# σ-Bonded Organic Derivatives of a Cobalt(III) Macrocyclic Complex

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Abstract: A new series of vitamin B_{12} coenzyme model compounds has been prepared. They contain 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene (CR) (structure I) as the planar ligand and σ-bonded alkyl groups (R) as one of the axial ligands, [RCo^{III}(CR)X]Y. The compounds have been characterized by elemental analysis, electrical conductivity, infrared spectra, and nmr spectra. Their electronic spectra exhibit significant features. The electronic spectral bands are tentatively assigned and correlated with the photolability, which is characteristic of this type of compound.

O f late several σ-bonded organo derivatives of first transition series metals in rather well-defined oxidation states have been reported. Examples are [(C$_2$H$_5$)$_2$Fe^{II}(bipy)$_2$],[2] [(C$_2$H$_5$)$_2$Ni^{II}(bipy)],[3,4] [RCo^{III}(DMG)$_2$L],[5] [RCo^{III}(BAE)],[6] [RCo^{III}(SALEN)],[7] [RCo^{III}(etioporphin)],[8] [RCo^{III}(CR)Br]Y,[9] and several derivatives of vitamin B_{12} coenzyme[10] (bipy is bipyridyl; DMG, dimethylglyoximato; BAE, bis(acetylacetone)ethylenediamine; SALEN, bis(salicylaldehyde)ethylenediamine; and CR, 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.11]-heptadeca-1(17),2,11,13,15-pentaene (structure I). The

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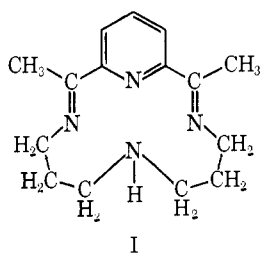
significance of the cobalt–alkyl complexes as models for vitamin B_{12} coenzyme has been discussed in some detail.[5,6] Pioneering studies in this area are due to Schrauzer.[5] In this report consideration is given to the nature and stability of the metal–carbon bond, taking [RCo^{III}(CR)Br]Y as the main example.

Experimental Section

Preparation of Co^{II}(CR)Br$_2$·H$_2$O. This procedure closely follows that of Karn for the preparation of Ni(CR)Br$_2$·H$_2$O.[11] Diacetylpyridine (16.3 g, 0.10 mole) is dissolved in 150 ml of hot

ethanol. Water (100 ml) is added. Cobalt(II) bromide (21.8 g, 0.10 mole) is added and dissolved in the hot mixed solvent. The solution is held at 65–75° and stirred as 3,3′-diaminodipropylamine (13.1 g, 0.10 mole) is added. The solution becomes cloudy on addition of the amine. Glacial acetic acid (4 ml) is added to clarify the solution. The dark red solution is stirred and heated at 65–75° for 4–6 hr. After removing about one-half of the ethanol under reduced pressure, the hot solution is filtered. A concentrated solution of lithium bromide in ethanol (50 ml) is added and the solution is set aside to cool to room temperature. The product is collected on a fritted-glass funnel and washed with ethanol. This product is recrystallized from hot ethanol with the addition of lithium bromide solution. Black needles of the monohydrate form and are filtered from the solution, washed with ethanol, and dried *in vacuo* over P$_4$O$_{10}$, yield 60%. *Anal.* Calcd for CoC$_{15}$H$_{22}$N$_4$Br$_2$·H$_2$O: C, 36.39; H, 4.85; N, 11.32; Br, 32.28. Found: C, 36.60; H, 4.78; N, 11.36; Br, 32.50.

[CH$_3$Co(CR)Br]PF$_6$. Co(CR)Br$_2$·H$_2$O (1 g, 0.002 mole) is dissolved in 50 ml of methanol in an erlenmeyer flask under nitrogen at room temperature. To this solution methyl iodide (about 3 molar equiv) is added, followed by 0.1 g of sodium borohydride. The color of the solution changes quickly from dark red-brown to blue-green and then to bright red upon the addition of sodium borohydride. The reaction is allowed to proceed for 5 min, although it seems to be complete in less than 1 min. The solution is filtered quickly and about 2 equiv of NH$_4$PF$_6$, in aqueous solution, is added to the filtrate. Nothing precipitates at this stage. The bulk of the methanol is removed rapidly by a means of rotary evaporator, and red crystals separate. They are collected on a filter funnel, washed with cold water and a small amount of cold methanol, and air-dried. The yield is 0.5 g (45%). *Anal.* Calcd: C, 34.31; H, 4.52; N, 10.06. Found: C, 34.48; H, 4.53; N, 9.95. Nmr: CH$_3$ at τ 9.47.

[C$_2$H$_5$Co(CR)Br]PF$_6$·$^{1}/_2$H$_2$O. The method described above is used except that ethyl bromide or ethyl iodide is used in place of methyl iodide, yield 25%. *Anal.* Calcd: C, 35.19; H, 4.86; N, 9.66. Found: C, 35.37; H, 4.91; N, 9.43. Nmr: CH$_3$ (of C$_2$H$_5$) at τ 10.33 (triplet, $J \sim$ 7.5 cps), CH$_2$ (of C$_2$H$_5$) at τ 8.45 (quartet, $J \sim$ 7.5 cps).

[*n*-C$_4$H$_9$Co(CR)Br]PF$_6$·xH$_2$O is obtained by the essentially same method using *n*-butyl bromide instead of ethyl iodide. This product has not been studied in detail (nmr, CH$_3$(CH$_2$)$_3$ at τ 9.3–8.4).

[ClCH$_2$Co(CR)Br]PF$_6$·$^{1}/_2$H$_2$O. This compound is prepared by essentially the same method described above. The formation reaction with CH$_2$Cl$_2$ is, however, rather slow and takes a few minutes to reach completion, yield 40%. *Anal.* Calcd: C, 31.99; H, 4.20; N, 9.33. Found: C, 32.27; H, 4.20; N, 9.55.

[CH$_2$=CHCo(CR)Br]PF$_6$·$^{1}/_2$H$_2$O. The method is the same as that used for the methyl derivative except that vinyl bromide is added instead of methyl iodide. The compound is isolated as a brown powder, yield 35%. *Anal.* Calcd: C, 35.31; H, 4.53; N, 9.69. Found: C, 35.21; H, 4.55; N, 9.55. Ir: ν(C=C) at 1608 cm^{-1}.

[C$_6$H$_5$CH$_2$Co(CR)Br]PF$_6$·H$_2$O. One gram of Co(CR)Br$_2$·H$_2$O is dissolved in 50 ml of methanol in an erlenmeyer flask under nitrogen at 0°. To this solution, benzyl chloride (1.5 molar equiv) is added, followed by 0.1 g of sodium borohydride. The color of the solution changes quickly from dark red-brown to blue-green and, finally, to brownish red, and a dark brown precipitate forms.

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(2) A. Yamamoto, Y. Morifuji, T. Saito, Y. Uchida, A. Misono, and G. Ikeda, *J. Am. Chem. Soc.*, 87, 4652 (1965).

(3) T. Saito, Y. Uchida, A. Misono, A. Yamamoto, Y. Morifuji, and S. Ikeda, *ibid.*, 88, 5198 (1966).

(4) G. E. Wilke and E. Herrman, *Angew. Chem.*, 78, 591 (1966).

(5) G. N. Schrauzer, *Accounts Chem. Res.*, 1, 97 (1968), and references cited therein.

(6) G. Costa, G. Mestroni, G. Tauzher, and L. Stefani, *J. Organometal. Chem.*, 6, 181 (1966); G. Costa and G. Mestroni, *ibid.*, 11, 325 (1968).

(7) G. Costa, G. Mestroni, and L. Stefani, *ibid.*, 7, 493 (1967); G. Costa, G. Mestroni, and G. Pellizer, *ibid.*, 11, 333 (1968).

(8) D. A. Clarke, R. Grigg, and A. W. Johnson, *Chem. Commun.*, 208 (1966).

(9) E. Ochiai and D. H. Busch, *ibid.*, 905 (1968).

(10) *Cf.* K. Bernhauer, O. Müller, and F. Wagner, *Angew. Chem. Intern. Ed. Engl.*, 3, 200 (1964); R. Bonnett, *Chem. Rev.*, 63, 573 (1963).

(11) J. L. Karn and D. H. Busch, *Nature*, 211, 160 (1966).

This precipitate is isolated by filtering, and about 3 molar equiv of NH_4PF_6 (in aqueous solution) is added to the filtrate. When the bulk of the methanol solvent is evaporated (rapidly) by means of a rotary evaporator, brownish red crystals form. They are collected on a filter funnel, washed with cold methanol, and air-dried, yield 30%. *Anal.* Calcd: C, 40.54; H, 4.78; N, 8.60. Found: C, 40.15; H, 4.81; N, 9.02. Ir: δ(CH) of benzyl at 739 and 695 cm^{-1}.

Other Compounds. The formation reaction of the allyl derivative, using allyl bromide, proceeds in close similarity to those cases mentioned above, but this substance is so reactive that no solid product has yet been isolated.

The reduction of $Co(CR)Br_2 \cdot H_2O$ with sodium borohydride in the presence of acrylonitrile, followed by the addition of an aqueous solution of NH_4PF_6, yields a brown compound, which has the composition $[NCCH_2CH_2Co(CR)Br]PF_6 \cdot \frac{1}{2}H_2O$. *Anal.* Calcd: C, 35.72; H, 4.50; N, 11.57. Found: C, 35.92; H, 4.41; N, 11.64. Ir: ν(C≡N) at 2240 cm^{-1}. This compound has not been studied in detail. $[RCo(DMG)_2L]$ complexes (R = CH$_3$, C$_2$H$_5$; L = H$_2$O, py) are prepared by a method similar to that of Schrauzer, *et al.*[5]

Measurement of the Rate of Photodecomposition. The reaction was effected in a quartz cell (1-cm path) using a conventional tungsten lamp and a solution of about 4.5×10^{-4} M concentration. The cell was placed in the same position in each experiment and the temperature was $24.5 \pm 1°$. The change in concentration of the compound in question was measured by the change in optical density at a suitable wavelength. All the photodecomposition reactions studied followed the first-order rate law quite well. The spectra were recorded with Cary Model 14 spectrophotometer.
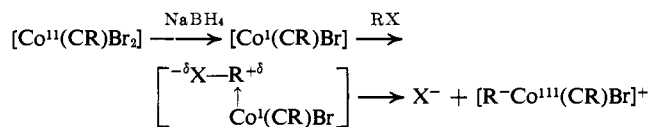
Results and Discussion

Preparation. The general method of preparation of these compounds involves the reduction of $Co^{II}(CR)$-$Br_2 \cdot H_2O$ with sodium borohydride in the presence of an appropriate alkyl halide. This procedure is, in essence, the same as the method used for the preparation of $[RCo(DMG)_2L]$,[5] $[RCo(BAE)]$,[6] and $[RCo(SALEN)]$.[7] The second general method of preparation that has been applied to the synthesis of carbon–metal σ-bonded compounds of this type is based on the use of strongly reducing alkylating agents, such as trialkylaluminum[2–4] and Grignard reagents.[5–7] The third general method which is applicable to the formation of transition metal-to-carbon σ bonds is the thermal odd electron (free radical) reaction that has been observed to occur between a d^4 (*e.g.*, Cr^{2+}) or d^7 (*e.g.*, Co^{2+}) metal ion in its complex and an alkyl halide.

In the first general method, prereduction generates the strongly nucleophilic low-valent metal atom, *e.g.*, Co^I (or Fe^0 or Mn$^-$). It is assumed that the high-energy (e$_g$)^2 electrons outside a (t$_{2g}$)^6 core attack the electrophilic carbon atom of the alkyl halide. The nucleophilicity of Co^I in the Co–DMG system has been discussed recently.[12] The second method might proceed similarly; however, it is also reasonable to assume that the carbanion from AlR$_3$ or RMgX simply displaces a ligand and coordinates with the metal ion. The last type of reaction has been observed with the d^4 and d^7 (low-spin) electronic configurations, both of which have one high-energy (e$_g$) electron outside of (t$_{2g}$)^3 or (t$_{2g}$)^6 cores. This electron behaves like the odd electron in a free radical.[13]

The mechanism of the first type of reaction is of immediate interest. It is well known[14] that the oxidative addition reactions of (for example) d^8 compounds are slower for coordinatively saturated deriv-

(12) G. N. Schrauzer, E. Deutsch, and R. J. Windgassen, *J. Am. Chem. Soc.*, **90**, 2441 (1968).
(13) J. Halpern, *Chem. Eng. News*, **46**, 68 (Oct 31, 1968).
(14) *E.g.*, *cf.* J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968).

atives, *i.e.*, five-coordinated, than for those that are coordinatively unsaturated; *i.e.*, four- (or less) coordinated. This is in accord with the expectation that vacant sites are necessary to the mechanisms of coordinative oxidative addition. In fact, many oxidative coordination reactions occur between four-coordinate d^8 complexes like $[Ir(CO)Cl(P\{C_6H_5\}_3)_2]$ and alkyl halides, hydrogen halides, the hydrogen molecule, etc. Though the present reaction amounts to an oxidative coordination, it takes place between a five-coordinate d^8 (Co^I) (coordinately saturated) species and the alkyl halides. That the reactive Co^I species are five-coordinate is substantiated by the fact that $[RCo(CR)Br]^+$ is obtained regardless of the nature of RX with X = Cl, Br, or I. This requires that the Co^I(CR) species which is formed by the reduction of $Co(CR)Br_2 \cdot H_2O$ with NaBH$_4$ retains one of the Br$^-$ ions in its coordination sphere during the reaction, *i.e.*, that it is at least five-coordinate. The reaction is very fast, reaching completion within a few minutes, as in the case of the Co(DMG)$_2$ system.[12] The reaction rate depends on the halide of the RX molecule, being slowest in the case of the chloride. This is in accord with a mechanism requiring nucleophilic attack of the Co^I species upon the carbon atom of the alkyl halide. Thus, the mechanism of the preparation reaction of these complexes is

$$[Co^{II}(CR)Br_2] \xrightarrow{\text{NaBH}_4} [Co^I(CR)Br] \xrightarrow{\text{RX}}$$

$$\left[\begin{array}{c} ^{-\delta}X\text{---}R^{+\delta} \\ \uparrow \\ Co^I(CR)Br \end{array} \right] \longrightarrow X^- + [R^-Co^{III}(CR)Br]^+$$

This mechanism, of course, does not invoke the principle of d^8 *unsaturatedness* mentioned above, because, in the formal sense, R$^+$ contributes no electrons to the complex upon coordination to coordinately saturated d^8 species. Thus, it should be noted that the nucleophilicity of the cobalt, or the existence of high-energy electrons (one in the case of d^4 or d^7; two in d^8, d^9, d^{10}, or possible d^5), is the more general essential requirement for oxidative addition reactions in metal complexes.

It is also well established that olefins act as alkylating agents in these systems. In fact, acrylonitrile reacts with $Co(CR)Br_2 \cdot H_2O$ in a procedure similar to that described above for alkyl halides, and forms $[NCCH_2$-$CH_2Co(CR)Br]^+$ (after addition of water). This reaction may involve a π complex between Co^I species and acrylonitrile as the intermediate in the first step, as postulated by Schrauzer.[5]

Characterization. The results of chemical analyses and infrared and nmr spectral data are recorded in the Experimental Section. The molar conductances of these complexes are reported in Table I. These conductance data show that the compounds $[RCo(CR)$-$Br]PF_6 \cdot nH_2O$ exist as 1:1 electrolytes in methanol solutions, as expected, and that they become 2:1 electrolytes in aqueous solutions. Thus, the coordinated bromide is readily replaced by water but not by methanol. This aquation is also inferred from visible spectral data. The position *trans* to the alkyl group in such complexes as $RCo(DMG)_2L$, $RCo(BAE)L$, and $RCo(SALEN)L$ is known to be very labile. In fact, even five-coordinate species like $RCo(DMG)_2$, $RCo(BAE)$, and $RCo(SALEN)$ are readily obtained, and rather stable. Though the coordination number

Table I. Molar Conductivities of [RCo(CR)Br]PF₆·nH₂O Complexesᵃ

Complex	Solvent	Molar conductivity, mho cm² mole⁻¹	Electrolyte type
[CH₃Co(CR)Br]PF₆·	MeOH	114	1:1
[CH₃Co(CR)Br]PF₆·	H₂O	201	2:1
[C₂H₅Co(CR)Br]PF₆·¹/₂H₂O	MeOH	109	1:1
[C₂H₅Co(CR)Br]PF₆·¹/₂H₂O	H₂O	205	2:1
[CH₂=CHCo(CR)Br]PF₆·¹/₂H₂O	MeOH	109	1:1
[ClCH₂Co(CR)Br]PF₆·¹/₂H₂O	MeOH	130	1:1
[C₆H₅CH₂Co(CR)Br]PF₆·H₂O	MeOH	100	1:1

ᵃ At 4.5 × 10⁻⁴ M, 25°

represented as the ion pair [CH₃Co(CR)]²⁺Br⁻. The reaction ascribed to the partial formation of a five-coordinate species is also observed in the case of [C₂H₅Co(CR)-Br]PF₆·¹/₂H₂O.

The nmr spectral data for the [RCo(CR)Br]⁺ complexes show the proton signals due to the R group at relatively high fields: CH₃ at τ 9.47 in [CH₃Co(CR)-Br]⁺ and τ 9.58 in [CH₃Co(DMG)₂H₂O];[17] and C₂H₅ at τ 10.33 and 8.45 in [C₂H₅Co(CR)Br]⁺, at τ 9.97 and 8.45 in [C₂H₅Co(DMG)₂(py)]. This suggests that the alkyl group bears more negative charge than the R group in ordinary organic compounds. This change might be smaller in the cases of [RCo(BAE)L] and [RCo(SALEN)L] than in [RCo(CR)Br]⁺ as is indicated by the nmr data.[18]

Table II. Electronic Spectra of σ-Bonded Organic Derivatives of Cobalt(III) Complexesᵃ

Complex	ν_IE	ν_IA	ν_II	ν_III	ν_IV	ν_V	Ref
[CH₃Co(CR)Br]⁺	20.4 (3.02)	21.4 sh (3.02)	25.5 (3.53)			36.0 (3.86)	This work
[CH₃Co(CR)(H₂O)]²⁺	20.6 (2.99)	21.8 sh (2.93)	26.2 (3.31)	sh	32.2 sh	35.3 (3.62)	This work
[CH₃Co(CR)(py)]²⁺	19.9 (3.05)	Obscured	24.6 (3.63)	29.4 (3.67)			This work
[CH₃Co(CR)(PPh₃)]²⁺	20.8 (3.07)	Obscured	27.0 sh			36.4 (3.97)	This work
[CH₃Co(CR)]²⁺	16.1 (2.72)	20.6 (3.08)	25.6 (3.42)			36.2 (3.87)	This work
[C₂H₅Co(CR)Br]⁺	20.6 (2.99)	Obscured	25.0 (3.30)		32.1 sh	35.7 (3.93)	This work
[C₂H₅Co(CR)(H₂O)]²⁺	20.8 (2.94)	Obscured	24.6 (3.09)		31.8 sh	35.7 (3.79)	This work
[C₂H₅Co(CR)]²⁺	15.7	20.5	24.5				This work
[n-C₄H₉Co(CR)(H₂O)]²⁺	20.4 (2.89)	Obscured	24.2 (3.07)	29.1 sh			This work
[ClCH₂Co(CR)Br]⁺	20.5 (2.86)	Obscured	25.3 (3.26)		32.8 sh	34.9 sh (3.99)	This work
[C₆H₅CH₂Co(CR)Br]⁺	19.1 (2.92)	Obscured	25.0 (3.53)			32.9 (4.14)	This work
[C₆H₅CH₂Co(CR)(H₂O)]²⁺	19.2 (2.91)	Obscured	25.6 (3.46)			33.6 (4.03)	This work
[Co(CR)Cl₂]⁺	17.7	21.6	25.0				12
[C₂H₅Co(BAE)]	14.8 (2.80)	22.3 sh (3.08)	25.2 (3.41)	28.6 (3.56)	31.6 (3.90)	36.6 (4.13)	7
[C₂H₅Co(BAE)(py)]	20.1 (2.75)	24.0 sh (3.35)	26.4 (3.57)				7
[CH₃Co(SALEN)]	15.4 (3.15)	22.0 sh (3.42)	25.4 (3.79)	29.2 (4.21)			8
[CH₃Co(SALEN)(py)]	20.4 (3.37)	22.7 sh (3.57)	25.4 (3.76)	28.4 (3.94)			8
[CH₃Co(DMG)₂(H₂O)]		22.0 (3.18)	26.0 (3.19)		31.2 sh	34.6 sh (3.76)	This work
[CH₃Co(DMG)₂(py)]		22.7 (3.06)	26.5 (3.25)			34.7 sh (3.78)	This work
[C₂H₅Co(DMG)₂(py)]		22.1 (3.13)	26.1 (3.24)		31.2 sh	34.7 (3.85)	This work

ᵃ ν in kK (log ε); sh = shoulder.

has not been proven for these substances, their distinct natures are apparent from electronic spectra (Table II). The *trans* effect[15] of alkyl groups, R⁻, in planar platinum complexes is known to be very large (between PR₃ and NO₂⁻), and this strong *trans* effect has been clearly shown in the case of derivatives of vitamin B₁₂.[16] The bromide ion in [RCo(CR)Br]⁺ also seems to be easily replaced by pyridine in that solvent as is inferred from changes in the visible spectra.

The electronic spectrum of methanol solutions of the complex [CH₃Co(CR)Br]PF₆ gradually changes in the dark, and after 15 hr it exhibits a pattern (see Table II) that is very similar to that of the five-coordinate complexes reported by others ([CH₃Co(BAE)] and [C₂H₅Co-(SALEN)]). Although the electrical conductivity of a methanol solution of [CH₃Co(CR)Br]PF₆ that has aged for 15 hr corresponds to expectation for a 1:1 electrolyte, the electronic spectrum strongly suggests the formation of a five-coordinate species. Again, there is a good chance that this distinctive change generates an alternate structure; however, we cannot think of a more likely possibility than that suggested. This might be

Electronic Spectra. The electronic spectra of these compounds are reported in Table II, together with those of closely related compounds. It should be noted that the spectra are quite similar to each other even among complexes of different in-plane ligands. There are two classes of spectra, those of the six-coordinate compounds and those of the supposed five-coordinate species. The spectra generally consist of three peaks (occasionally only two) in the visible region, one or two shoulders in the near-ultraviolet region, and one distinct absorption band at approximately 280 mμ. These general characteristics resemble those of the usual tetragonally distorted octahedral cobalt(III) complexes.[19] In strictly octahedral cobalt(III) complexes two d–d transitions (ν_I, ¹T₁g ← ¹A₁g; and ν_II, ¹T₂g ← ¹A₁g) usually appear in the visible region. Decreasing the symmetry splits the first of these peaks; for example, in the D₄h point group, the ¹T₁g level splits into ¹E_gᵃ and ¹A₂g. The second band, ¹T₂g, also splits to ¹E_gᵇ and ¹B₂g, but the separation between the latter two states is usually too small to detect. The splitting in ¹T₁g becomes larger as the difference in ligand field strength between the in-

(15) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967, p 355.

(16) G. C. Hayward, H. A. O. Hill, J. M. Pratt, N. J. Vanston, and R. J. P. Williams, *J. Chem. Soc.*, 6485 (1965).

(17) G. N. Schrauzer and R. J. Windgassen, *J. Am. Chem. Soc.*, **88**, 3738 (1966).

(18) H. A. O. Hill, K. G. Morale, G. Pellizer, G. Mestroni, and G. Costa, *J. Organometal. Chem.*, 11, 167 (1968).

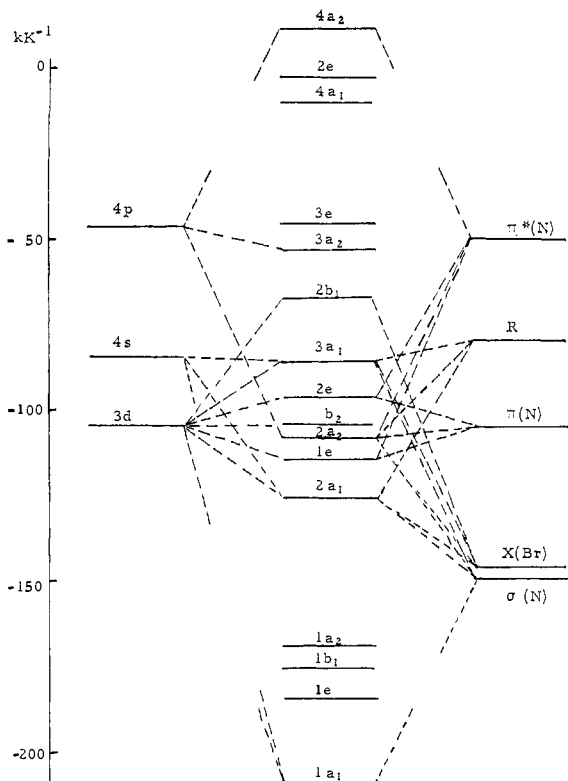(19) A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, 4, 704 (1965).

Figure 1. Molecular orbital energy level diagram for [CH₃Co^III-(CR)Br]PF₆ (qualitative).

Table III. Dq^z Value for the Alkyl Group in $[RCo(CR)X]^{n+}$ and Related Complexes

Complex	$Dq^z(R + X)$, cm⁻¹	$Dq^z(R)$,[a] cm⁻¹
[CH₃Co(CR)]²⁺	1330	2660
[CH₃Co(CR)Br]⁺	2350	3400
[CH₃Co(CR)(H₂O)]²⁺	2330	2940
[CH₃Co(CR)(py)]²⁺	2030	2740
[C₂H₅Co(CR)Br]⁺	2330	3360
[C₂H₅Co(CR)(H₂O)]²⁺	2370	3020
[C₆H₅CH₂Co(CR)Br]⁺	2030	2760
[C₆H₅CH₂Co(CR)(H₂O)]²⁺	2050	2380
[C₂H₅Co(BAE)]	1100	2200
[C₂H₅Co(BAE)(py)]	2160	3000
[CH₃Co(SALEN)]	1250	2500
[CH₃Co(SALEN)(py)]	2250	3180

[a] Additivity is assumed. $Dq^z(R + X) = \frac{1}{2}\{Dq^z(R) + Dq^z(X)\}$. Other values used are $Dq^z(py) = 1320$ cm⁻¹, $Dq^z(Br) = 1300$ cm⁻¹, and $Dq^z(H_2O) = 1720$ cm⁻¹.

plane ligand and the axial ligand increases. Since the complexes in question crudely approximate D₄ symmetry (the actual symmetry may not be higher than C₂), the following assignments may tentatively be made in the d–d transition region. The first peak around 14.5∼ 21.0 kK is ascribed to the transition ¹E^a ← ¹A₁, the second peak (shoulders in most cases) around 21.0– 22.0 kK to the transition ¹A₂ ← ¹A₁, and the third peak around 25.0 kK to the transition ¹E^b, ¹B₂ ← ¹A₁. Wentworth and Piper[19] devised a method of analysis of the d–d transitions in the spectra of tetragonal cobalt-(III) complexes. A formal application of their method gives the results shown in Table III. Dq^{xy}(BAE) and Dq^{xy}(SALEN) are estimated from the average value of ν_1A, and Dq^{xy}(CR) is taken from the analysis of the spectra of [Co^III(CR)XY]Z complexes.[12] This table shows that the ligand field strengths of the alkyl groups are rather high, being nominally around NO₂⁻ in the spectrochemical series, and that their behavior is consistent over those complexes with different in-plane ligands. It is also suggested that the ligand field strengths of the alkyl groups may be affected by the group *trans* to them. This in accord with the nmr data on these types of compounds.[17,18] Further application of this model, however, probably is not fruitful, for this analysis is based on a point charge model while the metal–ligand bonds in this type of compound almost certainly involve a high degree of covalency.

An approximate molecular orbital model[20] has been

applied to this system. The results of the calculations are depicted schematically in Figure 1. The d-orbital portion of this diagram is similar to that for the usual cobalt(III) complexes of D₄ symmetry. A distinctive characteristic of the present system is that there is a filled σ-bonding orbital, 2a₁, at a relatively high energy level, just below the d orbitals, which is due to the relatively high energy orbitals of the alkyl radicals, as estimated from their ionization potentials. They are 80.3 kK for CH₃·,[21] 70.2 kK for C₂H₅·,[22] and 62.6 kK for C₆H₅CH₂·.[23] The energy level diagram of Figure 1 can be correlated with the crystal field analysis of Wentworth and Piper[19] insofar as the energy level of the d orbitals and d–d transitions in spectra are concerned. The peaks in the near-ultraviolet and ultraviolet region of the spectra are not easy to assign. A number of transitions are expected to appear in this region: 3a₂ ← d_{yz}, d_{zz} (ligand p_π* ← d), 3a₁ ← ligand p_π, and 3a₁ ← 2a₁. The rough molecular orbital calculation, though highly qualitative, is useful in the rationalization of qualitative trends, for example, the variation of energy levels with the axial ligands. Assuming that no appreciable changes occur in the overlap integrals or the effective charge on the cobalt with the change in the Coulomb integral (or ionization potential) of the alkyl groups, the relative positions of several levels have been estimated for the several sets of matrix elements. The result for 3a₁ and 2a₁ levels is depicted in Figure 2. Although the actual values for the energy difference between the pairs of levels are probably poorly estimated, the trend may reflect the real situation. This trend suggests that this energy difference diminishes in the order ·CH₂Cl > ·CH₃ > ·C₂H₅ > ·CH₂C₆H₅. The same trend is observed in the ν_V peak of the [RCo(CR)Br]⁺ series. This strongly,

(20) (a) The assumptions made in this calculation are (*cf*. C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory," W. A. Benjamin, Inc., New York, N. Y., 1965): (1) Co^{0.5}; (2) $H_{ij} = KG_{ij}$. $(H_{ii} + H_{ij})/2$; (3) $K = 1.50$ for σ bonding, $K = 2.00$ for π bonding; (4) the distance R (metal–ligand) ≈ 2.0 Å; and (5) $G_{ij} = 0$, if i and j are orbitals of metal and ligand, respectively, except for the calculation of H_{ij}. (b) The values of matrix elements are estimated using the

above assumptions and the pertinent tables. They are: (1) Coulomb integrals (kK), $H_{\sigma(N)} = -140$, $H_{\pi(N)} = -106$, $H_{\pi*(N)} = -50$, $H_{\sigma(CH_3)} = -80$, $H_{\sigma(Br)} = -140$, $H_{4p} = -47$, $H_{4s} = -85$, and $H_{3d} = -106$; and (2) overlap integrals, $S(\sigma, 4s) = 0.22$, $S(\sigma, 4d_\sigma) = 0.14$, $S(\sigma, 4p_\sigma) = 0.40$, $S(p_\pi, 3d_\pi) = 0.05$, $S(p_\pi, 4p_\pi) = 0.16$. (c) The molecular orbitals 2a₁ and 3a₁ are: 2a₁ = 0.4984 (3d_z²) − 0.0868 (4s) + 0.7154 (σ(CH₃, Br)) − 0.4820 (σ(N)); 3a₁ = 0.7738 (3d_z²) − 0.3988 (4s) − 0.4428 (σ(CH₃, Br)) + 0.2147 (σ(N)).
(21) F. P. Lossing, K. U. Ingold, and I. H. S. Henderson, *J. Chem. Phys.*, **22**, 621 (1954).
(22) J. B. Farmer and F. P. Lossing, *Can. J. Chem.*, **33**, 861 (1955).
(23) J. B. Farmer, I. H. S. Henderson, C. A. McDowell, and F. P. Lossing, *J. Chem. Phys.*, **22**, 1948 (1954).

though not conclusively, suggests that this peak ν_V is due to the transition $3a_1$ (antibonding) ← $2a_1$ (bonding).

The high intensities of the absorption bands in the spectra of this type of compound, as compared to those of the ordinary cobalt(III) complexes, is a matter of importance. The d–d peaks usually have molar extinction coefficients of no more than 200 or so, except for azido and thiocyanato derivatives, while the absorption bonds for these alkyl derivatives have extinction coefficients of 650 to 3000. Although the theoretical interpretation of band intensity[24] has not yet been fully developed, there appear to be two main sources that are appropriate to explain the high intensities noted for these complexes. One is low symmetry and the other is covalency. The complexes of the type *trans*-[CoA₄X₂] are centrosymmetric and have relatively weak (orbitally forbidden) absorption intensities in d–d transitions. The complexes in question here are not centrosymmetric, and this will facilitate the interactions that make these transitions partly allowed (make the transition moment $\int x_1 \vec{r} x_2 \, d\tau$ nonzero). The value of the transition moment integral probably diminishes as x_1 and x_2 become more nearly pure d in character. In other words, the transition moment increases with increased mixing of the d orbitals and ligand orbitals. On this qualitative basis, the high intensity suggests that a high degree of covalency is involved in the bonding.

Photolability of the Cobalt–Carbon σ Bond. The complexes reported here are sensitive to light and undergo decomposition even in the diffuse light of the laboratory. The first decomposition step is believed to be the formation of an alkyl radical and a cobalt(II) species.[6] Detailed studies[25,26] on the photoreactions of [Co(NH₃)₅X] complexes led to the postulation of the following reaction as the first step in such processes. The intermediate complex [Co^{II}(NH₃)₅·X] reacts further

$$[Co^{III}(NH_3)_5X^-] \xrightarrow{h\nu} [Co^{II}(NH_3)_5 \cdot X]$$
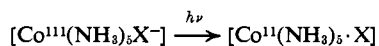
with either the formation of solvolyzed Co(III) species or the formation of Co(II) species and the free radical X. The latter reaction, photoreduction, is facilitated by light of shorter wavelengths.[25] Radiation corresponding to the charge-transfer band[26] is especially effective; the longer wavelengths which correspond to d–d transitions are less effective.

The rates of photodecomposition of these alkyl complexes have been measured, and the results are summarized in Table IV. The rate data conform quite well to the first-order rate law. Certain qualitative aspects of these data appear to be meaningful though no exact measurement of quantum yield has been attempted.

It is assumed that the photodecomposition is associated with the excitation of a particular electronic transition (or transitions). The series of compounds [RCo(CR)X]$^{n+}$ with R = CH₃, C₂H₅, and C₆H₅CH₂, and X = Br and H₂O, have similar absorption spectra, and correlation has been sought between the rate of photodecomposition and the spectral data. The reaction rate depends on the intensity of the incident light and the molar extinction coefficient ϵ in the per-

(24) C. J. Ballhausen, *Progr. Inorg. Chem.*, **2**, 251 (1960).
(25) A. W. Adamson, *Discussions Faraday Soc.*, **29**, 163 (1960).
(26) V. Balzani, R. Ballardini, N. Sabbatini, and L. Moggi, *Inorg. Chem.*, **7**, 1398 (1968).
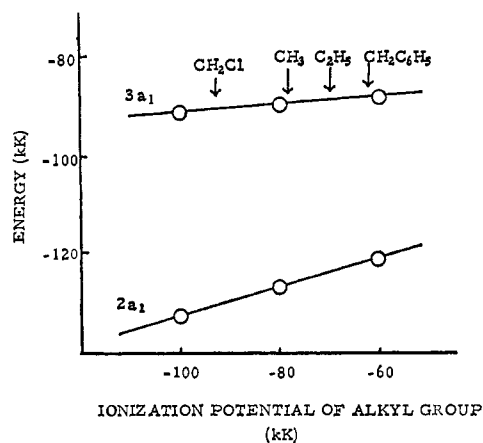

Figure 2. The variation in energy of the two levels $2a_1$ and $3a_1$ with the ionization potential of the alkyl group.

tinent wavelength range. The dispersion curve has not been determined for the conventional tungsten lamp used. From the usual dispersion of such lamps, the intensity may be assumed to be constant over narrow-wavelength ranges near 500 mμ, and to decrease linearly with the wavelength for short-wavelength ranges that fall in the region from around 400 to about 290 mμ.

Table IV. Photodecomposition[a] of [RCo(CR)X]$^{n+}$ Complexes and Related Complexes

Complex	Solvent	Rate constant, min^{-1}	In the dark,[b] min^{-1}
1. [CH₃Co(CR)Br]⁺	MeOH	8.8×10^{-3}	0[c]
2. [C₂H₅Co(CR)Br]⁺	MeOH	7.2×10^{-3}	0[c]
3. [C₆H₅CH₂Co(CR)Br]⁺	MeOH	19×10^{-3}	8.3×10^{-3}
4. [CH₃Co(CR)(H₂O)]²⁺	H₂O	2.1×10^{-3}	0
5. [C₂H₅Co(CR)(H₂O)]²⁺	H₂O	4.2×10^{-3}	0
6. [C₆H₅CH₂Co(CR)(H₂O)]²⁺	H₂O	9.0×10^{-3}	
7. [ClCH₂Co(CR)Br]⁺	MeOH	2.0×10^{-3}	0
8. [CH₃Co(CR)]²⁺	MeOH	12×10^{-3}	0
9. [C₂H₅Co(DMG)₂(py)]	MeOH	2.3×10^{-3}	0

[a] At 24.5 ± 1.0°; concentration $\sim$4.5 × 10^{-4} M. [b] 0; no appreciable decomposition within a few hours. [c] See section on characterization.

Thus, correlations have been sought between the rate constant k and ϵ at ν_{IE}, and between k and $\epsilon\lambda$ at ν_{II} and ν_V (Figure 3). There is no correlation in the case of ν_{IE}, a poor correlation for ν_{II}, and a relatively good correlation at ν_V for that series of compounds. This is consistent with the assumption that the photodecomposition is principally caused by the transition ν_V: $3a_1$ ← $2a_1$. This conclusion is in accord with that for well-known reactions, *e.g.*, [Co^{III}(NH₃)₅X]$^{n+}$.[25,26]

A few of the compounds do not conform to this correlation; they are [ClCH₂Co(CR)Br]⁺, [CH₃Co(CR)]²⁺, and [EtCo(DMG)₂py]. Each of these substances differs in some obvious way from the general series of complexes, [RCo(CR)Br]⁺ and [RCo(CR)(H₂O)]²⁺ (R = CH₃, C₂H₅, C₆H₅CH₂). The detailed energy level patterns may differ between [RCo(CR)X]⁺ and [RCo-(DMG)₂X]. In the case of [ClCH₂Co(CR)Br]⁺, the
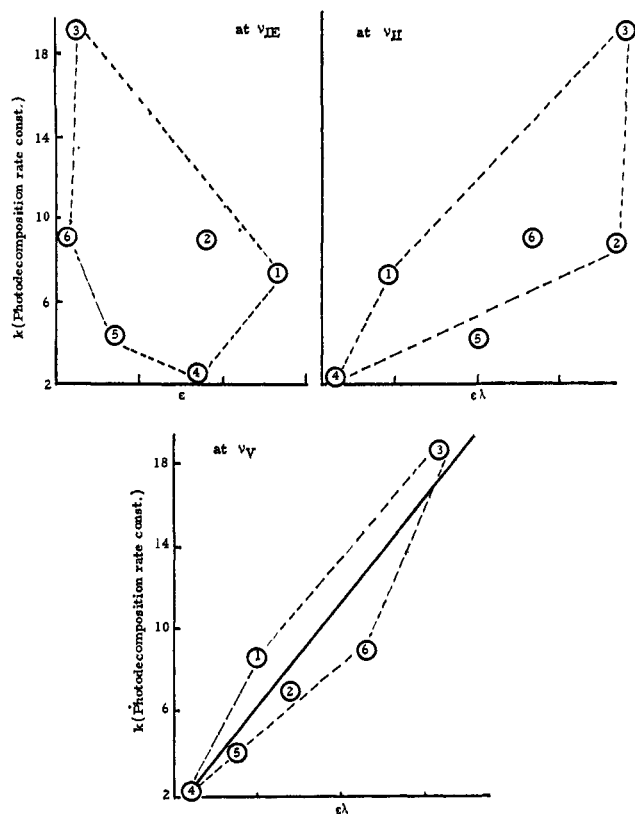
Figure 3. Correlation between the rate of photodecomposition and electronic transitions.

assignment of the spectral bands may not be correct. The shortest wavelength band at 34.6 (sh) kK (Table II) may be incorrectly assigned to the transition $3a_1 \leftarrow 2a_1$, since this is inconsistent with the rate data. This band is expected to occur at a much higher energy and may be hidden in the intense bands in the shorter wavelength region. The fact remains that a rather good correlation

exists between spectra and photolability for the six compounds of most closely related structures.

The benzyl derivative $[C_6H_5CH_2Co(CR)Br]^+$ decomposes thermally in solution in the dark at room temperature while the other compounds do not. The benzyl radical which is supposed to form as the result of the decomposition has a relatively great thermal stability, and this may appreciably decrease the activation energy for the first step in the decomposition process $[RCo^{III}(L)] \rightarrow [R \cdot Co^{II}(L)]$.

The photostability of the cobalt-to-carbon bond appears to be related to the energy difference between the $3a_1$ level (σ antibonding) and the $2a_1$ level (σ bonding), or possibly between $3a_1$ and $1e$ (d_{zz}, d_{yz}). Enhanced energy difference is expected to increase the photostability of the bond. Lowering the $2a_1$ level (or d_{zz}, d_{zz} level) in energy or raising the $3a_1$ level increases this energy difference. The conformance of the axial alkyl groups to this model was demonstrated above. A ligand which can withdraw electron density from the cobalt atom makes that atom more positive and may lower the energy of the $2a_1$ level. Such an effect may be exerted by an axial ligand *trans* to the alkyl group, such as pyridine or triphenylphosphine, or by an in-plane ligand (ligands) which has low-lying vacant π orbitals. The ligands that are known to stabilize cobalt–carbon σ bonds (BAE, SALEN, DMG, CR, the corin and porphyrin rings) all have vacant π orbitals. The same synthetic techniques have been applied to $[Co^{II}(CRH)X_2]$ complexes, where CRH is derived from CR by hydrogenation of the two azomethine linkages, but it has not yet been found possible to prepare alkyl derivatives with this ligand. Clearly, the removal of two-thirds of the unsaturated nitrogen donors has influenced the ease of formation of cobalt–carbon σ bonds.