Cobalt–Carbon σ Bond Formation Employing a High-Spin Cobalt(II) Complex as a Precursor

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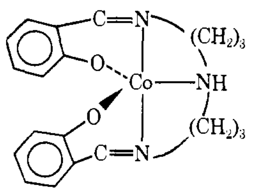
Abstract: A new series of vitamin B_{12} coenzyme model compounds has been prepared starting with the high-spin cobalt(II) chelate of the pentadentate Schiff base ligand derived from salicylaldehyde and bis(3,3′-aminopropyl)amine. The general method of preparation of these σ-bonded alkyl derivatives is the reduction of the cobalt complex with sodium borohydride in the presence of an alkyl halide. These compounds have been characterized by elemental and mass spectral analysis as well as infrared, visible, and nmr spectra. A six-coordinate pseudooctahedral structure is envisioned for these materials in the solid state. In poorly coordinating solvents, an equilibrium between five- and six-coordinate complexes is postulated. These σ-bonded organic derivatives appear to be quite thermally and photochemically stable.

The significance of cobalt–alkyl complexes as potential models for vitamin B_{12} coenzyme has been discussed in some detail.[1–4] Those systems from which stable Co–C links can be produced have been limited primarily to low-spin cobalt(II) square-planar complexes which employ tetradentate ligands with either all nitrogen donors or two nitrogen and two oxygen donor atoms.[5] The known exceptions in this regard are $[Co(CN)_5]^{3-}$,[6] the square-planar cobalt(II) complex of dimethylglyoxime (a bidentate ligand), and the five-coordinate vitamin B_{12} coenzyme (cobalamin) which contains a pentadentate ligand composed of a Corrin ring and a nucleotide side chain that terminates with a benzimidazole group, which may or may not be coordinated to the cobalt ion. The spin state of the cobalt(II) in these three cases is, however, found to be low spin.

The implications from a comparison such as this suggest that strong-field in-plane ligands are necessary for stable cobalt–carbon bond formation. The axial ligand trans to the bound carbon substrate is suspected of being just as important in determining the reactivity and stability of the C–Co link. While the influence of axial ligands on the nucleophilicity of the reactive cobalt species has been ably explored,[7] the preparation of model cobalt–alkyl complexes wherein the axial base is actually attached to the in-plane ligand is presently lacking. We wish to describe in this report the preparation of a series of cobalt–alkyl complexes starting with a cobalt complex which, on the surface, at least, does not satisfy our preconceived notion of a good precursor. In this paper consideration is given to the nature of the cobalt–carbon bond formed from the previously reported[8] high-spin five-coordinate cobalt(II) complex of the potentially pentadentate ligand derived from salicylaldehyde and bis(3,3′-aminopropyl)amine, hereafter referred to as Co(SALDPT), I.



I

Experimental Section

Materials. Bis(3,3′-aminopropyl)amine and salicylaldehyde were obtained from Aldrich Chemical Co., Milwaukee, Wis., and used without further purification. Palladium(II) chloride and $NaBH_4$ were obtained from Alfa Inorganics, Inc., Beverly, Mass. The preparation of Co(SALDPT) was accomplished by several procedures which are recorded elsewhere.[8–10] No oxygen was allowed to come in contact with the compound until the mother liquor had been washed away from the product with ether and allowed to dry to yield a golden yellow crystalline product. All other chemicals, including alkyl halides and solvents, were of reagent grade or equivalent.

Preparation of $CH_3Co(SALDPT)$. The method of Schrauzer[11] was employed for the preparation of these materials. Co(SALDPT) (1.0 g, 0.0025 mol) was dissolved in 75 ml of methanol and the solution flushed with N_2. Methyl iodide (1.07 g, 0.0075 mol) dissolved in 10 ml of methanol was added, followed by 2 drops of a 10% $PdCl_2$ solution in methanol along with 0.1 g of $NaBH_4$. Immediately there was a rapid evolution of H_2. After stirring for a short while, 4 ml of a 50% NaOH solution was added dropwise. Soon afterward, a red solid appeared. Stirring was continued for 1 hr. The material was filtered and dried *in vacuo* at 100° for 12 hr.

Preparation of $C_2H_5Co(SALDPT)$. Co(SALDPT) (1.0 g, 0.0025 mol) was dissolved in 75 ml of methanol and the solution flushed with N_2. A 10% $PdCl_2$ solution in methanol (2 drops) was added. Then ethyl iodide (1.17 g, 0.0075 mol) dissolved in 10 ml of methanol was added, followed by 0.1 g of $NaBH_4$. There was an immediate evolution of H_2. The solution was stirred for a few minutes; then 3 ml of a 50% aqueous NaOH solution was added. After a short while a red solid formed. It was isolated and dried as described above.

The remaining alkyl derivatives (*i.e.*, *n*-propyl, *n*-butyl, *n*-pentyl, *n*-hexyl, *n*-heptyl, *n*-octyl, and *n*-decyl) were prepared, isolated, and dried as described above using the appropriate alkyl iodide or bromide in each case.

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[2] G. N. Schrauzer, *Advan. Catal.*, **18**, 526 (1968), and references therein.

[3] G. N. Schrauzer, American Chemical Society–Chemical Institute of Canada Symposium on Bioinorganic Chemistry, Blacksburg, Va., June 1970.

[4] G. Costa, G. Mestroni, G. Taugher, and L. Itefani, *J. Organometal. Chem.*, **6**, 181 (1966).

[5] M. Green, J. Smith, and P. A. Tasker, *Discuss. Faraday Soc.*, **47**, 172 (1969).

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

[8] L. Sacconi and I. Bertini, *ibid.*, **88**, 5180 (1966).

[9] R. H. Bailes and M. Calvin, *ibid.*, **69**, 1886 (1947).

[10] C. Floriani and F. Calderazzo, *J. Chem. Soc. A*, 946 (1969).

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Table I. Analytical and Infrared Data on the Alkyl Derivatives

Compound		Anal, %				
		C	H	N	δ_{CH_3}[a]	γ_{CH_3}[b,c]
CH_3–Co(SALDPT)	Calcd	61.30	6.39	10.22	1385	2965
	Found	61.34	6.13	10.06		3890
C_2H_5–Co(SALDPT)	Calcd	62.10	6.65	9.88	1380	2970
	Found	62.35	6.44	9.73		2870
n-C_3H_7-Co(SALDPT)	Calcd	62.85	6.89	9.56	1380	2950
	Found	62.75	6.96	9.56		2860
n-C_4H_9–Co(SALDPT)	Calcd	63.56	7.13	9.27	1385	2955
	Found	63.37	7.18	9.22		2860
n-C_5H_{11}–Co(SALDPT)	Calcd	64.22	7.35	8.99	1388	2955 sh
	Found	63.95	7.28	8.88		2890
n-C_6H_{13}–Co(SALDPT)	Calcd	64.84	7.55	8.73	1388	2960 sh
	Found	64.59	7.49	8.68		2890 sh
n-C_7H_{15}–Co(SALDPT)	Calcd	65.43	7.74	8.48		2960
	Found	65.19	7.60	8.36	1385	2890
n-C_8H_{17}–Co(SALDPT)	Calcd	65.98	7.93	8.25		2960
	Found	65.75	7.79	8.11	1388	2890
n-$C_{10}H_{21}$–Co(SALDPT)	Calcd	67.01	8.27	7.82		2960
	Found	66.92	8.06	7.72	1385	2890

[a] Aliphatic carbon–hydrogen bending modes. [b] Aliphatic carbon–hydrogen symmetric and asymmetric stretching modes. [c] Shoulder = sh.

Physical Measurements. Infrared spectra were obtained in the region 5000–400 cm^{-1} using a Perkin-Elmer Model 621 spectrophotometer. Solid-state spectra were recorded as KBr pellets and as Nujol or hexachlorobutadiene mulls. Solution spectra were taken in spectroquality solvents using matched solution cells. Ultraviolet–visible–near-infrared spectra were obtained with a Cary 14 recording spectrophotometer. Spectra of solid samples were obtained by a diffuse transmittance technique[12] employing Nujol mulls impregnated on Whatman No. 1 filter paper. Solution spectra were obtained utilizing spectroquality organic solvents.

Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-7 double-focusing mass spectrometer using a solid inlet probe. The solid probe temperature was maintained at a value to prevent decomposition of the samples. The source temperature was maintained at approximately the temperature of the solid probe. Analyzer tube and ion source pressures of less than 10^{-6} Torr were employed. Where necessary, mass-to-charge ratios were calibrated with perfluorokerosene.

Nuclear magnetic resonance spectra were determined in deuterated chloroform and dimethyl sulfoxide, employing a Varian A60 nmr spectrometer with TMS as an internal standard.

Duplicate elemental analyses were performed in this laboratory using a Perkin-Elmer Model 240 carbon, hydrogen, nitrogen analyzer.

Results and Discussion

Highly crystalline, dark red σ-bonded organocobalt derivatives have been prepared starting with the cobalt(II) complex of the pentadentate ligand derived from salicylaldehyde and bis(3,3′-aminopropyl)amine, Co(SALDPT). The reactions have been carried out in methanol by chemically generating the highly nucleophilic cobalt(I) species in the presence of the appropriate alkyl halide. Reduction in methanol occurs only under highly alkaline conditions in the presence of $PdCl_2$ catalyst, suggesting a relatively high Co(II)|Co(I) reduction potential[11] for Co(SALDPT). Electrochemical studies involving Co(SALDPT) support this postulate. Accordingly, the Co(II)|Co(I) polarographic half-wave potential is observed at -2.8 V and the Co(I)|Co(0) potential of the same compound is at -3.1 V (in glyme, *vs.* Ag|0.10 *M* $AgNO_3$).[13] The similar reduction potentials in going from Co(II) to Co(I) and Co(I) to Co(0) also suggest a high-spin cobalt(II)[2] species in glyme. More direct evidence for the high-spin nature of Co(SALDPT) has been obtained by Fritz and Gretner,[14] who report a magnetic moment of 4.15 BM in $CHCl_3$ solution.

The alkyl derivatives are relatively stable in sunlight, air, and water, undergoing little or no noticeable decomposition. They are thermally stable melting above 150° and are quite soluble in chloroform and dimethyl sulfoxide but insoluble in alcohols and water. This behavior is in contrast to the photolability of the analogous R-Co(SALEN)[15] model compounds. Analytical data supporting their composition as RCo(SALDPT) are shown in Table I.

Calvin[9] and later, more definitively, Sacconi[8] reported Co(SALDPT) to be a high-spin five-coordinated complex in the solid state. Since to date all vitamin B_{12} model systems have been prepared starting with low-spin essentially square-planar cobalt(II) complexes, we have taken great care to show that our Co(SALDPT) is the same as that reported earlier. In agreement with Sacconi and Calvin we find that (1) the yellow-brown crude Co(SALDPT) is hydrated, (2) the water of hydration may be removed by drying at 100° for 12 hr under reduced pressure, (3) both crude and dried Co(SALDPT) exhibit repeatedly a magnetic moment around 4.2 BM, which falls in the range for high-spin five-coordinate cobalt(II) complexes,[16] and (4) the visible spectra are similar except for the absence of a band around 6000 cm^{-1} in our Co(SALDPT).

In contrast to Sacconi, we find that recrystallization from warm ethanol–water under nitrogen yields nicely formed green needles which, upon drying at 100° for 12 hr, change to dark brown needles. The recrystallized materials differ in several respects from the crude material. The infrared spectrum of our crude Co(SALDPT) differs significantly in the N–H stretching region from that reported earlier. A single band is observed at 3180 cm^{-1} and assigned to this vibrational mode. Sacconi,[7] in comparison, reports a band at 3250 cm^{-1}. The

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(12) R. H. Lee, E. Griswold, and J. K. Kleinberg, *Inorg. Chem.*, 3, 1278 (1964).

(13) R. E. Dessy and R. W. Koch, unpublished results.

(14) H. P. Fritz and W. Gretner, *Inorg. Nucl. Chem. Lett.*, 3, 141 (1967).

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(16) E. K. Barefield, D. H. Busch, and S. M. Nelson, *Quart. Rev., Chem. Soc.*, **22**, 457 (1968).

location of the N–H stretching mode at this frequency appears inconsistent with the secondary nitrogen being coordinated. This finding is substantiated by the fact that the N–H stretching mode in the free ligand, SALDPT, which we have prepared, occurs at 3255 cm^{-1}.

It is interesting to speculate concerning the exact nature of the green and brown recrystallized needles as opposed to the crude crystalline yellow-brown product. The two materials (recrystallized and crude) differ in several respects. Specifically, (1) visible spectra in solution as well as in the solid state are somewhat dissimilar, (2) the green and brown products are essentially diamagnetic ($\mu_{\text{eff}} \cong 1.0$ BM) and independent of field strength, (3) X-ray powder patterns of both show them to be different structures, and (4) C, H, and N analyses do not agree. Also, exposure of a saturated methanol solution of either of the recrystallized materials to air precipitates a black material which is suspected to be the oxygen adduct whereas the crude yellow-brown material, when treated in the same manner, does not yield a black precipitate. On the other hand, mass spectral measurements on all compounds under identical conditions give essentially superimposable mass spectra which include an isotopic cluster attributable to [Co(SALDPT)]$^+$. The infrared spectra except for the 3300-cm^{-1} region and reactivity with alkyl halides of both our "recrystallized" and crude material are also identical. The exact structure of these new materials obtained by recrystallization is highly conjectural. Elemental analyses on several different samples dried *in vacuo* at room temperature, 78°, and 100° yield data which strongly suggest the formulation [Co(SALDPT)]·3(H_2O). Even on drying *in vacuo* for 29 hr at 117°, the infrared spectrum of the dried material revealed a very strong broad band centered around 3350 cm^{-1} attributable to the presence of water. This would indicate that water is very tightly held in the crystal. From the results obtained to date, it seems reasonable to suggest magnetic isomers for the crude and recrystallized complexes, since there appears to be little difference in their elemental compositions except for the presence of water. The incorporation of water into the complex may (1) impose different packing features on the crystal, thereby introducing some low-symmetry component or intermolecular interaction which would reduce the magnetic moment, or (2) the degree of hydration may affect the distribution between spin states which has been postulated for complexes of some analogous Schiff base ligands.[17]

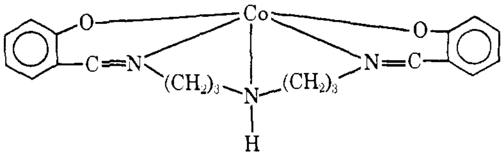
Infrared spectra of the ligand, precursor complex, and alkyl derivatives were obtained as KBr pellets and Nujol mulls. Of particular interest are the positions of the secondary N—H and the C=N stretching vibrational modes. All of the alkyl derivatives behave as the methyl derivative, so it will be discussed with the understanding that the discussion could well apply to all derivatives. The pertinent data are presented in Table II. The drop of 20 cm^{-1} in the position of the C=N stretch between the ligand and two complexes may be attributed to the fact that the imine nitrogen is coordinated, which reduces the bond order of the C=N and lowers the stretching frequency.

Table II. Infrared Data

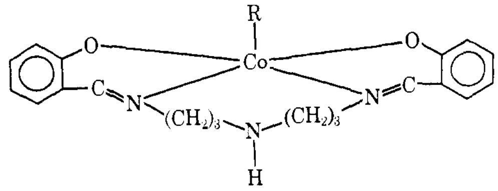
Compound	Frequency, cm^{-1}	Assignment
SALDPT	3255	N—Hst
Co(SALDPT)	3180	N—Hst
CH_3-Co(SALDPT)	3255	N—Hst
SALDPT	1640	C=Nst
Co(SALDPT)	1620	C=Nst
CH_3-Co(SALDPT)	1620	C=Nst

One will notice that this shift of 20 cm^{-1} is not as great as the shift of 35 cm^{-1} observed with Ni(SALDIEN) and Ni(SALDAES) complexes where axial perturbation is predicted to be very small[18] (SALDIEN, bis(salicylidene)-1,5-diamino-3-azapentane and SALDAES, bis(salicylidene)-1,5-diamino-3-thiopentane). It has been shown previously that coordination of a donor atom in an axial position weakens the in-plane ligand-field strength to a certain extent. In other words, the in-plane donor atoms are probably not coordinated as strongly as in the nonaxial perturbation case. This observation strengthens our contention that the secondary N–H in the Co(SALDPT) is coordinated.

Of particular interest is the fluctuating position of the N–H stretching mode. When Co(SALDPT) is converted to RCo(SALDPT), one observes that the N–H stretch returns to the position found in the free ligand. This suggests that RCo(SALDPT) may be a five-coordinate species or, at best, a six-coordinate structure in which the secondary nitrogen is very weakly bound to the cobalt. In other words, both Co(SALDPT) and RCo(SALDPT) may possibly be five-coordinate; however, the difference may be in the groups coordinated to the cobalt, structures IIa and IIb. It has been shown that alkyl ligands act as strong donors, often giving rise to five-coordinate complexes by greatly weakening the donor–metal bond trans to it.[19] The infrared spectra of all derivatives show peaks around 2965 and 2890 cm^{-1} which can be assigned to the aliphatic C–H stretching modes for a methyl group, Table I. Also, a band around 1385 cm^{-1} can be assigned to a methyl bending mode. These bands are totally unique to the alkyl derivatives (*i.e.*, they are not present in the spectrum of the parent complex) and this, coupled with the presence of a relatively strong secondary nitrogen–hydrogen stretching mode, supports the formulation as RCo(SALDPT).



IIa



IIb

Mass spectra were determined on the alkyl derivatives employing conditions described earlier. For deriva-

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[17] J. S. Judge and W. A. Baker, Jr., *Inorg. Chim. Acta*, 1, 68 (1967); C. T. Spencer and L. T. Taylor, unpublished results.

[18] L. T. Taylor and W. M. Coleman, submitted for publication.

[19] H. A. O. Hill, J. M. Pratt, and R. J. P. Williams, *Discuss. Faraday Soc.*, 47, 165 (1969).

Table III. Mass Spectral Data on the Alkyl Derivatives[a]

Compound	Molecular formula	Probe temp, °C	Isotopic cluster
CH_3–Co(SALDPT)	$C_{21}H_{26}N_3O_2Co$	120	411, 412
C_2H_5–Co(SALDPT)	$C_{22}H_{28}N_3O_2Co$	110	425, 426
n-C_3H_7–Co(SALDPT)	$C_{23}H_{32}N_3O_2Co$	145	439, 440
n-C_4H_8–Co(SALDPT)	$C_{24}H_{32}N_3O_2Co$	135	453, 454
n-C_5H_8–Co(SALDPT)	$C_{25}H_{34}N_3O_2Co$	125	467, 463

[a] Isotope patterns for ^{13}C were observed for the complexes but are not included here.

tives with R = CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9, and *n*-C_5H_{11}, *m/e* peaks were observed for (1) the parent ion, (2) the parent ion less R, and (3) the free ligand (Table III). In the cases of R = C_6, C_7, C_8, and C_{10}, no molecular ion was detected, but *m/e* corresponding to the complex Co(SALDPT) was observed. However, in every case there were patterns associated with fragmentation of the appropriate alkane. For instance, in the C_{10} derivative an *m/e* 142 corresponding to $C_{10}H_{22}^+$ was observed along with the fragmentation expected from this alkane. Each spectrum was scanned above the parent *m/e* to check for dimer formation, but no such peaks were observed, which lends strong support to a composition of RCo(SALDPT) in the gas phase.

Nuclear magnetic resonance spectra were obtained on the R = CH_3, C_2H_5, and C_3H_7 derivatives in dimethyl-d_6 sulfoxide. The set of data obtained from these spectra is presented in Table IV. Assignment of the alkyl methylene protons lying closest to the metal was not possible because they fell in the range found for the methylene protons on the backbone chain. This assignment is consistent with the methyl proton resonances found for $CH_3Co(SALEN)$[20] (SALEN = bis(salicylidene)ethylenediamine). Investigation of the free ligand offered no assistance in elucidating the position of the protons under consideration. However, the appearance at relatively high field of a triplet in the case of the ethyl derivative and a poorly resolved doublet in the spectrum of the propyl derivative confirms that the alkyl group is attached to the cobalt atom. The remaining assignments shown in Table V are consistent with the proposed ligand structure.

Table IV. Nmr Data on the Alkyl Complexes

Compound	Range or position, δ[a]	Assignment
CH_3–Co(SALDPT)	7.54–6.40	Vinyl and aromatic protons
	4.24	Proton on secondary N
	3.36–2.04	CH_3 bonded to metal and methylene protons on backbone chain
C_2H_5–Co(SALDPT)	7.64–6.2	Vinyl and aromatic protons
	4.24	Proton on secondary N
	3.32–2.00	α-Methylene protons on ethyl group plus methylene protons on backbone chain
	0.4 (t)	CH_3 group on ethyl group bound to the metal
C_3H_7–Co(SALDPT)	7.12–6.20	Vinyl and aromatic protons
	4.20	Proton on secondary N
	3.34–2.00	α- and β-methylene protons on propyl group plus methylene protons on backbone chain
	1.0 (d)	CH_3 protons on propyl group attached to Co

[a] t = triplet, d = doublet.

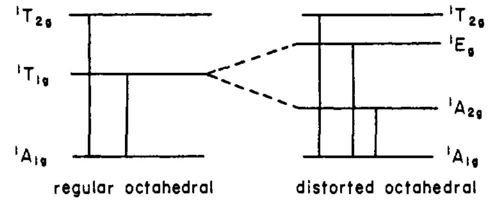

Figure 1. Correlation diagram of ligand-field states of cobalt(III) in octahedral and distorted octahedral fields.

Visible spectra in the solid state of the alkyl derivatives are consistent with a pseudooctahedral environment around a low-spin Co(III) ion,[21] Table V. Two Laporte-forbidden d–d transitions are predicted from the energy level diagram shown in Figure 1 for a regular octahedral Co(III) complex. However, in our case, nonequivalent donor atoms give rise to a structure of lower symmetry, thereby causing a splitting of the $^1T_{1g}$ level. The $^1T_{2g}$ is not split enough to be observed, as predicted by theoretical results.[22]

We observe three transitions in the visible region assignable to transitions from the $^1A_{1g}$ to the three excited states. This suggests a pseudooctahedral environment for the metal ion. The apparent contradiction with the infrared data may be explained by assuming that the secondary nitrogen does not form a ground-state bond with the metal atom but does offer some degree of perturbation.

When the alkyl derivatives are placed in $CHCl_3$ with a minimum exposure to any light, the visible spectrum exhibits the three previously discussed band maxima and a new band at *ca.* 15,500 cm^{-1}. Bands in this region have been assigned to transitions resulting from five-coordinate geometry.[21] It is therefore postulated that in $CHCl_3$ solution two species are present, one being five-coordinate and the other being six-coordinate.

If these same solutions are exposed to the normal daylight of the laboratory, an increase in intensity of the band at 15,500 cm^{-1} is observed along with a very marked increase in intensity of the 18,500-cm^{-1} band, which suggests that the predominant species is the five-coordinate one in $CHCl_3$ when exposed to light. A similar phenomenon is observed in dimethyl sulfoxide. We feel that the five-coordinate species might be the intact complex, R–Co(SALDPT), in which the secondary nitrogen–cobalt bond is not formed, structure IIb. Infrared data in the solid state certainly suggest this as a very likely possibility; Williams and coworkers[19] have demonstrated in a number of cases with physicochemical measurements that the group trans to the carbon substrate behaves essentially as if it were a free ligand. Alternatively, it may be argued that five-coordination could equally well arise from dealkylation of the molecule in the presence of light as a result of the known photochemical instability of most B_{12} model compounds. One observation which would rule against the latter

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

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

Table V. Electronic Spectra (cm^{-1}) of the Alkyl Complexes

Compound	Medium[a]	ν_1	ν_2	ν_3	ν_4
CH_3–Co(SALDPT)	Nujol	18,020 sh	22,990 sh	25,640 sh	
	$CHCl_3$ (NL)	15,630 sh 18,690 sh		26,140	35,710
	$CHCl_3$ (L)	15,680 sh		26,670	
C_2H_5–Co(SALDPT)	Nujol	18,350 sh	22,990 sh	25,970 sh	
	$CHCl_3$ (NL)	15,630 sh 18,520		25,970	35,710
	$CHCl_3$ (L)	15,810		25,970	39,600
n-C_3H_7–Co(SALDPT)	Nujol	18,520 sh	23,530 sh	26,320 sh	
	$CHCl_3$ (NL)	15,560 18,080		25,970	35,710
	$CHCl_3$ (L)	15,750		25,970	39,600
n-C_4H_9–Co(SALDPT)	Nujol	18,520 sh	23,810 sh	25,970 sh	
	$CHCl_3$ (NL)	15,680 18,350		25,030	35,710
	$CHCl_3$ (L)	15,630		25,970	39,600
n-C_5H_{11}–Co(SALDPT)	Nujol	18,180 sh	22,470 sh	24,690	
n-C_6H_{13}–Co(SALDPT)	Nujol	18,180 sh	22,470 sh	25,320	
n-C_7H_{15}–Co(SALDPT)	Nujol	18,180 sh	21,740 sh	22,730 sh	25,320
n-C_8H_{17}–Co(SALDPT)	Nujol	18,520 sh	21,980 sh	23,320	
n-$C_{10}H_{21}$–Co(SALDPT)	Nujol	18,180 sh	22,470 sh	25,320	

[a] NL = solution exposed to no light, L = solution exposed to light.

hypothesis is the fact that nmr spectra of $CDCl_3$ solutions of R–Co(SALDPT) when exposed to the light and not exposed to the light are identical.

The alkyl derivatives result only from the reactions of primary alkyl halides and not secondary or tertiary ones. Numerous reactions were attempted using secondary, tertiary, unsaturated, acyl, and dihalides but without success. It can be shown from molecular models that reaction of a secondary alkyl halide results in a group which is too bulky to occupy the sixth position. Secondary and tertiary halides place alkyl groups in sterically unfavorable positions which are very close to the region of the two benzene aromatic electron clouds. The benzene rings are forced to bend up and out of the CoN_2O_2 plane and away from the secondary nitrogen in order for the ligand to coordinate in a pentadentate manner. In this conformation the aromatic rings essentially encircle the vacant axial site. Hence, this prevents the formation of a σ alkyl carbon–cobalt bond with large and bulky organic groups. Alternatively, the highly alkaline conditions required for the reaction to occur may give rise to elimination of the hydrogen halide and formation of an alkene in a more rapid reaction than the competing metal alkylation reaction.

There is also a distinct dependence on the halide anion insofar as the rate is concerned. Chloro derivatives seem to give no reaction at all. Bromo derivatives react very slowly. However, iodo derivatives react very rapidly; in fact, the product forms almost immediately as soon as the pH is properly adjusted.

In conclusion complexes containing a cobalt–carbon linkage have been prepared and characterized starting with a high-spin cobalt(II) five-coordinate complex. Since the potentially B_{12} model compounds are prepared in methanol solution and the magnetic moment of the precursor has been demonstrated to depend on the degree of hydration, it is highly possible that the ground spin state of the starting material is not a quartet under the conditions of the reaction. Nevertheless, the reported complexes appear to be as stable, and in many cases, more stable than many of the previously reported cobalt–carbon bonded species.

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