***trans*-[Co(DIM)Br$_2$]ClO$_4$.**—Hydrobromic acid (3.26 g of 48% aqueous solution, 0.02 *M*) was added to a solution of *N,N'*-bis(3-aminopropyl)-1,2-diaminoethane (3.48 g, 0.02 *M*), followed by biacetyl (1.72 g, 0.02 *M*). After the solution had been stirred for 0.5 hr, resulting in a yellow-brown color, cobalt(II) acetate (2.49 g, 0.01 *M*) was added and the mixture was stirred under nitrogen for 4 hr. Excess hydrobromic acid was added to the purple solution, which turned green when air was bubbled through it. Addition of perchloric acid caused crystallization of the product as a bright green solid which was filtered, washed with methanol, and dried by vacuum desiccation.

***trans*-[Co(DIM)Br$_2$]PF$_6$.**—Addition of a saturated acetonitrile solution of [Co(DIM)Br$_2$]ClO$_4$ to a saturated aqueous solution of NH$_4$PF$_6$ caused precipitation of the PF$_6$ salt.

***trans*-[Co(DIM)Br$_2$]Br.**—Solid [Co(DIM)Br$_2$]ClO$_4$ was stirred in a saturated acetone solution of LiBr. Over a period of 1 hr the solid [Co(DIM)Br$_2$]ClO$_4$ disappeared and [Co(DIM)Br$_2$]Br precipitated.

***trans*-[Co(DIM)Cl$_2$]ClO$_4$ or -PF$_6$.**—Use of hydrochloric acid instead of hydrobromic acid in the procedure described above for the preparation of [Co(DIM)Br$_2$]ClO$_4$ leads to the corresponding *trans*-dichloro complex.

***trans*-[Co(DIM)(NO$_2$)$_2$]ClO$_4$.**—This was prepared by the addition of sodium nitrite to the bromo or chloro complex, in a manner identical with that described for the synthesis of the corresponding TIM complex.

Synthesis of 2,3-Dimethyl-1,4,8,11-tetraazacyclotetradecane (DMC).—Hydrogenation of [Ni(DIM)](ClO$_4$)$_2$ in methanol using active Raney nickel as catalyst gave [Ni(DMC)](ClO$_4$)$_2$ in good yield.[17] The free cyclic amine was then removed from nickel following the method of Curtis.[33] Decomposition of [Ni(DMC)](ClO$_4$)$_2$ was achieved with 5 equiv of sodium cyanide in a 1:1 ethanol–water solution. The ethanol was removed by rotary evaporation and the product was extracted into chloroform. Removal of the chloroform gave the crude product as an off-white solid, which was recrystallized from dioxane. This was analyzed as the hydrochloride salt. *Anal.* Calcd for C$_{12}$H$_{32}$N$_4$Cl$_4$: C, 38.5; H, 8.6; N, 15.0; Cl, 38. Found: C, 36.9; H, 8.3; N, 14.3; Cl, 36.2.

Complexes of DMC.—These complexes may be prepared from free ligand following the procedures used by Bosnich, Poon, and Tobe.[34] Alternatively, the cobalt complexes of DIM can be reduced directly. The case of [Co(DMC)Br$_2$]ClO$_4$ is given here as an example. Green [Co(DIM)Br$_2$]$^+$ changed to a red-yellow color in CH$_3$OH solution upon the addition of Raney nickel hydrogenation catalyst. The necessary 2 mol of hydrogen was absorbed in about 2 min at 50 lb H$_2$ pressure. The pale yellow solution was filtered in the presence of air and HBr was added. The resulting green solution was evaporated to a small volume and saturated with NaClO$_4$. Yellow-green [Co(DMC)Br$_2$]ClO$_4$ separated from solution. Recrystallization yielded yellow-green crystals.

Physical Measurements.—Using KBr plates infrared spectra were obtained with a Beckman IR-10 recording spectrophotometer and Perkin-Elmer Model 337 spectrophotometer as Nujol and halo oil mulls in the range 4000–400 cm^{-1}. A Cary Model 14R spectrophotometer was used for visible spectra in the range 12.5–33.0 kK. The electronic spectra of [Co(TIM)Cl$_2$]$^+$ and [Co(TIM)Br$_2$]$^+$ were resolved using a Du Pont 310 curve resolver programmed for gaussian distribution. Solution conductivities were obtained with an Industrial Instruments, Inc., Model RC-16B2 conductivity bridge at 25 ± 0.1°.

Pmr spectra were run on a Varian HA-60/DA-60 and a Varian HA-100 spectrometer at ambient temperature. Elemental analyses were determined by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach über Engelskirchen, West Germany, Galbraith Laboratories, Inc., and Chemalytics, Inc.

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[33] N. F. Curtis, *J. Chem. Soc.*, 2644 (1964).

[34] B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, **4**, 1102 (1965); C. K. Poon and M. L. Tobe, *J. Chem. Soc. A*, 2069 (1967); 1549 (1968).

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Monoalkyl Derivatives of the Cobalt(III) Complexes of a Tetradentate Macrocyclic Ligand Containing α-Diimine Groups

By KEITH FARMERY and DARYLE H. BUSCH*

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The tetradentate macrocycle 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene (abbreviated Me$_4$[14]-1,3,8,10-teteneN$_4$ or more simply Me$_4$[14]teteneN$_4$), in which two conjugated α-diimine functional groups are coordinated about the metal in a planar array, has been used to produce cobalt(III) complexes containing a σ-bound alkyl group (R) as one of the axial ligands. These complexes have been prepared by standard methods *via* the corresponding cobalt(I) derivatives Co^{I}(Me$_4$[14]teteneN$_4$)X (X = halide). Direct reaction between the cobalt(II) derivatives [Co(Me$_4$[14]teteneN$_4$)X]$^+$ and alkyl halides results in formation, in ~50% yield, of the same alkylcobalt(III) complexes—a reaction which is rationalized in terms of the free-radical-like nature of the d^7 metal ion. These complexes have been identified as six-coordinate alkylcobalt(III) complexes by use of analytical, electrical conductivity, and spectral (nmr, infrared, and electronic) data.

Introduction

As part of an extensive investigation of the use of synthetic macrocyclic ligands in providing chemical foundations for the understanding of the behavior of natural macrocyclic complexes,[1] we have been examining the ligand structural parameters that are responsible for the successful synthesis of compounds containing Co(III)–C bonds.[2] Among the factors that might be important in this respect are the nature of the donor atoms, the sizes of chelate rings, the charge on the macrocyclic ligand, and the nature and extent of delocalization of any unsaturation in the system. There are now several noncyclic polydentate ligand

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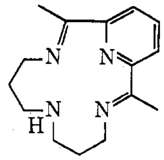
[1] D. H. Busch, K. Farmery, V. L. Goedken, V. Katovic, A. C. Melnyk, C. R. Sperati, and N. Tokel, *Advan. Chem. Ser.*, **100**, 44 (1971).

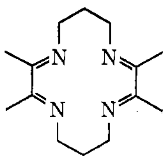
[2] D. Crowfoot-Hodgkin, *Proc. Roy. Soc., Ser. A*, **288**, 294 (1965).

systems which have been used in the formation of well-characterized alkylcobalt(III) derivatives.[3] However, cyclic ligands, into which class the natural ligand systems fall, have recently been shown to bestow upon their complexes properties which are significantly different from those produced by the more common open-chain polydentate ligands. Among these are the constraint upon the metal ion that arises from purely mechanical effects[1,4] and their uncommon kinetic and thermodynamic inertness.[1,5] So far, only one uncharged synthetic macrocycle has been used successfully in the formation of alkylcobalt derivatives. This is the tetradentate ligand 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene (CR)[3] (structure I). We report here attempts to synthesize organocobalt(III) complexes of the 14-membered tetradentate macrocycle having structures II–IV, which vary both in the number of C=N functions and in the extent of conjugation between these groups.[6] We have been concerned only with those reactions that have been most often used to generate alkyl derivatives of the B_{12} complex and its analogs under moderate conditions. These are the nucleophilic attack by a cobalt(I) derivative on an alkyl halide[7] and the reaction of the cobalt(II) complex with an alkyl halide to yield equimolar amounts of alkylcobalt derivative and of halocobalt complex.[8] Under these conditions only the complex of the tetraimine Me_4[14]tetene N_4 yielded alkyl derivatives. Although other reactions might yield other results, comparisons between the subject reactions of the complexes of Me_4[14]teteneN$_4$ and those of the two dienes are illuminating. The cobalt complexes used in this work have been characterized in earlier studies.[9]



I

(CR)

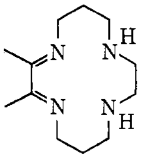


II

Me_4[14]teteneN$_4$

or

"tetene"

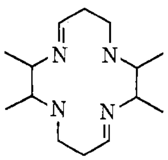


III

Me_2[14]1,3dieneN$_4$

or

"1,3diene"



IV

Me_6[14]4,11dieneN$_4$

or

"4,11diene"

Results and Discussion

Preparations.—The most generally useful method for the synthesis of alkylcobalt(III) complexes containing a stabilizing planar ligand system is *via* the corresponding cobalt(I) complex. It is now well established[10,11] that reaction between this cobalt(I) center and the alkyl halide proceeds by an S$_N$2 mechanism. The electron pair in the d_{z^2} orbital (assuming here that the planar ligand occupies the xy plane) is directed, through vacant coordination sites in the cobalt ion, toward the electrophilic carbon atom of RX. The term "supernucleophile" has been coined[10] to describe its very high reactivity. For convenience, the cobalt(I) complex is often generated in the presence of the alkyl halide by use of sodium borohydride as reducing agent in a protic medium (alcohols or water). Prereduction with sodium amalgam in an inert solvent (*e.g.*, acetonitrile or tetrahydrofuran), followed by the addition of alkyl halide, has also been used with success. We have used these two methods to generate the corresponding cobalt(I) complex from both the cobalt(III) derivatives $[Co(tetene)X_2]^+$ and the cobalt(II) compounds $[Co(tetene)X]^+$ (X = halide). When the reactions were performed in methanol or methanol–acetone mixtures, the intermediate was probably the five-coordinate Co(tetene)X, since the alkyl product finally isolated always contained the halide (X) present in the initial cobalt complex, not the halide from the organic halide. When the reductions were performed in the presence of acetonitrile, either as part of a mixed solvent system (borohydride reduction) or as the pure solvent (sodium amalgam reduction), the reduced species appears to have been $[Co(tetene)(CH_3CN)_2]^+$ since the alkylated product was of the form $[RCo(tetene)(CH_3CN)]^{2+}$.

Initially certain difficulties were experienced in the preparation of pure monoalkyl complexes of Me_4[14]teteneN$_4$ especially when the borohydride method was used. These problems were associated with two features of the chemistry of this particular system. First, the ligand itself readily undergoes hydrogen addition to one or more of its imine functions under these conditions. Thus, when the stoichiometric quantity of $NaBH_4$ is added to either the Co(II) or the Co(III) complex of tetene in methanol solution, there is a very rapid color change to the deep blue color of Co^I(tetene)X. However, over a period of 1–2 min, this solution turns to a deep green color, and cobalt complexes isolated from this solution appear to have undergone imine hydrogenation.

This hydrogenation phenomenon, by virtue of its rapidity, imposed the practical constraint that Co^I(tetene)X species have to be consumed as quickly as possible when they are formed by the borohydride

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[3] E. Ochiai, K. M. Long, C. R. Sperati, and D. H. Busch, *J. Amer. Chem. Soc.*, **91**, 3201 (1969), and references therein.

[4] G. R. Brubaker and D. H. Busch, *Inorg. Chem.*, **5**, 2114 (1966).

[5] (a) D. K. Cabbiness and D. W. Margerum, *J. Amer. Chem. Soc.*, **92**, 2151 (1970); (b) *Chem. Eng. News*, **48**, 9 (June 29, 1970).

[6] We have adopted a general system of abbreviations for macrocyclic ligands based on the lengthy names of the substances. The total abbreviation contains all significant locants and can be used to generate the structures, *e.g.*, 2,3,9,10-Me_4[14]-1,3,8,10-tetene-1,4,8,11-N_4. In any given report we will use only as much of the abbreviation as is necessary to distinguish it from other structures discussed therein—*i.e.*, "Me_4[14]teteneN$_4$" or merely "tetene." The old abbreviations for the ligands of structures II–IV were totally trivial, TIM, DIM, and 1,7-CTH, respectively.

[7] (a) K. Bernhauer, O. Müller, and G. Müller, *Biochem. Z.*, **336**, 102 (1962); (b) E. L. Smith, L. Mervyn, A. W. Johnson, and N. Shaw, *Nature (London)*, **199**, 1175 (1962).

[8] (a) J. Halpern, *Chem. Eng. News*, **46**, 68 (Oct 31, 1968); (b) W. G. Marzelli, P. A. Marzelli, and J. Halpern, *J. Amer. Chem. Soc.*, **92**, 5752 (1970).

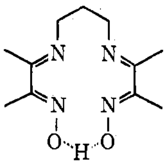
[9] (a) S. C. Jackels, K. Farmery, E. K. Barefield, N. J. Rose, and D. H. Busch, *Inorg. Chem.*, in press; (b) N. Sadasivan, J. A. Kernohan, and J. F. Endicott, *ibid.*, **6**, 770 (1967).

[10] G. N. Schrauzer and E. Deutch, *J. Amer. Chem. Soc.*, **91**, 3341 (1969).

[11] F. R. Jensen, V. Madan, and D. H. Buchanan, *ibid.*, **92**, 1414 (1970).

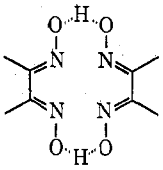
method. Therefore, we routinely performed the reduction reactions in the presence of a very large excess (100-fold) of alkyl halide so that the alkylation reaction was complete within a few seconds after reduction. Under these conditions only a small fraction of the ligand was reduced ($<5\%$ by ir) and its complexes were easily removed by recrystallization of the major product.

A second problem encountered in the synthesis of these derivatives was that the intended reaction products (*i.e.*, monoalkylcobalt(III) derivatives) were themselves susceptible to reduction at the cobalt, to give alkylcobalt(I) complexes of stoichiometry RCo(tetene). We have reported[12] the isolation and characterization of representatives of this new class of complexes both of the ligand tetene and of the ligand 2,12-dimethyl-3,7,11-17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,-13,15-pentaene (CR, structure I) whose normal alkylcobalt(III) derivatives have already been described.[3] These deep green derivatives RCo(tetene) react very rapidly with alkyl halide, which is always present in excess in the reaction mixture, to yield a third type of σ-bound organocobalt complex,[13] of formulation *trans*-$[R_2Co(tetene)]^+$. These complexes, in which the two equivalent alkyl groups occupy axial coordination sites on the cobalt(III) ion, are red or brown and have solubilities and other properties similar to those of the monoalkyl derivatives. Consequently, they represent impurities which are difficult to remove. It was therefore found to be imperative that only the exact stoichiometric quantity of sodium borohydride be used and that the reaction mixture be stirred as vigorously as possible during its addition. It is interesting that while the macrocycles CR (structure I), $Me_4[14]teteneN_4$ (structure II), and the linear tetradentate ligand derived by condensation of 1,3-diaminopropane and biacetylmonooxime[13] (structure V) will stabilize *trans*-dialkylcobalt(III) complexes, formed *via* alkylcobalt(I) derivatives, neither the bisdimethylglyoxime ligand system (structure VI, in the so-called cobaloximes) nor the corrin ring itself (the ligand in coenzyme B_{12}) has yielded analogous complexes. This may be a simultaneous function of the charge and nature of the ligand unsaturation. The dialkyl derivatives will be reported in detail later.



V

PDG



VI

$(DMG)_2$

As we mentioned above, the formation of alkylcobalt(III) complexes *via* cobalt(I) intermediates requires that the d^8 system be less than six-coordinate and low spin with two electrons paired in the high-energy d_{z^2} orbital. If a similar situation obtains for a d^7 system, the odd electron in the d_{z^2} orbital confers free-radical-like behavior on the complex.[8] The cobalt(II) derivatives of the ligand tetene fall within this category,[9] and they indeed react directly with alkyl halides according to the equations

$$2[Co(tetene)X]BPh_4 + RY \xrightarrow{acetone} [RCo(tetene)X]BPh_4 + [Co(tetene)XY]BPh_4$$
$$(X, Y = halide)$$

$$2[Co(tetene)X]BPh_4 + RY + NaBPh_4 \xrightarrow{CH_3CN} [RCo(tetene)(CH_3CN)](BPh_4)_2 + [Co(tetene)XY]BPh_4 + NaX$$

Half of the cobalt was isolated from such reaction systems as the alkyl complex, the other half having formed the usual *trans*-diacidocobalt(III) complex. Therefore the products of these reactions are entirely consistent with homolytic cleavage of the carbon–halogen bond, each half going to a different cobalt ion. The exact nature of the mechanisms of such reactions is ambiguous in the absence of detailed information.[8]

The two components of the product mixture can be separated by fractional crystallization, but we found a more efficient separation procedure by utilization of their different densities. For example, crystals of the benzyl complexes all float on methylene chloride (in which they are slightly soluble) and can be decanted from the crystals of the *trans*-diacido complexes. Final purification was then effected by normal recrystallization.

Characterization of the New Compounds.—The results of elemental analyses clearly reveal the stoichiometries of these complexes. In solution in the presence of air they are all light sensitive, as are all other cobalt(III) alkyls, but they appear to be indefinitely stable in the solid state. The alkyl complexes where $R = CH_3$ or $C_6H_5CH_2$ were prepared, but attempts to form the ethyl or higher homologs were unsuccessful. This appears to be due, in part, to the fact that reaction between Co^I(tetene)X and these halides was very slow, the blue color of the cobalt(I) species being discharged only over several hours even in the presence of enormous quantities of alkyl halide. In addition the solutions are particularly light sensitive and the compounds may spontaneously decompose, even in the dark.

The resonance positions of the methyl protons in the nmr spectra of the methyl complexes are also reported in the Experimental Section. The other features such as the resonances associated with the methylene groups in the macrocycle are not included since they merely serve to confirm the structures of the ligands and they have been discussed in greater detail elsewhere.[9a] Measurements of the intensities of the peaks in the nmr spectra verify that there is one cobalt alkyl group per ligand. The relatively high field position of the unique methyl groups confirms that they are bound directly to the cobalt ion. However, the positions are not quite as high as has been observed for most of the methylcobalt(III) complexes reported to date, for which τ values greater than 9 are typical. This small variation may be due to a combination of several factors. First, the overall charge on complexes of tetene is more positive than on complexes of the other ligands which themselves are negatively charged. Second, the extent of delocalization of the unsaturation in the ligand may be significant. It is perhaps a little surprising that there is no real variation in the position of the methyl resonances as the axially opposite ligand

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[12] K. Farmery and D. H. Busch, *Chem. Commun.*, 1091 (1970).

[13] G. Costa, G. Mestron, T. Licari, and E. Mestroni, *Inorg. Nucl. Chem Lett.*, **5**, 561 (1969).

TABLE I

ELECTRONIC SPECTRA AND SPECTRAL PARAMETERS FOR THE COMPLEXES[a]

Complex	Solvent	ν_E	ν_A	Dq(R)
$[CH_3Co(tetene)Cl]^+$	Acetone	20.0 (2300)	24.2 (4600)	2.42
$[CH_3Co(tetene)Br]^+$	Acetone	20.3 (2900)	24.8 sh	2.70
$[CH_3Co(tetene)I]^+$	Acetone	20.0 (4300)	25.0 (8500)	2.88
$[C_6H_5CH_2Co(tetene)Cl]^+$	Acetone	19.9 (1700)	24.1 (4500)	2.39
$[C_6H_5CH_2Co(tetene)Br]^+$	Acetone	19.6 (1500)	24.4 (4500)	2.42
$[C_6H_5CH_2Co(tetene)I]^+$	Acetone	20.2 (2400)	23.8 (6000)	2.96
$[CH_3Co(tetene)(CH_3CN)]^{2+}$	Solid	22.4	24.8	
	Acetonitrile	22.5 sh	24.4 (3000)	
	Nitromethane	22.3 sh	24.6 (3000)	
	Acetone	20.6 (2000)	23.9 (1500)	
	Methanol	20.5 (2000)	23.8 (1450)	
$[C_6H_5CH_2Co(tetene)(CH_3CN)]^+$	Acetonitrile	22.0 sh	25.0 (6300)	
	Nitromethane	22.0 sh	24.9 (6000)	
	Acetone	19.5 (2700)	24.0 (6400)	
	Methanol	19.3 (2600)	23.7 (6000)	

[a] All values of ν and Dq are in kK; ϵ values are in parentheses; sh = shoulder.

varies through the halides, since small but significant changes have been observed in other systems.[14] The noticeable reduction in $\tau(CH_3)$ both for ligand (7.1–6.9) and cobalt methyls (8.8–8.3) in the complex $[CH_3Co(tetene)(CH_3CN)](BPh_4)_2$ probably reffects the higher positive charge on the central metal ion in this case.

All the haloalkyl complexes exhibit normal 1:1 electrolyte behavior in nitromethane solution while the acetonitrile–alkyl derivatives are 2:1 electrolytes in this solvent. In acetonitrile solution, solvent rapidly displaces the halide ligands, resulting in conductivity values corresponding to 2:1 electrolytes. Since the electronic spectra of these acetonitrile solutions are identical with those of the authentic complexes which contain acetonitrile in their primary coordination sphere, all the complexes are six-coordinate under these conditions.

Electronic Spectra.—The electronic spectra of all of the alkyl–halo complexes $[RCo(tetene)X]^+$ (R = CH_3, $C_6H_5CH_2$; X = Cl, Br, I) consist of two major, well-resolved bands around 20 and 25 kK, respectively, together with very intense (charge-transfer) bands in the ultraviolet region. The assignment and interpretation of the two lower energy bands in the visible region are of major interest here.

Ochiai, *et al.*,[3] in the interpretation of this region of the spectra of the complexes $[CH_3Co(CR)L]^{n+}$ (L = monodentate ligand), assigned a peak at ~20 kK to the transition to the ^1E component[15] of the first band and a shoulder on the high-energy side of this band (around 22 kK) to the transition to the ^1A component. This led to a $Dq^z(CH_3)$ value (*i.e.*, the contribution of the methyl group to the axial ligand field) in the 3000-cm^{-1} region (for example 3400 cm^{-1} when trans to Br$^-$). However recent studies on the spectra of broad ranges of macrocyclic complexes have shown that there are special problems in interpreting the spectra of both the Co(III) and Ni(II) complexes of CR.[16] The spectra of the complexes of $Me_4[14]teteneN_4$ having the general form *trans*-$[Co(tetene)X_2]^{n+}$ are relatively well behaved.[9a,16] These complexes[9a] give Dq^{xy} values for tetene of 2800–2900 cm^{-1} assuming the Racah parameter C is about 3800 cm^{-1}.[15] This accords with the assignment of the transition at about 24 kK in $[RCo(tetene)X]^+$ to $^1A_{2g} \leftarrow {}^1A_{1g}$ and the lower energy band to $^1E \leftarrow {}^1A_1$. Use of these assignments leads to the values for $Dq(CH_3)$ given in Table I. The average value of ν_A (24.4 kK) was used in the calculations. The calculations assume axial averaging (pseudo-D_{4h} symmetry) for the complex and Dq^z values for halides as follows: Cl$^-$, 1460 cm^{-1}; Br$^-$, 1300 cm^{-1}; I$^-$, 1000 cm^{-1}. Our calculated values provide crude approximations to the lower limits of Dq values for alkyl groups bound to cobalt(III). Within these limitations, the CH_3 or $C_6H_5CH_2$ group exerts a rather strong ligand field, somewhere between those of thiocyanate ($Dq^z \approx 2100$ cm^{-1}) and nitrite ($Dq^z \approx 3000$ cm^{-1}). The apparent variation of Dq(R) with the nature of the trans ligand is undoubtedly explained in terms of the amount of charge donated by the ligand to the cobalt through the σ bond.[17]

The low-energy band assigned to the transition $^1E \leftarrow {}^1A_1$ is somewhat unsymmetrical in the complexes containing a CH_3 group. This is evidence for lower symmetry splitting beyond the fourfold symmetry assumed in the discussion above. A gaussian fit between the observed and calculated spectra was only achieved when one of the component gaussians was placed to the *low*-energy side of the first observed maximum (Table II).[15]

TABLE II

COMPONENTS OF THE E BAND AS CALCULATED BY GAUSSIAN ANALYSIS[a]

Complex	ν_1	ν_2
$CH_3Co(tetene)Cl^+$	17.6 (140)	20.0 (2300)
$CH_3Co(tetene)Br^+$	17.6 (360)	20.3 (2900)
$CH_3Co(tetene)I^+$	17.5 (240)	20.0 (4300)

[a] All values of ν are in kK; extinction coefficients are given in parentheses.

In view of these results for $[CH_3Co(tetene)X]PF_6$, we prepared a fresh sample of $[CH_3Co(CR)Br]PF_6$ and subjected its spectrum to a similar examination. We found that any shoulder at 21.4 kK (assigned[3] as the ν_A band) may well be a result of the tailing of a higher energy band into this region of the spectrum. In addition, there appears to be a weak shoulder on the low-energy side of the 20.4-kK band, so that the spectrum of $[CH_3Co(CR)Br]PF_6$ is quite similar, in this region,

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[14] H. A. O. Hill, K. G. Morallee, G. Pellizer, G. Mestroni, and G. Costa, *J. Organometal. Chem.*, **11**, 167 (1968).

[15] A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965).

[16] C. R. Sperati, A. M. Tait, and D. H. Busch, unpublished results.

[17] R. A. Firth, H. A. O. Hill, J. M. Pratt, R. G. Thorp, and R. J. P. Williams, *Chem. Commun.*, 400 (1967).

to that of [$CH_3Co(tetene)Br]PF_6$. Gaussian analysis of this band resolved it into bands at 20.0 kK (ϵ 1050) and 17.6 kK (ϵ 150) while attempts to synthesize a spectrum including a band between 20.5 and 25 kK were unsuccessful.

The electronic spectra of all of the complexes containing halide ligands quickly change in acetonitrile solution into spectra identical with those produced by the authentic acetonitrile-containing complexes in this solvent. As Table I shows, in CH_3CN or CH_3NO_2 solvents the spectrum of $[CH_3Co(tetene)(CH_3CN)]^{2+}$ consists of one highly asymmetric band slightly below 25 kK which has one prominent low-energy shoulder (around 22 kK) and probably at least one other shoulder. Since these spectra are essentially identical with the solid-state spectra, we assume that they are associated with those complexes in which the acetonitrile is coordinated to cobalt in the position trans to the alkyl ligand. In methanol or acetone, two well-resolved bands around 20 and 24 kK were observed. This type of spectrum we ascribe to a species containing the new solvent in the sixth coordination site, since, upon the addition of CH_3CN, the spectrum reverts to that of the genuine acetonitrile complex. We do not believe the complexes can be five-coordinate in these solvents, since alkyl complexes with this geometry usually have a fairly intense band in the 14–17-kK region of the spectrum.[18]

The high intensities of the two main bands in the visible region of these spectra (*i.e.*, the $^1A_2 \leftarrow {}^1A_1$ and $^1E \leftarrow {}^1A_1$ transitions) are worthy of further discussion. The alkyl ligands carry a large charge density and have only a low electronegativity and therefore should be rather polarizable. Consequently, the main factor contributing to the high transition moment is likely to be the high covalent character of the Co–C bonds. This is to some extent analogous to the situation found in iodocobalt(III) complexes, where incorporation of one iodide ligand in the complex also increases the intensity of these same two bands by a factor of 5 or 6 compared to the corresponding chloro complexes. Interestingly, there are very few complexes of cobalt(III) known in which iodide is found as an axial ligand. However, almost without exception, these few also form stable alkylcobalt(III) complexes. Apparently the electronic factors responsible for the existence of these two types of complexes are closely related.

Attempted Synthesis of Alkyl Complexes of the Other Macrocycles.—We have applied the same synthetic techniques to the cobalt(II) and -(III) complexes of the macrocyclic tetradentate amines $Me_6[14]$-4,11-dieneN_4 and $Me_2[14]$-1,3-dieneN_4 without success. Solutions of the cobalt(II) complexes slowly darkened when heated (temperature variations up to 100° were used) in the presence of alkyl halides, but no alkyl products could be isolated. At first this might appear surprising since the complexes [Co(1,3-diene)X]BPh_4 and [Co(tetene)X]BPh_4 are similar in most respects[9a] other than in their alkylation reactions. In addition the complexes $[Co(4,11\text{-diene})X]^+$ also have the d-electron distribution and basic geometry necessary for participation in a free-radical-like reaction.[19]

Attempts to synthesize alkylcobalt complexes *via* cobalt(I) intermediates were equally unsuccessful in these cases. Reaction between Co(4,11-diene)$(ClO_4)_2$ and $NaBH_4$ does not appear to yield the Co(I) complex but involves a variety of processes including the formation of a borohydride complex [Co(4,11-diene)-$BH_4]ClO_4$.[19] The same reaction with [Co(1,3-diene)-X]BPh_4 leads to a pale brown cobalt(I) solution (*cf.* the very intense blue color of most of the other cobalt(I) derivatives) from which complexes containing only reduced ligand were obtained. Alkyl halides do react with those solutions but do not produce substantial yields of compounds containing Co–C bonds. It seems more likely that a simple redox reaction occurs. In acetonitrile, sodium amalgam appears to reduce the cobalt ion in both of these complexes to the 1+ state, the 4,11-diene complex being blue-green and the 1,3-diene complex, green-brown, but, again, derivatives containing Co–C bonds were not isolated after the addition of alkyl halide. We therefore conclude that there is an important difference between the cobalt(I) complexes of these ligands and the cobalt(I) complexes of the more saturated ligands. The former may be six-coordinate and/or have triplet ground states, or they may act too strongly as reducing agents. In any case, the principal requirements for the desired nucleophilic reaction of the cobalt(I) complexes with alkyl halides appear to be absent. Studies aimed at clarifying this point are currently in progress.

Experimental Section

All reactions and manipulations involving cobalt(I) or cobalt(II) complexes were performed entirely under an atmosphere of prepurified nitrogen. The preparation of cobalt(II) and -(III) complexes of the ligands tetene and 1,3-diene have been discussed elsewhere.[9a,20] Samples of the cobalt complexes of 4,11-diene were generously provided by Dr. V. L. Goedken. Sodium borohydride was kept under a nitrogen atmosphere. A 1% sodium analgam was prepared by dissolving hexane-washed sodium metal in mercury under nitrogen, and reactions involving this material were performed in a two-necked vessel which had, blown into the bottom, a stopcock through which excess amalgam could be removed upon completion of the reaction. Solvents were purified by standard procedures. Alkyl complexes were protected from light at all stages in their synthesis.

[CH_3Co(tetene)Cl]BPh_4. (a) **From [Co(tetene)Cl]BPh_4.**—To a slurry of 1.0 g (1.5 mmol) of the cobalt complex in 300 ml of an acetone–methanol mixture (4:1 by volume) was added rapidly, against a countercurrent of nitrogen, 0.06 g (1.6 mmol) of sodium borohydride. The mixture was stirred as vigorously as possible during the addition. As soon as the deep blue color of the cobalt(I) derivative was fully formed (~5 sec), a very large excess of methyl iodide (~10 ml) was added, also with vigorous stirring. When the solution had completely turned red-orange (a few seconds), it was rapidly filtered and the acetone was removed by rotary evaporation under subdued light, until orange crystals formed. These were collected, washed with methanol and ether, dried in a desiccator, and then recrystallized from nitromethane by the addition of alcohol. *Anal.* Calcd: C, 69.2; H, 7.0; N, 8.3; Cl, 5.2. Found: C, 69.5; H, 7.3; N, 8.4; Cl, 5.0. **Nmr** (DMSO-d_6 solution): CH_3 of ligand at τ 7.18 (intensity 4), Co CH_3 at τ 8.83 (intensity 1).

(b) **From [Co(tetene)Cl_2]ClO_4.**—The orange solution of the alkyl compound was produced by a procedure identical with that described above, except that twice the molar quantity of sodium borohydride is needed to reduce Co(III) to Co(I). Addition of excess sodium tetraphenylborate followed by partial solvent removal gives the product as orange crystals. Addition of an aqueous solution of ammonium or potassium hexafluorophosphate, followed by removal of solvent, gave the corresponding

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[18] See ref 3 for examples and references.

[19] V. Goedken and D. H. Busch, *Inorg. Chem.*, in press.

[20] K. Farmery and D. H. Busch, to be submitted for publication.

hexafluorophosphate salt. *Anal.* Calcd: C, 35.8; H, 5.4; N, 11.1. Found: C, 35.7; H, 5.5; N, 11.1.

[$\mathrm{CH_3}$Co(tetene)Br]$\mathrm{BPh_4}$. (a) **From [Co(tetene)Br]$\mathrm{BPh_4}$.**—This red complex was prepared in a manner entirely analogous to that used for the methylation of [Co(tetene)Cl]$\mathrm{BPh_4}$ above; yield 70%. *Anal.* Calcd: C, 64.9; H, 6.6; N, 7.8; Br, 1.1. Found: C, 65.1; H, 6.8; N, 7.8; Br, 10.8. **Nmr** (DMSO-d_6 solution): $\mathrm{CH_3}$ of ligand at τ 7.10 (intensity 4), Co $\mathrm{CH_3}$ at τ 8.86 (intensity 1).

(b) **From [Co(tetene)$\mathrm{Br_2}$]$\mathrm{ClO_4}$.**—Alkylation of this complex was achieved exactly as described above for [Co(tetene)$\mathrm{Cl_2}$]$\mathrm{ClO_4}$. *Anal.* Calcd for the $\mathrm{PF_6}$ salt: C, 32.9; H, 5.0. Found: C, 33.0; H, 5.0.

[$\mathrm{CH_3}$Co(tetene)I]$\mathrm{BPh_4}$ and [$\mathrm{CH_3}$Co(tetene)I]$\mathrm{PF_6}$.—Synthesis of these deep red-brown complexes from either [Co(tetene)I]$\mathrm{BPh_4}$ or Co(tetene)$\mathrm{I_3}$ was achieved by use of procedures identical with those above. *Anal.* Calcd for $\mathrm{BPh_4}$ salt: C, 61.0; H, 6.2; N, 7.3; I, 16.5. Found: C, 61.0; H, 6.2; N, 7.2; I, 16.7. Calcd for $\mathrm{PF_6}$ salt: C, 30.3; H, 4.6; I, 21.4. Found: C, 30.8; H, 4.7; I, 21.1. **Nmr** (DMSO-d_6 solvent): $\mathrm{CH_3}$ of ligand at τ 7.10 (intensity 4), Co $\mathrm{CH_3}$ at τ 8.85 (intensity 1).

[$\mathrm{CH_3}$Co(tetene)($\mathrm{CH_3CN}$)]($\mathrm{BPh_4}$)$_2$ and [$\mathrm{CH_3}$Co(tetene)($\mathrm{CH_3CN}$)]($\mathrm{PF_6}$)$_2$.—These bright yellow complexes were prepared from both cobalt(II) and cobalt(III) starting materials by methods entirely analogous to those above, except that a 1:1 mixture of acetonitrile and methanol was used as solvent and the products were recrystallized from acetonitrile by addition of ether. *Anal.* Calcd for $\mathrm{BPh_4}$ salt: C, 77.9; H, 7.0; N, 7.0. Found: C, 77.7; H, 7.2; N, 7.0. Calcd for $\mathrm{PF_6}$ salt: C, 31.3; H, 4.6; N, 8.6. Found: C, 31.3; H, 5.0; N, 8.8. **Nmr** of [$\mathrm{CH_3}$Co(tetene)($\mathrm{CH_3CN}$)]$\mathrm{BPh_4}$ ($\mathrm{CH_3CN}$-d_3 solvent): $\mathrm{CH_3}$ of ligand at τ 6.93 (intensity 4), Co $\mathrm{CH_3}$ at τ 8.30 (intensity 1), $\mathrm{CH_3}$ of acetonitrile at τ 8.06. **Ir:** ν(C$\equiv$N) 2320, 2288 (coordinated $\mathrm{CH_3CN}$).

[$\mathrm{C_6H_5CH_2}$Co(tetene)Cl]$\mathrm{BPh_4}$ and [$\mathrm{C_6H_5CH_2}$Co(tetene)Cl]$\mathrm{PF_6}$.—The methods used in the synthesis of these orange-brown complexes were identical with those above, except that cobalt was introduced as [Co(tetene)Cl]$\mathrm{BPh_4}$ or [Co(tetene)$\mathrm{Cl_2}$]$\mathrm{ClO_4}$ and $\mathrm{C_6H_5CH_2Cl}$ was used as the alkylating agent. *Anal.* Calcd for $\mathrm{BPh_4}$ salt: C, 71.8; H, 6.8. Found: C, 72.1; H, 7.0. Calcd for $\mathrm{PF_6}$ salt: C, 43.6; H, 5.4; N, 9.7; Cl, 6.1. Found: C, 43.4; H, 5.5; N, 10.0; Cl, 5.9.

[$\mathrm{C_6H_5CH_2}$Co(tetene)Br]$\mathrm{BPh_4}$ and [$\mathrm{C_6H_5CH_2}$Co(tetene)Br]$\mathrm{PF_6}$.—These red-brown crystalline salts were prepared from [Co(tetene)Br]$\mathrm{BPh_4}$ or Co(tetene)$\mathrm{Br_3}$ and $\mathrm{C_6H_5CH_2Br}$ in an entirely analogous manner. *Anal.* Calcd for $\mathrm{PF_6}$ salt: C, 40.5; H, 5.0; N, 9.0; Br, 12.8. Found: C, 40.4; H, 5.1; N, 8.7; Br, 12.7.

[$\mathrm{C_6H_5CH_2}$Co(tetene)I]$\mathrm{BPh_4}$ and [$\mathrm{C_6H_5CH_2}$Co(tetene)I]$\mathrm{PF_6}$.—These brown crystalline solids were prepared from Co(tetene)$\mathrm{I_3}$ and $\mathrm{C_6H_5CH_2Br}$ by the methods above. *Anal.* Calcd for $\mathrm{BPh_4}$ salt: C, 64.0; H, 6.1; I, 15.0. Found: C, 64.0; H, 6.1; I, 14.7. Calcd for $\mathrm{PF_6}$ salt: C, 37.6; H, 4.7; N, 8.4; I, 18.9. Found: C, 37.5; H, 4.9; N, 8.5; I, 19.1.

[$\mathrm{C_6H_5CH_2}$Co(tetene)($\mathrm{CH_3CN}$)]($\mathrm{PF_6}$)$_2$·$\mathrm{CH_3CN}$.—Yellow needles of this complex were obtained using $\mathrm{C_6H_5CH_2Br}$ in the procedure used above for the synthesis of the methyl analog. *Anal.* Calcd: C, 39.0; H, 4.8; N, 10.9. Found: C, 39.0; H, 4.9; N, 11.0. **Ir:** ν(C$\equiv$N) 2320, 2295 (coordinated $\mathrm{CH_3CN}$), 2245 cm^{-1} ($\mathrm{CH_3CN}$ of crystallization).

Preparation of Alkylcobalt Compounds by Sodium Amalgam Prereduction.—The cobalt(II) or cobalt(III) complexes were stirred under $\mathrm{N_2}$ with excess sodium amalgam in acetonitrile until reduction to the deep blue cobalt(I) complex was complete. The mercury amalgam was then poured off through the stopcock on the bottom of the flask. Addition of the appropriate alkyl halide then led, within a few minutes, to the formation of the corresponding alkyl complex [RCo(tetene)($\mathrm{CH_3CN}$)]$^{2+}$, which was isolated by addition of the appropriate anion (*i.e.*, $\mathrm{NaBPh_4}$ or $\mathrm{NH_4PF_6}$ in aqueous solution) and partial removal of solvent. The complexes were characterized by comparing their spectral properties (ir, nmr, and electronic) with those of the complexes prepared by the borohydride method above.

Preparation of Alkylcobalt Compounds by Direct Reaction of [Co(tetene)X]$\mathrm{BPh_4}$ with Alkyl Halides. (a) **With Benzyl Halides.**—A slurry of the cobalt(II) complex was stirred overnight with large excess of $\mathrm{C_6H_5CH_2Br}$ in an acetone–acetonitrile mixture under nitrogen. The resulting yellow-brown solution was filtered and the solvent was evaporated. The crude product was copiously washed with ether and then dissolved in acetonitrile containing acetone (25%). The volume of solution was doubled by addition of water containing 1 mol of $\mathrm{NaBPh_4}$ and the mixture was cooled in the refrigerator. The resulting solid, which was a mixture of deep green and red-brown needles, was filtered off and washed with ethanol and ether. Methylene chloride (20 ml) was then poured onto the mixture in a beaker, and the floating brown needles were decanted from the green crystals and recrystallized from acetonitrile by the addition of ether. The product was characterized by comparison of its spectral properties with those of the corresponding complex prepared as above.

If the same reaction was performed in acetone only, the corresponding complexes [$\mathrm{C_6H_5CH_2}$Co(tetene)X]$\mathrm{BPh_4}$ (X = Cl, Br, I) were obtained and isolated in a similar manner.

(b) **From Methyl Iodide.**—The cobalt(II) complex was warmed to 50° under nitrogen in acetonitrile with excess methyl iodide in a flask equipped with a reflux condenser. After 3 hr, the solution was cooled and 1 mol of $\mathrm{NaBPh_4}$ was added. Upon doubling the solution volume with water deep red crystals of the complex [Co(tetene)XI]$\mathrm{BPh_4}$ (X = Br, Cl) separated. These were removed by filtration and more water was added until the crystalline product was yellow-brown and contained no red crystals. This product was recrystallized from acetonitrile by addition of ether to yield yellow needles of the product. Again, this product was characterized by comparison of its spectral properties with those of an authentic sample of [$\mathrm{CH_3}$Co(tetene)($\mathrm{CH_3CN}$)]($\mathrm{BPh_4}$)$_2$.

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