamides coordinated with cyano group or groups are cited from: Firth, R. A.; Hill, H. A. O.; Pratt, J. M.; Thorp, R. G.; Williams, R. J. P. *J. Chem. Soc. A* **1968**, 2428–2433. [b] In reference to the classification of optical spectra for corrin complexes (Firth, R. A.; Hill, H. A. O.; Pratt, J. M.; Williams, R. J. P.; Jackson, W. R. *Biochemistry* **1967**, *6*, 2178–2189), the longest wavelength band and the immediate higher energy band in the visible region were assigned respectively to α- and β-bands and the longest wavelength band of significant intensity in the near-UV region to γ-band for the BDHC complex. [c] Shoulder. [d] α- and β-bands are not well separated in the region of $(20.0–20.8) \times 10^3$ cm^{-1}.

Table II. ESR Spin Hamiltonian Parameters for Cobalt(II) Complexes at 77 K

complex	medium	$10^4 \times A_\parallel^{Co}$/ cm^{-1}	$10^4 \times A_\parallel^{N}$/ cm^{-1}	ref
Co^{II}(BDHC)	$CHCl_3$–C_6H_6 (2:1 v/v)	127		this work
py-Co^{II}(BDHC)	$CHCl_3$–C_6H_6 (2:1 v/v)	101	17.1	this work
O_2-Co^{II}(BDHC)	$CHCl_3$–C_6H_6 (2:1 v/v)	18		this work
(py)(O_2)-Co^{II}(BDHC)	$CHCl_3$–C_6H_6 (2:1 v/v)	12		this work
Co^{II}(cobinamide)	H_2O	135		*a*
py-Co^{II}(cobinamide)	CH_3OH	105	17.7	*a*
vitamin B_{12r}	H_2O	102.7		*b*
O_2-vitamin B_{12r}	H_2O	14.0		*b*

[a] Bayston, J. H.; Looney, F. D.; Pilbow, J. R.; Winfield, M. E. *Biochemistry* **1970**, *9*, 2164–2172. [b] Bayston, J. H.; King, N. K.; Looney, F. D.; Winfield, M. E. *J. Am. Chem. Soc.* **1969**, *91*, 2775–2779.

(BDHC)] are shown in Figures 2 and 3, and the absorption maxima for the α-, β-, and γ-bands are summarized in Table I along with those for the corresponding cobinamide complexes. The extent of band shift caused by a given set of axial ligands is nearly the same for both systems. That the BDHC and corrinoid complexes have closely related electronic structures was further confirmed by examination of the ESR parameters for their Co(II) complexes and their nitrogen-base and oxygen adducts (Table II) and by comparison of the NMR chemical shifts for the cobalt-

(16) Firth, R. A.; Hill, H. A. O.; Mann, B. E.; Pratt, J. M.; Thorp, R. G.; Williams, R. J. P. *J. Chem. Soc. A* **1968**, 2419–2428.
(17) Offenhartz, P. O.; Offenhartz, B. H.; Fung, M. M. *J. Am. Chem. Soc.* **1970**, *92*, 2966–2973.

Table III. Reduction and Oxidation Potentials (V vs. SCE) for BDHC, TDHC, and Corrinoid Complexes

complex	medium	Co(III)/Co(II)	Co(II)/Co(I)	Co(I)/$[Co^{II}L]^-$ [a]	$(CN)_2Co^{III} \rightarrow$ Co(I)
Co(BDHC)	CH_3OH	+0.47	−0.71		
	DMF		−0.55		
	CH_2Cl_2		−0.57		
Co(TDHC)	CH_3OH	+0.59 (+0.54)[e]	−0.25 (−0.27)[e]		
	DMF		−0.11	−1.31	
	CH_2Cl_2	+0.97	−0.13	−1.57	
vitamin B_{12} [b]	H_2O	*ca.* +0.3	−0.742		
$(CN)_2Co^{III}$(TDHC)	DMF				−0.58
	CH_2Cl_2				−0.73
$(CN)_2Co^{III}$(BDHC)	DMF				−1.38
	CH_2Cl_2				<−1.45
$(CN)_2Co^{III}$(cobinamide)	DMF				−1.14
$(CN)_2Co^{III}$(cobinamide)[c]	H_2O				−1.18
$(CN)_2Co^{III}$(cobalamin)[d]	H_2O				−1.33

[a] $Co(I)/[Co^{II}L]^-$ is the redox potential for $Co^I(TDHC) \rightleftharpoons [Co^{II}(TDHC)]^-$. [b] (a) Lexa, D.; Saveant, J. M. *J. Am. Chem. Soc.* 1976, *98*, 2652–2658. (b) Lexa, D.; Saveant, J. M.; Zickler, J. *Ibid.* 1977, *99*, 2786–2790. [c] Hogenkamp, H. P. C.; Holmes, S. *Biochemistry* **1970**, *9*, 1886–1892. [d] Reference 6. [e] Elson, C. M.; Hamilton, A.; Johnson, A. W. *J. Chem. Soc., Perkin Trans. 1* 1973, 775–781.

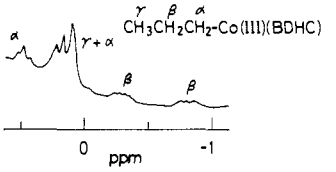


Figure 4. NMR spectrum of $[(n\text{-}C_3H_7)Co^{III}(BDHC)]I$ in $CDCl_3$. Only the high field region, where the proton signals due to the *n*-propyl group are observed, is shown here.

bound alkyl protons in $[(n\text{-}C_3H_7)Co^{III}(BDHC)]^+$ (Figure 4: a triplet at δ +0.48, an unresolved multiplet at δ +0.3–0, and multiplets at δ −0.31 and −0.81) with those for the corresponding cobinamide complex.[18]

The cyclic voltammograms for both $[Co^{II}(BDHC)]ClO_4$ and $[Co^{II}(TDHC)]ClO_4$ in methanol involved clearly distinguishable redox pairs of reversible or quasi-reversible character: Co(III) $\rightleftharpoons$ Co(II) and Co(II) $\rightleftharpoons$ Co(I). The TDHC complex showed another redox pair attributable to $Co^I(TDHC) \rightleftharpoons [Co^{II}(TDHC)]^-$ in an aprotic solvent. The reduction of the dicyanocobalt(III) complexes of TDHC and BDHC was referred to a two-electron process occurring in a cathodic region, while the cyanocobalt(III) complex, $[(CN)Co^{III}(BDHC)]^+$, underwent a one-electron reduction in methanol at around −0.5 V vs. SCE $[(CN)Co^{III} \rightarrow$ Co(II)] which was followed by the reversible waves for the Co(II) $\rightleftharpoons$ Co(I) redox couple. The Co(II)/Co(I) redox potential and the reduction potential for $(CN)_2Co$(III) species observed for the BDHC complexes exhibit significant cathodic shifts relative to those for the corresponding TDHC complexes and are comparable to those for the cobinamide and cobalamin complexes measured in water or DMF as shown in Table III.

In order to characterize the BDHC complex from its axial coordination behavior, we carried out spectrophotometric titrations to determine the acid-dissociation constants for coordinated water in $[(H_2O)_2Co^{III}(BDHC)]^{2+}$ and $[(CN)(H_2O)Co^{III}(BDHC)]^+$ and the equilibrium constants for substitution of coordinated water in the latter complex with pyridine bases. The results are summarized in Table IV along with those for the cobinamide complexes. Again, the respective values for the two complex systems are comparable. A linear free-energy correlation of the equilibrium constant with pK_a for a series of 4-substituted pyridines has been established: $\log K = 0.32pK_a + 0.50$ from least-squares analysis. A similar relationship was also noted for coordination of pyridine bases with $[Co^{II}(BDHC)]ClO_4$ in dichloromethane (Table V). The data also indicate a significant steric inhibition for coordination of 2-methyl-substituted pyridines.

Alkylation of Co^I(BDHC). The reduction of $(CN)_2Co^{III}$(BDHC) in tetrahydrofuran–water (1:1 or 2:1 v/v) with sodium hydroborate ($NaBH_4$) resulted in the formation of air-sensitive Co^I(BDHC), which was readily converted to a photolabile organometallic derivative upon treatment with an alkyl iodide or bromide.[14]

Table IV. Acid Dissociation Constants for Coordinated Water and Stability Constants for Coordination of Pyridine Bases in Aqueous Media at 25.0 ± 0.1 °C[a,b]

quantity	pyridine base	BDHC complex	cobinamide
pK_{a_1}		6.2	6.0[c]
pK_{a_2}		11.2	*d*
pK_{a_3}		11.3	11.0[c]
log *K*	py	2.17	2.6[e]
log *K*	4-Me-py	2.57	
log *K*	4-NH_2-py	3.38	
log *K*	4-CN-py	1.04	

[a] $Co^{III}(H_2O)_2 \rightleftharpoons (K_{a_1})\ Co^{III}(H_2O)(OH) \rightleftharpoons (K_{a_2})\ Co^{III}(OH)_2$. $Co^{III}(CN)(H_2O) \rightleftharpoons (K_{a_3})\ Co^{III}(CN)(OH)$. [b] $K = [(CN)(py)\text{-}Co^{III}X]/[(CN)(H_2O)Co^{III}X][py]$; X refers to an equatorial ligand. [c] Hayward, G. C.; Hill, H. A. O.; Pratt, J. M.; Vanston, N. J.; Williams, R. J. P. *J. Chem. Soc.* 1965, 6485–6493. [d] Not reported; a spectral change was observed in the pH range of 11. [e] Hayward, G. C.; Hill, H. A. O.; Pratt, J. M.; Williams, R. J. P. *J. Chem. Soc. A* 1971, 196–200.

Table V. Stability Constants for the Coordination of Pyridine Bases to $[Co^{II}(BDHC)]ClO_4$ in Dichloromethane at 25.0 ± 0.1 °C

pyridine base	pK_a[a]	K/L mol^{-1}
py	5.19	2.7×10^3
4-Me-py	6.02	5.1×10^3
4-NH_2-py	9.12	6.1×10^3
4-CN-py	1.90	2.1×10^2
2-Me-py	5.97	9.1
2,4,6-Me_3-py	7.48	8.4

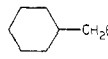
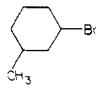
[a] Cited from Jencks, W. P.; Regenstein, J. "Handbook of Biochemistry and Molecular Biology"; Fasman, G. D., Ed.: CRC Press: Cleveland, Ohio 1976; Vol. 1.

The second-order rate constants for reactions of Co^I(BDHC) with alkyl halides at 25 °C were determined spectrophotometrically at 400 nm as listed in Table VI along with those reported for Co^I(corrinoid) (vitamin B_{12s}) in methanol at 25 °C.[19] The data indicate that the S_N2-type mechanism, which is believed to be concerned with the reaction of B_{12s},[19] is also operative in the reaction of Co^I(BDHC); the iodides are more reactive with the cobalt complex than the corresponding bromides, and the rate decreases with increasing bulkiness of an alkyl donor. The steric effect is far more pronounced on the reaction of Co^I(BDHC) than that of vitamin B_{12s} as confirmed by the rate ratios for Co^I(BDHC)

(18) Brodie, J. D.; Poe, M. *Biochemistry* **1971**, *10*, 914–922. Reported chemical shifts in $[^2H_6]Me_2SO$: δ +0.46, +0.26, +0.05, −0.25, and −0.85.

(19) Schrauzer, G. N.; Deutsch, E. *J. Am. Chem. Soc.* **1969**, *91*, 3341–3350.

Table VI. Second-Order Rate Constants for Reactions of $Co^{I}(BDHC)$[a] and Vitamin B_{12s}[b] with Alkyl Halides[c]

alkyl halide	k(BDHC)/ M^{-1} s^{-1}	$k(B_{12s})$/ M^{-1} s^{-1}	k(BDHC)/ $k(B_{12s})$
CH_3I	3.0×10^4	3.4×10^4	0.88
CH_3CH_2I	3.1×10^2		
$CH_3CH_2CH_2I$	1.1×10^2		
$(CH_3)_2CHI$	0.71	2.3×10^2	3.1×10^{-3}
CH_3Br	8.5×10^2	1.6×10^3	0.53
CH_3CH_2Br	3.9	3.1×10	0.13
$CH_3CH_2CH_2Br$	1.8	1.4×10	0.13
$(CH_3)_2CHBr$	7×10^{-4}	1.8	4×10^{-4}
$CH_3(CH_2)_{11}Br$	3.0×10^{-1}		
$CH_3CHBr(CH_2)_5CH_3$	4×10^{-4}		
	2.1×10^{-2}		
	5×10^{-4}		

[a] With CH_3X, CH_3CH_2X, $CH_3CH_2CH_2X$, and $(CH_3)_2CHX$ (X, Br, I); in THF-water (1:1 v/v). With the rest of alkyl halides; in THF-water (2:1 v/v). [b] In methanol containing 0.10 M NaOH (cited from ref 19). [c] $Co^{I}(BDHC)$, at 25.0 ± 0.1 °C; vitamin B_{12s}, at 25 ± 2 °C with ethyl, *n*-propyl, and isopropyl halides and at 25.0 °C with methyl halides.

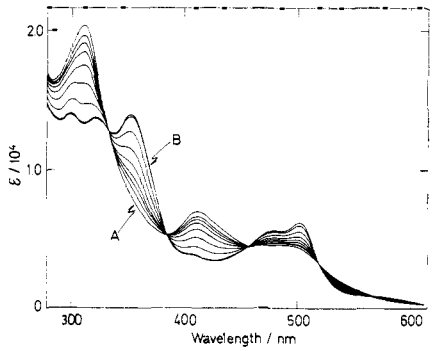


Figure 5. Spectral change for the aerobic photolysis of $[(CH_3)Co^{III}(BDHC)]^+$ in water containing 1.0% (v/v) methanol at pH 4.43 (acetate buffer): irradiated with a 200-W tungsten lamp from a distance of 60 cm; duration of photolysis 0, 10, 20, 40, 85, 175, 355, 955, 1285 s (read from A to B).

vs. B_{12s}, k(BDHC)/$k(B_{12s})$ (Table VI).

Cleavage of the Carbon–Cobalt Bond. The alkylated-BDHC complexes are in general very unstable and can not be isolated in pure form. Even a simple extraction procedure with organic solvents resulted in more or less decomposition of the carbon–cobalt bond. Thus, the decomposition behavior of the alkylated complexes was investigated as they were prepared in aqueous media, after decomposition of excess $NaBH_4$ with acid in the presence of excess alkyl halide. One of the characteristic features of the alkylated-BDHC complexes is their acid lability which apparently depends on the bulkiness of alkyl ligands. The methylcobalt complex, $[(CH_3)Co^{III}(BDHC)]^+$, in strongly acidic media (pH 1.33) was converted to $[(H_2O)_2Co^{III}(BDHC)]^{2+}$ under aerobic conditions in the dark, whereas the cyclohexylmethylcobalt complex was more readily decomposed in tetrahydrofuran–water (1:1 v/v) at pH 2.40 under otherwise identical conditions. The observation of isosbestic points during these decompositions, coupled with the fact that the rate of autoxidation of $Co^{II}(BDHC)$ under identical experimental conditions[20] was comparable to or smaller than those of acid-catalyzed decomposition of the alkylcobalt complexes, rules out the existence of the Co(II) intermediate. The isopropylcobalt complex was even more susceptible to acid decomposition and was gradually converted to $[(H_2O)_2Co^{III}(BDHC)]^{2+}$ at pH 2.3 in the dark even under anaerobic conditions.

(20) The rate of autoxidation of $[Co^{II}(BDHC)]ClO_4$ in water is proportional to hydrogen ion concentration in the pH range 2.24–4.18.

Table VII. Half-lives[21] for Photolysis of Alkylated BDHC Complexes[a,b]

alkyl moiety	$\tau_{1/2}$ (aerobic)/ min	$\tau_{1/2}$ (anaerobic)/ min
CH_3	1.7	ca. 3×10^2
CH_3CH_2	2.4	7
$(CH_3)_2CH$	0.5	0.5

[a] In water containing 1.0% (v/v) methanol at pH 2.3; initial concentration of each complex, 4.0×10^{-5} M. [b] Irradiated with a 200-W tungsten lamp from a distance of 60 cm.

The aerobic photolysis of the methylcobalt complex provided clean spectral changes (Figure 5) leading to the formation of $[(H_2O)_2Co^{III}(BDHC)]^{2+}$ with the rate independent of pH (2.37–4.99). The anaerobic photolyses of the methyl- and ethylcobalt complexes gave $Co^{II}(BDHC)$ whereas, in a marked contrast, the isopropylcobalt complex was photolyzed to afford the Co(III) complex, $[(H_2O)_2Co^{III}(BDHC)]^{2+}$. Another aspect, which distinguishes the isopropylcobalt complex from the methyl- and ethylcobalt complexes, is the oxygen effect on the photolysis rate[21] (Table VII); a significant acceleration due to oxygen observed for photolyses of the methyl- and ethylcobalt complexes is no longer seen for that of the isopropylcobalt complex.

Although the cyanide ion in the concentration range of the present investigation has no influence on the absorption spectrum of the methylcobalt complex, the ion greatly enhanced the photolysis of the complex under otherwise identical, anaerobic conditions at pH 9.93 (carbonate buffer) as the half-life[21] indicates the following: without CN^-, $\sim 3 \times 10^2$ min; 1.2×10^{-4} M CN^-, 7.8 min; 1.0×10^{-3} M CN^-, 7.3 min. The reaction afforded $(CN)_2Co^{III}(BDHC)$ and no stable intermediate was present since clear isosbestic points were observed. The cyanide ion also enhanced the photolysis in acidic media from which $[(CN)(H_2O)Co^{III}(BDHC)]^+$ was obtained. The oxidation of $Co^{II}(BDHC)$ was much slower than the photolysis under the same conditions and hence the photolysis must afford directly the $Co^{III}(CN)$ derivative without intermediacy of Co(II) species.

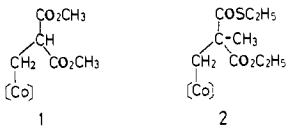
Fate of Axial Alkyl Ligands. According to recent model studies, cobalamins coordinated with an alkyl moiety bearing two β-alkyl esters (**1** and **2** where [Co] stands for cobalamin) undergo 1,2-rearrangement of the substituent in the dark.[4a,b] The reaction of $Co^{I}(BDHC)$ with dimethyl bromomethylmalonate afforded dimethyl methylmalonate, the reductive debromination product, likely through formation of a metastable alkylated-cobalt complex analogous to **1** as an intermediate since dimethyl methylmalonate was not detected in the absence of the BDHC complex. The reaction of bromo thioester (**3a**) with $Co^{I}(BDHC)$ yielded an alkylated complex (**3b**) which was identified by spectroscopic means. Decomposition of this species dissolved in water or in an aqueous micelle of hexadecyltrimethylammonium bromide also gave the reductive debromination product (**3c**) in the dark or under irradiation. In neither case was the rearrangement product (succinate or thioester of butyric acid) detected.

The BDHC complex with a simpler axial alkyl ligand also predominantly underwent reductive debromination. Thus, the dodecylcobalt complex of BDHC, prepared from dodecyl bromide and $Co^{I}(BDHC)$ followed by addition of acid to decompose excess

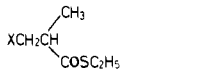
(21) The photolysis conditions were chosen to assure reasonable absorbance of the incident light by the sample solutions. This was achieved by using an intense light source (200 W) and dilute solutions of the complexes (4.0×10^{-5} M). We do not mean by "half-life" that the photolysis critically follows first-order kinetics on the basis of general criteria for photochemical reactions, although similar photolysis reactions with corrinoid[22] and cobaloxime[23] complexes were analyzed in terms of first-order kinetics. The kinetic studies of the homolytic bond cleavage itself has no primary concern here. We intend to show that nonphotochemical trapping of the homolytically cleaved species by oxygen or cyanide ion rather than the primary photochemical process producing radicals determines the apparent photolysis rate for the methyl complex, but not for the isopropyl complex.

(22) Pailes, W. H.; Hogenkamp, H. P. C. *Biochemistry* **1968**, *7*, 4160–4166.

(23) Schrauzer, G. N.; Lee, L. P.; Sibert, J. W. *J. Am. Chem. Soc.* **1970**, *92*, 2997–3005.



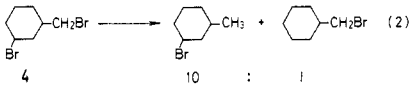
1 2



3 (a) : X = Br
(b) : X = Co(III)(BDHC)
(c) : X = H

$NaBH_4$, was irradiated under nitrogen. The main reaction product was dodecane (ca. 50% yield based on the cobalt complex) and the oxygenated materials such as dodecanol and dodecanal were, if any, only in a trace amount.

The alkylation of Co^I(BDHC) with an alkyl bromide forming an alkylcobalt complex was subjected to a significantly large steric interaction between the reactants (perhaps the largest ever known for related reactions), the primary bromide being favored over the secondary (Table VI). The resulting alkylcobalt complex derived even from a primary bromide yielded the hydrogenation (or reduction) product as described above. Combination of these two unique properties of the BDHC complex leads us to expect that the complex can be used as a catalyst for reductive debromination of primary alkyl bromides at high selectivity by utilizing $NaBH_4$ as the stoichiometric reducing agent as shown in Scheme I. In fact, when 1-dodecyl bromide was used as a substrate in aqueous CTAB micelle, dodecane was obtained in 500% yield based on the BDHC complex used; the reaction is catalytic with respect to the BDHC complex. When 1-dodecyl bromide was put into competition with 2-octyl bromide in the reaction with the above catalytic process, only dodecane was detected practically as the debromination product. Furthermore, the reaction of 1-bromo-3-(bromomethyl)cyclohexane (**4**), having both primary and secondary bromo groups, with the BDHC catalyst resulted in the formation of 1-bromo-3-methylcyclohexane and (bromomethyl)cyclohexane at a 10:1 molar ratio (eq 2); the high selectivity for the primary bromide should be noted.

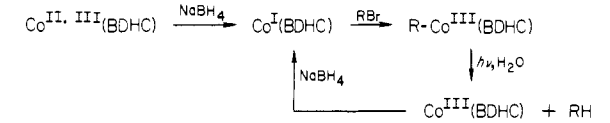


4 10 : 1 (2)

Discussion

Electronic Effects. On the basis of the preceding results, the BDHC complexes are quite analogous to the corrinoids as far as the electronic properties of the macrocyclic chromophore (separation of the π–π^* levels, extent of the electronic perturbation on π and π^* levels by axial ligands, and diamagnetic shielding effect provided by the macrocycle) and the nuclear cobalt (redox potential and spin distributions in the Co(II) complex and its pyridine and oxygen adducts) as well as the axial coordination behaviors (stability constants for the pyridine-base adducts and pK_a for the coordinated water molecule) are concerned. Far from analogous to the corrinoids, on the contrary, are the TDHC complexes despite their apparently related structures. What is most characteristic of the TDHC system is the surprising stability of the Co(I) state as reflected on the Co(II)/Co(I) redox potential and the reduction potential for $(CN)_2Co^{III}$(TDHC); significant anodic shift relative to those for the corresponding corrinoid complexes. The enhanced stability of lower oxidation states may bring about the lack of reactivity in the nucleophilic or electron-donating reactions at the nuclear cobalt. In fact, no oxygen adduct of Co^{II}(TDHC) was detected at 77 K and no evidence was obtained for the formation of an organometallic derivative in the reaction of Co^I(TDHC) with methyl iodide. Thus, the effects of peripheral double bonds are provided in various ways depending on their locations; the double bonds at the periphery of A and D rings of the macrocycle are practically of isolated character (confirmed with BDHC), while those of B and C rings are in conjugation with the interior double bonds (confirmed with TDHC) extending conjugation of the π-bond system. The extended π conjugation would induce further diamagnetic shielding and, in fact, the NMR signals for meso protons (at 5, 10, and 15 positions) of $(CN)_2Co^{III}$(TDHC) are shifted to downfield by ca. 1 ppm relative to those of $(CN)_2Co^{III}$(BDHC).

Scheme I



Although the redox properties are of crucial significance for vitamin B_{12} models, it is not well understood how a given type of equatorial ligand affects redox potentials of the nuclear cobalt. The present TDHC and BDHC, etioporphyrin, and octaalkylcorrole constitute an interesting family of closely related cyclic tetrapyrroles which carry 1–, 2–, and 3– charges, respectively, when coordinated to cobalt. In this family, the Co(III)/Co(II) potentials in non- or weakly coordinating solvents span more than 1 V; +0.97 V for TDHC in CH_2Cl_2 as one extreme through +0.30 V for porphyrin in butyronitrile[24] to −0.26 V for corrole in CH_2Cl_2[25] as the other extreme. The significant charge effect may be understood on the basis of electrostatic consideration and/or solvation effect. Such a charge effect is effective in controlling the Co(II)/Co(I) potential as well: for the etioporphyrin complex, −1.04 V in DMF.[26] A big difference in Co(II)/Co(I) potential between the TDHC and BDHC complexes may provide a clear evidence for the following concept: as the lower oxidation state of cobalt is stabilized, the π-conjugation effect, among other things, comes into play in such a manner that the lower π^* level in highly conjugated TDHC may accept an electron from the 4p or 3d orbital of Co(I). Such a nephelauxetic effect tends to stabilize the Co(I) state so that its nucleophilic reactivity toward an alkyl ligand can not be exercised. It is interesting to note that further reduction of Co^I(TDHC) results in the formation of $[Co^{II}$(TDHC)$]^-$; instead of reducing the nuclear cobalt, two electrons are transferred to the π^* level of TDHC and cobalt is rather oxidized to the bivalent state.[27]

The corrin ring acting as a monoanionic ligand with a unique type of conjugation system is so constructed by nature as to provide a ligand effect for the proper redox potential of cobalt. If a vitamin B_{12} model is to mimic the redox behavior of the nuclear cobalt, the BDHC complex is assumed to be a good model judging from their Co(II)/Co(I) potentials regardless of the difference in solvent for the measurement (Table III).

Steric Effects. The correlation, although qualitative, has been demonstrated between kinetic nucleophilicity of cobalt(I) species and their thermodynamic instability as judged by the Co(II)/Co(I) potentials.[7] On this basis, Co^I(BDHC) and Co^I(corrinoid) (B_{12s}) should have comparable nucleophilicity. This is true only for reactions with the least bulky alkyl donors, methyl iodide and bromide (Table VI). With bulkier alkyl donors, the reaction of Co^I(BDHC) is subjected to a more pronounced steric retardation than that of B_{12s} is, as reflected on the rate ratio, k(BDHC)/k(B_{12s}). What is most noteworthy for the BDHC system is that the reactivity of secondary alkyl halides is surprisingly depressed; the rate ratios for reactions with isopropyl bromide to those with ethyl bromide: Co^I(BDHC), 1.8×10^{-4}; B_{12s}, 5.8×10^{-2};[19] (tributylphosphin)cobaloxime(I), 6.9×10^{-2};[19] and bromide ion (bromide exchange or Finkelstein reaction), 1.1×10^{-2}.[28] The additional and significant steric effect observed for the reactions of the BDHC complex seems to arise from the interaction between angular methyl groups placed at C(1) and C(19) positions situated on the opposite sides of the macrocycle[14] and an approaching alkyl donor which is finally bound to the cobalt atom, the significance

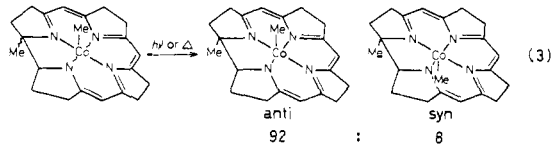
(24) Stanienda, A.; Biebl, G. *Z. Phys. Chem. (Wiesbaden)* **1967**, *52*, 254–275.
(25) Conlon, M.; Johnson, A. W.; Overend, W. R.; Rajapaksa, D.; Elson, C. M. *J. Chem. Soc., Perkin Trnas. 1* **1973**, 2281–2288.
(26) Felton, R. H.; Linschitz, H., *J. Am. Chem. Soc.* **1966**, *88*, 1113–1116.
(27) Hush, N. S.; Woolsey, I. S. *J. Am. Chem. Soc.* **1972**, *94*, 4107–4114.
(28) Gould, E. S. "Mechanism and Structure in Organic Chemistry"; Henry Holt and Co.: New York, 1959; pp 274–277.

Table VIII. Steric Repulsion Energies for Alkylation of Co^{I}(BDHC) with RBr and RI[a]

	repulsion energy/kcal/mol			
	with RBr		with RI	
R	R-CH_3	R-skeleton	R-CH_3	R-skeleton
CH_3	1.4	0[b]	1.4	0[b]
CH_3CH_2	2.2	2.4	2.8	1.3
$(CH_3)_2CH$	5.7	4.0	4.8	3.0

[a] For definitions and derivations, see ref 30. [b] The steric repulsion energy between the methyl group and the macrocyclic skeleton (BDHC) is assumed to be negligible.

of such an interaction being well-established in organic stereochemistry as the 1,3-diaxial interaction. The corrinoid complex possesses one angular methyl only at C(1), and, consequently, an alkyl halide may approach from the less hindered side of the equatorial skeleton to avoid the steric interaction with CH_3 at C(1). The methylated complex of cobyric acid is in an equilibrium under photolytic or thermal condition to give anti and syn forms at a 92:8 molar ratio (eq 3). This ratio is also identical with the kinetic



92 : 8 (3)

ratio for methylation of Co^{I}(cobyric acid). The anti to syn form ratio for the ethylated complex is 99:1.[29] According to the X-ray crystallographic analysis, the benzimidazole group and even the cyanide coordinated to the corrinoid complex at the side where the angular methyl group is sticking out assume a configuration so as to minimize the steric interaction with the methyl group.[6] Thus, all of these results point out the significance of a steric effect provided by the angular methyl.

The steric effect is the primary factor determining the reactivity in S_N2 type reactions[28] and in the present particular case of the alkylation of Co^{I}(BDHC). The overall steric effect involves the steric interactions between the axial alkyl ligand and the angular methyl and between the axial alkyl ligand and the macrocyclic skeleton. Contribution of each steric effect to selected reactions can be evaluated separately from the rate data listed in Table VI coupled with the kinetic and thermodynamic isomer ratios for methylated and ethylated cobyric acids as mentioned above under the following assumptions: (1) alkylations of B_{12s} with the rate constants listed in Table VI take place from the less hindered side and hence are free from steric interaction with the angular methyl, the macrocyclic skeleton providing the sole origin of the steric effect; (2) the steric energies due to interactions between the axial ligands and the macrocyclic skeleton are the same for the BDHC and corrinoid complexes; (3) the steric energies due to interactions between the axial ligands and the angular methyl in the BDHC complexes are identical with those in the corrinoid complexes; and (4) the steric interaction between the axial methyl ligand and the macrocyclic skeleton can be neglected for simplicity. In Table VIII are shown the estimated steric repulsion energies contributing to the activation processes in the methylation, ethylation, and isopropylation of Co^{I}(BDHC) with the corresponding alkyl bromides or iodides.[30,31]

Nature of the Carbon–Cobalt Bond. The homolytic cleavage of a carbon–cobalt bond upon photolysis of organocobalt derivatives is well documented.[10,22,23,32-34] In this respect, the methyl- and ethylcobalt derivatives, $[(CH_3)Co^{III}(BDHC)]^+$ and $[(C_2H_5)Co^{III}(BDHC)]^+$, behave normally: the anaerobic photolysis affords $[Co^{II}(BDHC)]^+$. In a marked contrast, the anaerobic photolysis of the isopropylcobalt complex, $[(i\text{-}C_3H_7)Co^{III}(BDHC)]^+$, gives rise to $[(H_2O)_2Co^{III}(BDHC)]^{2+}$ rather than the Co(II) complex. A significant increase in the photolysis rate for the methylcobalt complex by changing condition from anaerobic to aerobic is due to the trapping of a methyl radical with oxygen. This trapping effect inhibits recombination of the radical with the Co(II) species (eq 4) as has been suggested[7d] and con-

$$(CH_3)Co^{III}(BDHC) \overset{h\nu}{\rightleftharpoons} Co^{II}(BDHC) + CH_3\cdot \xrightarrow{O_2} CH_3\text{-}O\text{-}O\cdot \quad (4)$$

firmed[35] recently for the photolysis of methylcobalamin. Such an effect by oxygen is also seen in the photolysis of the ethylcobalt complex even though to a lesser extent.[36] On the other hand, the isopropylcobalt complex photolyzes at an identical rate irrespective of conditions, aerobic or anaerobic. These observations, when coupled with the fact that a cyclohexyl bromide (**4**) is indeed converted to the hydrogenation product *via* complex formation with the Co^{I}(BDHC) (eq 2), indicate that the carbon–cobalt bond in the secondary alkylcobalt complexes of BDHC undergoes heterolytic cleavage: an intrinsic heterolysis to yield the Co(III) complex and a carbanionic intermediate or an initial homolysis followed by rapid electron transfer from cobalt to carbon before the radical is trapped with oxygen. The novel bond-cleavage behavior of the isopropylcobalt complex may reasonably be ascribed to the significant steric strain involved in the complex. Such a steric effect would also explain the general instability of the alkylated-BDHC complexes, particularly their acid lability. Unfortunately, the isopropylcobalt complex decomposes gradually even under anaerobic conditions in aqueous media without light. Such prominent instability prohibits us from performing the detailed study on the photolysis mechanism and the role of acid involved therein.[37] Such being the case, it is important to discuss the kinetic pathway from the energetic viewpoint.

The heterolytic carbon–cobalt bond cleavage or the electron transfer from Co(II) to an organic radical (eq 5) is thermody-

$$Co(II) + R\cdot \rightarrow Co(III) + R^- \quad (5)$$

namically very unfavorable and does not take place unless other effects come into play.[5b,39-41] Factors affecting the reaction

(29) Friedrich, W.; Messerschmidt, R. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1969**, *24B*, 465–467.

(30) $E(CH_3/alkyl)$ and $E(sk/alkyl)$ are defined, respectively, as the steric repulsion energy between axial alkyl ligand and angular methyl and that between axial alkyl ligand and macrocyclic skeleton. For the alkylation with alkyl bromide, the following equations can be utilized: $[E(CH_3/C_2H_5) + E(sk/C_2H_5)] - E(CH_3/CH_3) = RT \ln (8.5 \times 10^2/3.9)$, $[E(CH_3/i\text{-}C_3H_7) + E(sk/i\text{-}C_3H_7)] - E(CH_3/CH_3) = RT \ln (8.5 \times 10^2/7 \times 10^{-4})$, $E(sk/C_2H_5) = RT \ln (1.6 \times 10^3/3.1 \times 10)$, $E(sk/i\text{-}C_3H_7) = RT \ln (1.6 \times 10^3/1.8)$, $E(CH_3/CH_3) = RT \ln (92/8)$. For the alkylation with alkyl iodide: $[E(CH_3/C_2H_5) + E(sk/C_2H_5)] - E(CH_3/CH_3) = RT \ln (3.0 \times 10^4/3.1 \times 10^2)$, $[E(CH_3/i\text{-}C_3H_7) + E(sk/i\text{-}C_3H_7)] - E(CH_3/CH_3) = RT \ln (3.0 \times 10^4/0.71)$, $E(CH_3/C_2H_5) = RT \ln (99/1)$.

(31) The 1,3-diaxial methyl–methyl interaction energy in *cis*-1,3-dimethylcyclohexane is 3.7 kcal/mol: Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. "Conformational Analysis"; Wiley: New York, 1965; Chapter 2.

(32) Hogenkamp, H. P. C. *Biochemistry* **1966**, *5*, 417–422.

(33) (a) Pratt, J. M. *J. Chem. Soc.* **1964**, 5154–5160. (b) Pratt, J. M.; Whitear, B. R. D. *J. Chem. Soc. A* **1971**, 252–255.

(34) (a) Giannotti, C.; Gaudemer, A.; Fontaine, C. *Tetrahedron Lett.* **1970**, 3209–3212. (b) Giannotti, C.; Bolton, J. R. *J. Organomet. Chem.* **1974**, *80*, 379–383.

(35) Endicott, J. F.; Ferraudi, G. F. *J. Am. Chem. Soc.* **1977**, *99*, 243–245.

(36) The faster rate for anaerobic photolysis of the ethyl derivative relative to the methyl derivative is attributed partly to the olefin formation, a reaction well-known for ethylcobalt complexes.[32] Also refer to: (a) Dolphin, D.; Johnson, A. W.; Rodrigo, R. *J. Chem. Soc.* **1964**, 3186–3193; (b) Yamada, R.; Shimizu, S.; Fukui, S. *Biochim. Biophys. Acta* **1966**, *124*, 197–200.

(37) Although the acid-catalyzed carbon–cobalt cleavage is rather common for alkyl complexes having an electronegative substituent on β-carbon,[38] there is little evidence for the direct attack of proton on the α-carbon of an organic ligand (Costa, G.; Mestroni, G.; Cocevar, C. *J. Chem. Soc., Chem. Commun.* **1971**, 706–707).

(38) (a) Reference 7d, pp 69–73. (b) Reference 13. (c) Silverman, R. B.; Dolphin, D.; Carty, T. J.; Krodel, E. K.; Abeles, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 7096–7097. (d) Silverman, R. B.; Dolphin, D. *Ibid.* **1976**, *98*, 4633–4639.

(39) Sibert, J. W.; Schrauzer, G. N. *J. Am. Chem. Soc.* **1970**, *92*, 1421–1423.

(40) Schrauzer, G. N.; Sibert, J. W.; Windgassen, R. J. *J. Am. Chem. Soc.* **1968**, *90*, 6681–6688.

energetics are the reduction ability of Co(II) reflected on its oxidation potential, the electron-accepting power of a radical reflected on its reduction potential, and the extent to which the developing carbanion is protonated at the transition state of electron transfer. An extra reducing agent such as a dithiol[39] or a highly coordinating ligand such as CN^- has been shown to induce the heterolytic methyl–cobalt bond cleavage in the methylated cobaloxime, and the Co(II) species coordinated with CN^- has been claimed as an intermediate which is able to reduce the methyl radical.[40] In conformity with this, the methylcobalt complex of BDHC undergoes conversion into the cyanocobalt(III) derivative under photolytic condition in the presence of cyanide. The reaction must involve the $Co^{II}CN$ species (eq 6) which is in fact a very powerful reductant; its oxidation potential would be at around −0.5 V vs. SCE judging from the reduction potential for $[(CN)(H_2O)Co^{III}(BDHC)]^+$ in methanol and is shifted to the cathodic direction by 1 V relative to *naked* $Co^{II}(BDHC)$.

$$(CH_3)Co^{III}(BDHC) \overset{h\nu}{\rightleftharpoons} [CH_3\cdot + Co^{II}(BDHC)] \xrightarrow{CN^-}$$

$$CH_3\cdot + \underset{\underset{CN}{|}}{Co^{II}(BDHC)} \longrightarrow CH_3^- + \underset{\underset{CN}{|}}{Co^{III}(BDHC)} \quad (6)$$

An anodic shift of the oxidation potential of Co(II) is expected to result in reduction of its reducing power. However, we are not certain about the limiting Co(III)/Co(II) potential which allows an electron transfer from Co(II) species to an alkyl radical. The ferrous complex of octaethylporphyrin (OEP) is known to reduce the methyl radical in an organic solvent containing 1% acetic acid[42] (eq 7). The Fe(II)/Fe(III) redox potential for the OEP complex

$$Fe^{II}(OEP) + CH_3\cdot \longrightarrow Fe^{III}(OEP) + CH_3^- \xrightarrow{H^+} CH_4 \quad (7)$$

in dimethylacetamide is at around 0 V vs. SCE.[43,44] From a purely electrochemical viewpoint, neglecting the difference in metal species involved, a Co(II) complex having a redox potential at around 0 V vs. SCE must reduce an alkyl radical. The Co(II)/Co(III) redox potential for the BDHC complex without any potent axial ligand is +0.5 V vs. SCE (Table III). Even if the nuclear cobalt in the BDHC complex does not have a high reducing ability, it can reduce an alkyl radical (isopropyl radical) upon securing an energy gain of some 12 kcal/mol (corresponding to the potential difference between 0 and +0.5 V) from other sources. If this energy gain is provided by the release of steric strain pertaining to the alkylated complex and to the Co^{II}–radical pair in the electron transfer and subsequent protonation processes, the amount of energy release should meet the above energy requirement (12 kcal/mol). The estimated steric energy at the transition state of the reaction between $Co^{I}(BDHC)$ and isopropyl bromide is ca. 10 kcal/mol (Table VIII). Thus, the strain-energy release upon Co–C bond cleavage for the isopropyl complex must be over 10 kcal/mol. Consequently, the strain-energy release must be a sole origin of the high reducing ability of $Co^{II}(BDHC)$.

Even for the BDHC complexes bearing a relatively bulky primary alkyl ligand, the carbon–cobalt cleavage seems not to be homolytic in nature judging from the predominant formation of the hydrogenation (or reduction) product in the decomposition of the complexes derived from 1-dodecyl bromide, bromomethylmalonate, **3a**, and **4**. The incorporation of hydrogen into the products can hardly take place through the radical mechanism since the methyl radical and presumably other radicals do not abstract a hydrogen atom from water[45,46] and the methyl radical formed by photolysis of the methyl–cobalt bond does not abstract, at least for the cobaloxime complex, the methyl–hydrogen of the peripheral methyl groups.[47] The reductive debromination of alkyl bromides via complex formation with the BDHC complex has an apparent usage for synthetic purposes. Since the reduction of bromo compounds usually requires drastic conditions, the present method prevails over the alternatives in the following respects: (1) the BDHC complex acts as a catalyst, (2) the method is selectively efficient for primary alkyl bromides, (3) it is performed in aqueous media, and (4) alkyl bromides bearing other functional groups can be treated without destroying these groups.

Finally, it needs to be pointed out that while these BDHC complexes are good B_{12} models, they do not catalyze the 1–2 migrations. The BDHC system failed to induce 1,2-rearrangement of the ester or the thioester group in **1** ([Co] = $Co^{III}(BDHC)$) and **3b** in marked contrast to the behavior of the corresponding or related cobalamin complexes.[4a,b] It may indeed be due to the steric repulsion of the angular methyl groups which prevents the initially formed alkyl fragments from staying close to the cobalt.

Experimental Section

General Analyses and Measurements. Elemental analyses were performed at the Microanalysis Center of Kyushu University. Infrared, ^1H NMR, and X-band ESR spectra were taken on a JASCO 403G grating spectrophotometer, Bruker WH-90 FT spectrometer, and JEOL JES-ME-3 spectrometer equipped with a 100-kHz modulation unit, respectively. Elimination of oxygen from the ESR sample solutions was performed by freeze–pump–thaw cycles. Electronic spectra were obtained with thermostated quartz cells of 1-cm path length set in either a Union Giken SM-401 high-sensitive spectrophotometer or a Hitachi 124 spectrophotometer. A Union Giken stopped-flow spectrophotometer RA-401 was used for rapid kinetic measurements. Gas chromatographic analyses were made with a Shimadzu GC-2C gas chromatograph using helium as a carrier gas. Identification of the reaction products was performed by coinjection with authentic samples, using two or three different columns (silicone DC-550, poly(ethylene glycol) 6000, and dioctyl phthalate). Hydrogen ion concentrations (pHs) of aqueous solutions were measured with a Beckman expandomatic SS-2 pH meter equipped with a Metrohm EA-125 combined electrode after calibration with a combination of appropriate aqueous standard buffers.

Cyclic Voltammetry. A Yanagimoto polarograph assembled with P8-PT and P8-ES units was equipped with a three-electrode cell having a platinum working electrode (TOA HP-105, disk area 20 mm^2), an auxiliary platinum electrode (Metrohm EA-211b, area 100 mm^2), gas inlet and outlet tubes, and a saturated KCl–agar bridge connected to a saturated calomel electrode (SCE). For most measurements concentrations of the cobalt complex and tetrabutylammonium perchorate (supporting electrolyte) contained in sample solutions were adjusted at 5×10^{-4} and 5×10^{-2} M, respectively, in methanol, DMF, or dichloromethane. Argon gas saturated with the solvent vapor was bubbled through each sample solution at least for 1 h before voltammetry was performed at room temperature. The sweep rate was changed in the range 5–200 mV/s. The Co(II)/Co(I) potential observed in the voltammetry of $[Co^{II}(BDHC)]ClO_4$ and $[Co^{II}(TDHC)]ClO_4$ in methanol or DMF showed a separation of 70–130 mV (depending on sweep rate) between the corresponding cathodic and anodic peaks, while the separation was slightly larger in dichloromethane. The peak separation for the Co(III)/Co(II) redox couple was somewhat larger and in some cases the cathodic or anodic wave split into two peaks.

Solvents, Alkyl Halides, and Axial Bases. Water was deionized and distilled with a Pyrex distilling apparatus. Methanol, dichloromethane, and DMF as solvents for electrochemistry and THF for kinetic runs were dried by standard procedures and distilled just before use. Commercial alkyl halides of the best grade available were fractionally distilled just before use. (Bromomethyl)cyclohexane and 1-bromo-3-methylcyclohexane were obtained by bromination of the corresponding alcohols with PBr_3. 3-Hydroxymethylcyclohexan-1-ol obtained by reduction of 3-hydroxycyclohexane-1-carboxylic acid with B_2H_6 was converted to 1-bromo-3-(bromomethyl)cyclohexane. Purification of pyridine and substituted pyridines was described previously.[15]

Dimethyl Bromomethylmalonate. This compound was prepared by a reported procedure.[4a]

(41) The reduction potential for saturated alkyl radicals must be more negative than −2 V vs. SCE (Mann, C. K.; Barnes, K. K. "Electrochemical Reactions in Nonaqueous Systems"; Marcel Dekker: New York, 1970; Chapter 7). The standard free-energy change for reaction 5 is estimated to be over 58 kcal/mol if the $Co^{II}(BDHC)/Co^{III}(BDHC)$ redox potential is +0.5 V vs. SCE in methanol.

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S-Ethyl β-Bromo(isobutane)thioate. β-Bromoisobutanoic acid (5.5 g) was converted to the corresponding acid chloride by refluxing it in thionyl chloride for 4 h: yield 5.0 g (77%); bp 60–62 °C (13.5mmHg); IR (neat) 1795 cm^{-1} (C=O str). Into a refluxing solution of the acid chloride (22.3 g) and pyridine (9.5 g) in benzene (50 mL) was added dropwise a solution of ethyl mercaptan (8.9 g) in benzene (50 mL) in a period of 1 h, and the mixture was further refluxed for 5 h. The organic layer was separated after addition of water, washed successively with dilute hydrochloric acid (pH 1) (200 mL × 5), aqueous sodium bicarbonate (pH 8) (200 mL × 5), and water (200 mL × 5), and dried over sodium sulfate. The solvent was evaporated off, and the residue was distilled to give the thioester: yield 3.2 g (13%); bp 90–92 °C (16mmHg); IR (neat) 1695 cm^{-1} (C=O str); NMR ($CDCl_3$, Me_4Si) δ 1.27 (3 H, t, CH_2CH_3), 1.32 (3 H, d, $CHCH_3$), 2.91 (2 H, q, CH_2CH_3), 3.06 (1 H, m, $CHCH_3$), and 3.50 (2 H, d, CH_2Br); M^+ *m/e* 212 and 210. Anal. Calcd for $C_6H_{11}BrOS$: C, 34.13; H, 5.25. Found: C, 34.11; H, 5.18.

Authentic Thioesters. The following thioesters were prepared from the corresponding acid chlorides and ethyl mercaptan in a manner as described above. *S*-Ethyl butanethioate: bp 37.5 °C (12mmHg); IR (neat) 1700 cm^{-1} (C=O str). *S*-Ethyl isobutanethioate: bp 80.5 °C (65mmHg); IR (neat) 1695 cm^{-1} (C=O str). *S*-Ethyl 2-methylpropenethioate (thioester of methacrylic acid): bp 50.5 °C (14mmHg); IR (neat) 1670 (C=O str) and 1640 cm^{-1} (C=C str). *S*-Ethyl *trans*-2-butenethioate (thioester of crotonic acid): bp 43 °C (27mmHg); IR (neat) 1675 (C=O str) and 1638 cm^{-1} (C=C str). *S*-Ethyl propanethioate: bp 115–118 °C; IR (neat) 1700 cm^{-1} (C=O str).

Cobalt Complexes of 8,12-Diethyl-1,2,3,7,13,17,18,19-octamethyl-*AD*-didehydrocorrin (BDHC). (8,12-Diethyl-1,2,3,7,13,17,18,19-octamethyltetradehydrocorrinato)cobalt(II) perchlorate ($[Co^{II}(TDHC)]ClO_4$)[14,15] (1.0 g) in methanol (150 mL) containing acetic acid (1.5 g) was hydrogenated over 10% palladium carbon (0.8 g) at 80–85 °C and the initial hydrogen pressure of 85 kg/cm^2 for 4 h. Evaporation of the solvent followed by preparative TLC on silica gel (type 60, E. Merck, Darmstadt) with chloroform containing acetic acid (1% v/v) afforded $[Co^{II}(BDHC)]ClO_4$: yield ca. 20%; IR (KBr disk) 1090 (ClO_4^- str) and 618 cm^{-1} (ClO_4^- def). Anal. Calcd for $C_{31}H_{41}ClCoN_4O_4$: C, 59.28; H, 6.58; N, 8.92. Found: C, 58.11; H, 6.58; N, 8.30. Slight disagreement in the analytical data is attributed to slow oxidative decomposition during the analysis, which was independently noticed. The product was readily autoxidized in aqueous media to give $[(H_2O)_2Co^{III}(BDHC)]^{2+}$, while it was quite resistant to autoxidation in organic solvents. A dichloromethane solution of $[Co^{II}(BDHC)]ClO_4$ was degassed without changing the visible spectrum, indicating that the oxygen complex was not present in a detectable amount at room temperature.

The reaction mixture, which was obtained by the hydrogenation of $[Co^{II}(TDHC)]ClO_4$ (0.6 g), was poured into water (350 mL) containing NaCN (3.5 g), extracted with chloroform, and dried over magnesium sulfate. The solvent was removed, and the residue was subjected to repeated preparative TLC on silica gel (type 60, E. Merck, Darmstadt) containing NaCN (2.3% by weight). Chloroform containing acetic acid (1% v/v) or chloroform–methanol (10:1 v/v) was used as eluant. The reddish purple fraction was extracted with chloroform, and the extract was evaporated at room temperature by bubbling through it with dry nitrogen after addition of NaCN (50 mg). Reextraction with chloroform followed by precipitation with petroleum ether gave $(CN)_2Co^{III}(BDHC)$: yield ca. 10%; IR (KBr disk) 2123 cm^{-1} (CN str); NMR ($CDCl_3$, Me_4Si) δ 5.97 (2 H, s, C(5)–*H* and C(15)–*H*), 5.91 (1 H, s, C(10)–H), 3.7–2.7 (4 H, broad, H's on saturated carbons C(7), C(8), C(12), and C(13)), 2.11 and 2.29 (12 H, s, CH_3 s on unsaturated carbons C(2), C(3), C(17), and C(18)), 1.55–1.1 (10 H, d centered at 1.41, CH_3's on saturated carbons C(7) and C(13); and overlapping m, CH_2CH_3), 0.97 (6 H, t, CH_2CH_3), 0.84 (6 H, s, C(1)–CH_3 and C(19)–CH_3), and 1.65 (4 H, broad s, H_2O; integrated intensity corresponds to about two molecules and disappeared upon deuteration). Anal. Calcd for $C_{33}H_{41}CoN_6 \cdot 2H_2O$: C, 64.29; H, 7.03; N, 13.63. Found: C, 64.01; H, 7.02; N, 13.02.

Into a solution of $(CN)_2Co^{III}(BDHC)$ (50 mg) in water (30 mL) was added a minimal amount of acetic acid which caused a spectral change. The resulting solution of $[(CN)(H_2O)Co^{III}(BDHC)]^+$ was freed from hydrogen cyanide by bubbling through it with nitrogen for 5 h; the electronic spectrum of an aliquot taken and made alkaline showed no sign for the existence of $[(CN)_2Co^{III}(BDHC)]$, indicating complete removal of hydrogen cyanide. The solution thus prepared was used for equilibrium studies. The whole solution was evaporated to give a dark brown solid; IR (KBr disk) 2195 cm^{-1} (CN str).

Determination of Equilibrium Constants. The stability constant for coordination of a pyridine base to $[(CN)(H_2O)Co^{III}(BDHC)]^+$ in water was determined by measuring spectral changes for a series of solutions containing the cobalt complex (6.4×10^{-5} M) and varying amounts of a pyridine base. With all the substituted pyridines, clear isosbestic points were observed. Plot of a reciprocal absorbance change at a wavelength in the α-band range of the pyridine adduct against a reciprocal concentration of the free-base form of a pyridine yielded a straight line. The stability constant was determined from the slope and the intercept by using a Benesi–Hildebrand type correlation.[48] The stability constant for coordination of a pyridine base to $[Co^{II}(BDHC)]^+$ in dichloromethane was also determined spectrophotometrically. The spectra were recorded for a series of solutions of $[(CN)(H_2O)Co^{III}(BDHC)]^+$ and $[(H_2O)_2Co^{III}(BDHC)]^{2+}$ in aqueous buffers at various pHs. The absorbance change at α- or γ-band was plotted against pH, and the pK_a values for acid dissociation of the coordinated water were determined graphically. Buffer components were as follows: acetate (or borate)–phosphate for pH 4.74–6.96 and borate–carbonate, phosphate–NaOH, or NaOH for pH 9.86–12.20.

Kinetic Runs. A solution of $(CN)_2Co^{III}(BDHC)$ (2.0×10^{-5} M) in water–THF (1:1 or 1:2 v/v) was prepared in a spectrophotometric cell of 1-cm path length which was thermostated at 25.0 ± 0.1 °C. The solution was deoxygenated with argon stream. Into the solution was added 20 μL of an aqueous solution of $NaBH_4$ (2 M). Reduction of the complex to the Co(I) state was instantaneous. Either an alkyl halide itself or a solution of an alkyl halide in THF was injected, the mixture was quickly shaken, and the decrease in absorbance at 400 nm characteristic of $Co^I(BDHC)$ was monitored. In all cases except for methyl bromide, an alkyl halide was used in excess to maintain pseudo-first-order kinetics. The reaction with methyl iodide was followed by the stopped-flow technique. The reaction with methyl bromide was carried out under second-order conditions. In all cases, clear isosbestic points were observed during conversion of the Co(I) complex to the corresponding alkylated complexes. Reactions under pseudo-first-order conditions provided straight-line correlations for ln ($OD_t - OD_\infty$) vs. time, and the slopes (pseudo-first-order rate constants) were divided by the initial concentrations of the alkyl halides to give the second-order rate constants. For runs under second-order conditions, a value of

$$\ln \frac{(OD_t - OD_0)[Co(I)]_0 + (OD_0 - OD_\infty)[RX]_0}{(OD_t - OD_\infty)[Co(I)]_0}$$

was plotted against time. The second-order rate constant was evaluated from the slope by

$$k = (\text{slope})/([RX]_0 - [Co(I)]_0)$$

Control experiments showed that even the isopropylcobalt complex, once formed, was stable in the dark under the kinetic conditions.

Photolyses. Solutions of the methyl-, ethyl-, and isopropylcobalt complexes in water containing 1% (v/v) methanol were prepared by prereduction of $Co^{II}(BDHC)$ (4.0×10^{-5} M) with 20 μL of an aqueous solution of $NaBH_4$ (2 M), treatment with an excess amount of the corresponding alkyl iodides, and finally addition of 30 μL of 1 N HCl to decompose excess $NaBH_4$. The pH of the resulting solution was observed to be 2.3. Appropriate amounts of formate or acetate were added for runs at other pHs. For aerobic photolysis, no care was taken to eliminate oxygen in all experimental procedures including preparation of sample solutions, and each solution was irradiated with a 200-W tungsten lamp from a distance of 60 cm. The solution spectra were measured at appropriate time intervals, and the photolysis rate or the half-life was evaluated from the change in absorbance in the 400-nm range which is characteristic of an alkylcobalt complex. The anaerobic photolysis was carried out by using a specially designed cell. A solution of $Co^{II}(BDHC)$ in water was placed in the cell. Argon gas was introduced into the cell first. Then, the reagents ($NaBH_4$, alkyl halide, HCl, and KCN if necessary) were injected with a microsyringe under argon atmosphere, and argon was further bubbled through the sample solution for 40 min for most runs. The solution was irradiated after any openings of the cell were closed.

Reaction of Co^I(BDHC) with Bromo Thioester (3a). A solution of $(CN)_2Co^{III}(BDHC)$ (200 mg) in water (1 L) was deoxygenated by bubbling through it with nitrogen, and $NaBH_4$ (200 mg) was added to the solution. After the solution was allowed to stand for 10 min, the complete formation of $Co^I(BDHC)$ was confirmed by electronic spectroscopy. Then, the bromo thioester (**3a**) (400 mg) was added to it. The formation of the alkylated-BDHC complex (**3b**) was confirmed by electronic spectroscopy. The mixture was stirred for 24–48 h under nitrogen in the dark and then extracted with ether. After usual workup, the reaction mixture was analyzed by means of gas chromatography. The thioester of isobutyric acid (**3c**) and the thioester of methacrylic acid in a less amount were detected. The above reaction was also carried out under the following modified conditions: $[Co^{II}(BDHC)]ClO_4$ in place of $(CN)_2Co^{III}(BDHC)$; medium, water–THF (1:1 v/v) or aqueous hex-

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adecyltrimethylammonium bromide (CTAB) solution (2.5×10^{-3} M); buffer, phosphate–borate (0.01 M) at pH 7; under irradiation for some reactions. In all of these experiments, the products were identical with those obtained without modification; and the thioester of butyric acid, the isomerization product, was not detected in any case. A control reaction, for which only the cobalt complex was absent, yielded the thioester of methacrylic acid, but that of isobutyric acid (**3c**) was not detected.

Reaction of Co^{I}(BDHC) with Dimethyl Bromomethylmalonate. The reaction was carried out in a similar manner as described above for the one with the bromo thioester (**3a**). At the end of the reaction, the solution was acidified (pH 1) by adding hydrochloric acid. The mixture was continuously extracted with ether (200 mL) for 20 h.[4a] After evaporation of the solvent, the residue was treated wtih diazomethane and analyzed by means of gas chromatography; dimethyl methylmalonate was detected, whereas dimethyl succinate, the isomerization product, was not. A control experiment without the cobalt complex yielded no detectable amount of dimethyl methylmalonate under otherwise identical reaction conditions.

Catalytic and Selective Reduction of Primary Alkyl Bromides. $(C-N)_2Co^{III}$(BDHC) (30 mg, 0.05 mmol) in aqueous CTAB solution (2.5×10^{-2} M, 70 mL) was reduced with $NaBH_4$ (60 mg, 1.6 mmol) to the Co(I) state. 1-Dodecyl bromide (250 mg, 1.0 mmol) was added to the solution under nitrogen. The mixture was cooled down with ice water, irradiated with a 250-W tungsten lamp from a distance of 20 cm for 4 h, and extracted with ether (100 mL × 4). The ether extract was washed with water (100 mL × 3), dried over sodium sulfate, and evaporated to dryness. The residue was chromatographed on a column of silica gel (Wako gel C-100) with petroleum ether (300 mL) as eluant: an oil (200 mg), a 1:2.5 mixture of dodecane and 1-dodecyl bromide by gas chromatographic and NMR analyses. The yield of dodecane was 0.25 mmol or 500% based on the amount of the cobalt complex used. The reductive debromination of 1-bromo-3-(bromomethyl)cyclohexane (0.25 mmol) with $NaBH_4$ (0.75 mmol) as catalyzed by $[Co^{II}(BDHC)]ClO_4$ (0.025 mmol) and the competitive debromination of 1-dodecyl bromide (0.13 mmol) and 2-octyl bromide (0.13 mmol) with $[Co^{II}(BDHC)]ClO_4$ (0.025 mmol) and $NaBH_4$ (0.75 mmol) were carried out, and the products were analyzed in a similar manner.

Preparation of Monocyclopentadienyl Benzylidene Complexes of Tantalum and the Crystal Structure of $Ta(\eta^5\text{-}C_5Me_5)(CHPh)(CH_2Ph)_2$[1a]

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Abstract: A benzylidene complex, $Ta(\eta^5\text{-}C_5Me_5)(CHPh)(CH_2Ph)Cl$, can be prepared by adding LiC_5Me_5 to $Ta(CH_2Ph)_3Cl_2$. The analogous $\eta^5\text{-}C_5H_5$ complex apparently is unstable but a relative, $Ta(\eta^5\text{-}C_5H_4Me)(CHPh)(CH_2Ph)_2$, can be prepared by dehydrohalogenating $Ta(\eta^5\text{-}C_5H_4Me)(CH_2Ph)_3Cl$ with $Ph_3P{=}CH_2$ while $Ta(\eta^5\text{-}C_5Me_5)(CHPh)(CH_2Ph)_2$ can be prepared from $Ta(\eta^5\text{-}C_5Me_5)(CHPh)(CH_2Ph)Cl$ and $Mg(CH_2Ph)_2$. Adding LiC_5Me_5 to $Ta(CH_2Ph)_2Cl_3$ gives $Ta(\eta^5\text{-}C_5Me_5)(CH_2Ph)_2Cl_2$ which can be forced to eliminate toluene by pyrolysis or photolysis to give $Ta(\eta^5\text{-}C_5Me_5)(CHPh)Cl_2$ in low yield. An X-ray structural determination of $Ta(\eta^5\text{-}C_5Me_5)(CHPh)(CH_2Ph)_2$ shows a molecule of the expected "three-legged stool" type. The benzylidene ligand's large $Ta{-}C_\alpha{-}C_\beta$ angle (166°) and short $Ta{=}C_\alpha$ bond (1.88 Å) make it seem more like a benzylidyne ligand. We believe this circumstance is due primarily to the metal's need for more electron density (which it acquires from the $C{-}H_\alpha$ bond) and that any contribution to the large $Ta{=}C_\alpha{-}C_\beta$ angle due to steric interaction between the benzylidene's phenyl ring and the $\eta^5\text{-}C_5Me_5$ ring is relatively small.

Introduction

In the past few years, we have found that certain complexes of Ta(V) and Nb(V) which contain at least two neopentyl groups decompose to yield neopentane and neopentylidene complexes by a process which we have called α-hydrogen abstraction.[2] One of the best studied examples is $Ta(\eta^5\text{-}C_5H_5)(CHCMe_3)Cl_2$.[3] This type of species also seems to be more interesting than one of the 18-electron, dicyclopentadienyl variety (e.g., $Ta(\eta^5\text{-}C_5H_5)_2(CHCMe_3)Cl$)[4] since it is electron deficient (14 electrons) and therefore reacts more readily with small molecules such as olefins.[5]

In contrast, the number of analogous benzylidene complexes is small. The only known example is 18-electron $Ta(\eta^5\text{-}C_5H_5)_2(CHPh)(CH_2Ph)$ which is formed when TlC_5H_5 is added to $Ta(CH_2Ph)_3Cl_2$.[4] There is also evidence that $Ta(CHPh)(CH_2Ph)_3$ (cf. $Ta(CHCMe_3)(CH_2CMe_3)_3$[6]) is formed when $Ta(CH_2Ph)_5$ decomposes in a first-order manner,[7] but it is apparently unstable under the reaction conditions.[8] One type of electron-deficient benzylidene complex which should be stable toward intermolecular decomposition reactions is one containing a single cyclopentadienyl ring, e.g., $Ta(\eta^5\text{-}C_5H_5)(CHPh)(CH_2Ph)Cl$, a possible intermediate in the reaction which gives $Ta(\eta^5\text{-}C_5H_5)_2(CHPh)(CH_2Ph)$. Therefore we set out to prepare this or related species by adding a cyclopentadienyl ring to benzyl complexes.

Results

Preparation of $Ta(CH_2Ph)_yCl_{5-y}$ (y = 1, 2, or 4). The only reported benzyl complexes of this type are $Ta(CH_2Ph)_3Cl_2$,[9]

(1) (a) Multiple Metal-Carbon Bonds. 17. For Part 16 see: Wengrovius, J. H.; Schrock, R. R.; Churchill, M. R.; Missert, J. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 4515. (b) MIT; Dow Predoctoral Fellow, 1976–1978. (c) MIT; Camille and Henry Dreyfus Teacher-Scholar Grant Recipient, 1978. (d) Present address: Sandia Laboratories, Alburquerque, New Mexico.

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