Notes

Synthesis, Characterization, and Reactivity of a New Mononuclear Benzyl−Cobalt Complex Containing Mixed Tridentate Imino−Oxime and Diamine Ligands

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*Summary: The complex [$C_6H_5CH_2Co(L)(LR)]ClO_4$ (**3**), where L = 2-((2-pyridylethyl)imino)-3-butanone oximato and LR = 2-((2-pyridylethyl)amino)-3-aminobutane, has been prepared by reduction with $NaBH_4$ of the complex [$Co^{III}(L)_2]ClO_4$, followed by addition of $C_6H_5CH_2Cl$. The compounds was characterized in the solid state by X-ray analysis. The complex undergoes Co−C homolytic cleavage under acidic conditions, giving dibenzyl under a nitrogen atmosphere and benzaldehyde in the presence of air.*

Introduction

The ability to form stable alkylcobalt complexes is typical of tetradentate chelating ligands, such as bis(dimethylglyoximato) and dianions of tetradentate Schiff bases.[1] These complexes have been widely studied over the past few decades since their reactivity pattern[1a] and their structural properties[1b] are similar to those of the vitamin B_{12} system and, for this reason, they are considered vitamin B_{12} models. Much less attention has been devoted to organocobalt derivatives containing tridentate imine ligands.[2] Recently, we have shown that also imino−oximato tridentate ligands are able to stabilize the Co−C bond.[3] In particular, we have recently reported that the cobalt(III) complex [$Co^{III}(L)_2]ClO_4$[4] (**1**) (Scheme 1), containing the monoanionic tridentate imino−oximato ligand L = 2-((2-pyridylethyl)imino)-3-butanone oximato, can be employed to obtain stable hydroxo-bridged dinuclear organocobalt complexes of the type **2** (Scheme 1).[3] The synthetic procedure is similar to that used to prepare alkylcobaloximes and other alkylcobalt complexes[1] and involves the in situ generation of a Co(I) species starting from complex **1** and successive addition of the appropriate alkyl iodide RI. Formation of μ-hydroxo dinuclear organocobalt species is observed for R = CH_3, C_2H_5,[3] CH_2CF_3, and CH_2Cl.[5] When $C_6H_5CH_2Cl$ is used as the alkylating agent instead of the corresponding diorganocobalt complex, the mononuclear species **3** (Scheme 1) is obtained and isolated as the perchlorate salt. The synthesis, structure, and some aspects of the reactivity of this new complex are reported here.

Results and Discussion

Addition of $NaBH_4$ to a MeOH solution of [$Co^{III}(L)_2$]-ClO_4, made alkaline with NaOH, under a nitrogen atmosphere resulted in a rapid darkening of the initial red color, denoting the formation of the [$Co^{I}(L)_2]^-$ nucleophilic species. By addition of benzyl chloride the solution turned brownish red to give the complex [C_6H_5-$CH_2Co(L)(LR)]ClO_4$ (**3**; LR = 2-((2-pyridylethyl)amino)-3-aminobutane), isolated and purified as described in the Experimental Section. The complex has been characterized by elemental analysis and X-ray diffraction.

The crystals of **3** are built up by [$C_6H_5CH_2Co(L)(LR)]^+$ cations and ClO_4^- anions. The ORTEP drawing of the cation is shown in Figure 1. The L tridentate ligand in a *mer* configuration coordinates Co through its N-donors in a way similar to that found in the parent complex **1**, whereas the LR neutral ligand (vide infra) chelates Co through its amino N(3) and N(5) donors. The sixth coordination position is occupied by the σ-bonded C_6H_5-CH_2 group, trans to N(3). The analysis of bond lengths and angles indicates (Table 2) single bonds and tetrahedral geometries around C(26) and C(28) (Figure 1), suggesting that LR is formed from L by reduction of both the iminic and oximic functions to the aminic one. Both *R* and *S* configurations of C(28), one of the two chiral centers of LR, are present, as shown by the half-occupancy of the C(28)-bonded methyl group in the equatorial (C(291)) and axial (C(292)) positions. The pendant pyridyl group is anchored through N(6) to the other chiral center N(3) by a hydrogen bond of 2.915(5) Å. The L and LR ligands interact through a hydrogen bond of

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[1] (a) Toscano, P. J.; Marzilli, L. G. *Prog. Inorg. Chem.* **1984**, *31*, 105. (b) Bresciani Pahor, N.; Forcolin, M.; Marzilli, L. G.; Randaccio, L.; Summers, M. F.; Toscano, P. J. *Coord. Chem. Rev.* **1985**, *63*, 1. (c) Randaccio, L.; Bresciani-Pahor, N.; Zangrando, E.; Marzilli, L. G. *Chem. Soc. Rev.* **1989**, *18*, 225.

[2] (a) Levitin, I. Ya.; Tsikalova, M. V.; Bakhmutov, V. I.; Yanovsky, A. I.; Struchkof, Yu. T.; Vol'pin, M. E. *J. Organomet. Chem.* **1987**, *330*, 161. (b) Levitin, I. Ya.; Yatsimirskij, A. K.; Vol'pin, M. E. *Metalloorg. Khim.* **1990**, *3*, 865; *Organomet. Chem. USSR* **1990**, *3*, 442.

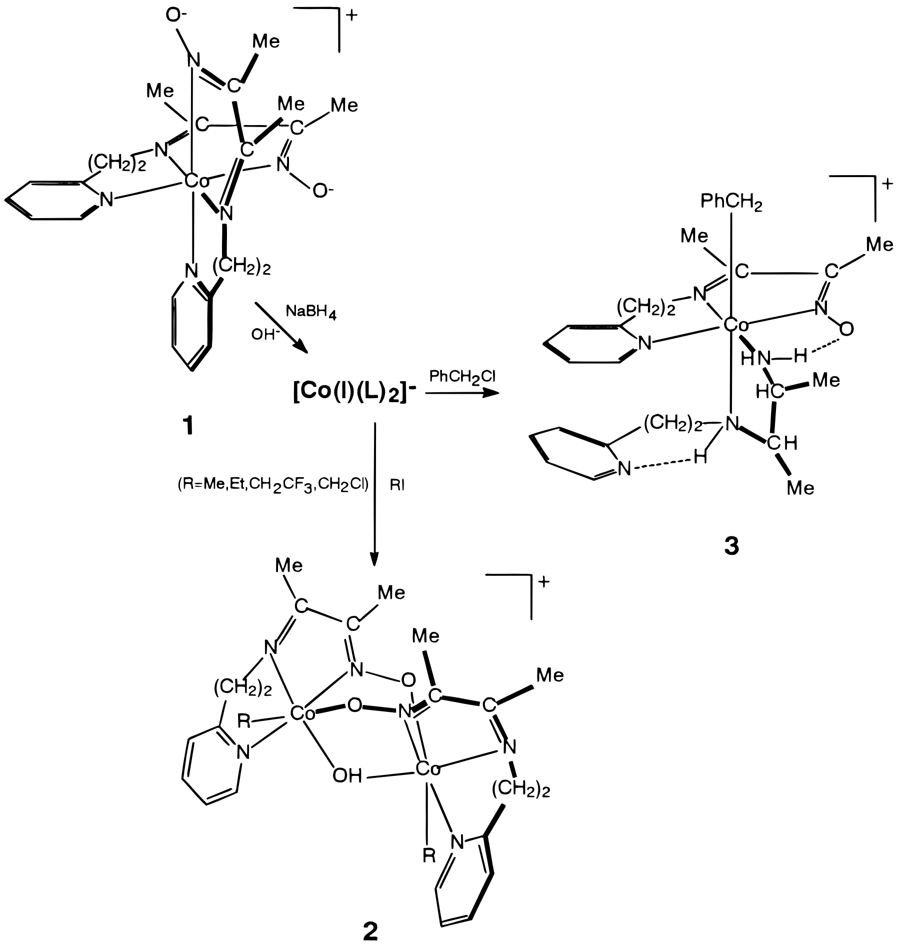
[3] Dreos, R.; Tauzher, G.; Trendafilova, D. H.; Nardin, G.; Randaccio, L. *Inorg. Chem.* **1996**, *35*, 2715.

[4] (a) Uhlig, E.; Schneider, D.; Hildebrandt, H. *Z. Anorg. Allg. Chem.* **1966**, *346*, 173. (b) Pajunen, A.; Pajunen, S. *Acta Crystallogr., Sect. C* **1983**, *39*, 852.

[5] Ongoing studies on the species **2**, containing other alkyl R groups, indicate that the formation of **2** occurs also when R = CH_2Cl, CH_2-CF_3.

S0276-7333(97)00967-9 CCC: $15.00

Scheme 1



2.724(5) Å between O(1) and N(5) (Figure 1), which contributes to the stabilization of the complex. The long Co−N(3) bond length of 2.135(4) Å is due to the *trans* influence of the benzyl group, which binds to Co through the Co−C distance of 2.044(5) Å and the Co−C−Ph angle of 118.8(4)° (Table 2).

The reason two different kinds of complexes (dinuclear and mononuclear), (Scheme 1) are formed in the alkylation reaction is not clear at the present time, and it is under study. We have previously suggested[3] that the formation of the dinuclear complex **2** proceeds through the reduction of **1**, leading to the $[Co^{I}(L)_2]^-$ monoanion, without any structural rearrangement. This nucleophilic species under alkylation conditions gives a mononuclear alkyl derivative as the precursor of **2**, losing one L unit, which is found reduced at the iminic function in the reaction mixture as free 2-((2-pyridylethyl)amino)-3-butanone oxime, LH. In the case of **3,** after alkylation of the $[Co^{I}(L)_2]^-$ species with C_6H_5-CH_2Cl, the complete reduction of one L ligand of the Co(I) intermediate to LR occurs. The latter ligand remains still coordinated with displacement of only the pyridyl ligand out of the metal coordination sphere (Scheme 1). Assuming that the $[Co^{I}L_2]^-$ ion has the same geometry as **1** (Scheme 1), on the basis of the structure of **3** (Scheme 1), it can be suggested that the benzyl attack to the metal center occurs at the side of the coordinated *N*-oxime donor and not on the side of the *N*-pyridyl one.

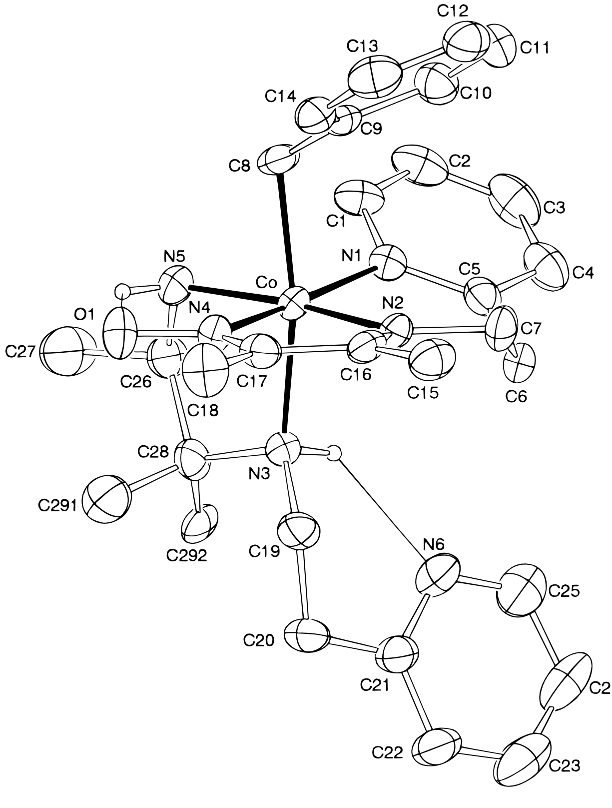


Figure 1. ORTEP drawing of the cation of **3**, $[C_6H_5CH_2$-$Co(L)(LR)]^+$, with 30% probability thermal ellipsoids, showing the numbering scheme.

Table 1. Crystal Data and Structure Refinement Details for 3

identification code	$[C_6H_5CH_2Co(L)(LR)]ClO_4$
empirical formula	$C_{29}H_{40}N_6O_5ClCo$
fw	647.04
temp	293(2) K
wavelength	0.710 73 Å
cryst syst	monoclinic
space group	$P2_1/n$
unit cell dimens	$a = 9.515(2)$ Å $b = 28.120(8)$ Å $c = 11.442(2)$ Å $\alpha = 90°$ $\beta = 90.56(2)°$ $\gamma = 90°$
V	3061.3(12) Å ^{3}
Z	4
density (calcd)	1.402 Mg/m^3
abs coeff	0.696 mm^{-1}
F(000)	1370
cryst size	0.4 × 0.2 × 0.8 mm
θ range for data collection	2.26−27.99°
no. of rflns collected	7718
no. of indep rflns	7370 [R(int) = 0.0418]
refinement method	full-matrix least squares on F^2
no. of data [$I > 2\sigma(I)$]/ restraints/params	2914/0/393
goodness of fit on F^2	0.858
final R indices [$I > 2\sigma(I)$]^a	R1 = 0.0835, wR2 = 0.1710
largest diff peak and hole	0.517 and −0.375 e Å^{-3}

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for 3

(a) Bond Lengths

Co−N(1)	2.014(5)	N(3)−C(28)	1.497(7)
Co−N(2)	1.909(4)	N(5)−C(26)	1.478(7)
Co−N(3)	2.135(4)	C(26)−C(28)	1.527(8)
Co−N(4)	1.871(5)	O(1)···N(5)	2.724(5)
Co−N(5)	1.961(4)	N(3)···N(6)	2.915(5)
Co−C(8)	2.044(5)		

(b) Bond Angles

N(1)−Co−N(2)	93.9(2)	N(4)−Co−C(8)	85.8(2)
N(1)−Co−N(3)	90.8(2)	N(5)−Co−C(8)	87.3(2)
N(1)−Co−N(4)	174.1(2)	Co−C(8)−C(9)	118.8(4)
N(1)−Co−N(5)	95.1(2)	N(5)−C(26)−C(27)	111.8(6)
N(1)−Co−C(8)	90.6(2)	N(5)−C(26)−C(28)	108.0(5)
N(2)−Co−N(3)	97.1(2)	C(27)−C(26)−C(28)	113.9(5)
N(2)−Co−N(4)	81.8(2)	N(3)−C(28)−C(26)	107.0(4)
N(2)−Co−N(5)	170.9(2)	N(3)−C(28)−C(291)	113.8(6)
N(2)−Co−C(8)	94.5(2)	N(3)−C(28)−C(292)	115.3(8)
N(3)−Co−N(4)	93.7(2)	C(291)−C(28)−C(292)	102.5(9)
N(3)−Co−N(5)	81.0(2)	C(26)−C(28)−C(291)	109.5(6)
N(4)−Co−N(5)	89.4(2)	C(26)−C(28)−C(292)	108.7(8)

The complex **3**, in a manner similar to the other alkylcobalt derivatives, is sensitive to the light.[1] However, it undergoes ready decomposition at room temperature upon acid treatment, in contrast with alkylcobalt compounds containing bis-glyoximate and tetradentate Schiff base ligands, which are acid-resistant even under vigorous conditions, unless the alkyl group has an O substituent on its β-carbon atom.[1a] The decomposition of **3** gives dibenzyl under an N_2 atmosphere and benzaldehyde in the presence of air, suggesting the homolytic cleavage of the Co−C bond. The yields, obtained by HPLC and UV spectrophotometry, were 65% and 75% of the theoretical amounts for dibenzyl and benzaldehyde, respectively. The organic products of the acid decomposition are those observed in the thermal homolysis of benzylcobalamin under aerobic and anaerobic conditions.[6]

Preliminary kinetic experiments indicate that the reaction of **3** with acids is biphasic and can be described by two exponential decays. The corresponding k_1^{obs} and k_2^{obs} kinetic constants were determined spectrophotometrically in the presence of oxygen and under pseudo-first-order conditions with respect to the complex (see Experimental Section). Only the first process is believed (vide infra) to be responsible for the production of benzaldehyde, and k_1^{obs} depends on [H$^+$], as shown in eq 1.

$$k_1^{obs} = a[H^+]/(b + [H^+]) \qquad (1)$$

Scheme 2 can be suggested for this process. Rapid steps of oxidation of the benzyl radical to benzaldehyde follow.[6] Hence, on the basis of eq 1 and Scheme 2, $a \equiv k = 0.02 \pm 0.01$ s^{-1} and $b \equiv K = 0.011 \pm 0.003$ M^{-1}.

Scheme 2

$$[C_6H_5CH_2Co^{III}(L)(LR)]^+ + H^+ \overset{K}{\rightleftharpoons} [C_6H_5CH_2Co^{III}(LH)(LR)]^{2+}$$

$$[C_6H_5CH_2Co^{III}(LH)(LR)]^{2+} \xrightarrow{k} [Co^{II}(LH)(LR)]^{2+} + C_6H_5CH_2^{\bullet}$$

k_2^{obs} ((7.5 ± 0.8) × 10^{-4} s^{-1}) is not pH-dependent and is likely associated with the reoxidation of $[Co^{II}(LH)(LR)]^{2+}$. According to the Scheme 2, the homolytic cleavage of the Co−C bond is preceded by the reversible addition of H$^+$ to the O(1) oxygen of the L ligand (Figure 1). This interaction, involving the breaking of the O(1)···N(5) hydrogen bond, leads to a decrease in electron density at the central metal atom as a consequence of the decreased electron-donating property of the ligand.[2b] Thus, an increase in the relative stability of the product $[Co^{II}(LH)(LR)]^{2+}$ with respect to the starting alkylcobalt complex is expected with a consequent lowering of the Co−C bond dissociation energy.[7] In addition, the breaking of the intramolecular hydrogen bond should contribute in destabilizing the whole Co(III) alkyl complex.

The behavior of **3** makes this compound a good reservoir of alkyl radicals which are released under acidic conditions. In this respect, it is similar to that of some alkylcobalt complexes containing one tridentate Schiff base and one diamine as ligands.[2] Further experiments are in progress, aimed at clarifying the mechanistic aspect of the homolytic cleavage reaction as well as obtaining complexes analogous to **3**, containing other alkyl groups.

Experimental Section

Synthesis of $[C_6H_5CH_2Co(L)(LR)]ClO_4$. To a solution of $[Co^{III}(L)_2]ClO_4$ (1.00 g, 1.86 mmol) in 150 mL of MeOH, made alkaline by addition of 0.1 g of NaOH in 5 mL of water under an inert atmosphere and stirring, was added 0.1 g $NaBH_4$ (2.64 mmol) in 5 mL of water. After 30−40 min of stirring at 40 °C, when no further darkening of the initial red color was detectable, an excess of benzyl chloride was added (0.5 mL). When the solution turned brownish red, the stirring was

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stopped and the solvent was evaporated nearly to dryness in air. The residue was taken up in CH_2Cl_2, precipitated with *n*-pentane, and filtered. The solid was redissolved in a minimum amount of water and reprecipitated by dropwise addition of saturated $NaClO_4$ solution (***Caution!*** **Perchlorate salts of complexes containing organic ligands are potentially explosive and should be handled only in small quantities!).** The solid was collected by filtration and dried under vacuum. Anal. Calcd for $C_{29}H_{40}N_6O_5ClCo$: C, 53.8; H, 6.23; N, 13.0. Found: C, 53.0; H, 6.15; N, 12.8.

Structure Determination of 3. Red-brown crystals of **3** were obtained by slow diffusion of pentane in a CH_2Cl_2 solution of **3**. Data were collected on an Enraf-Nonius CAD4 four-circle automated diffractometer with graphite-monochromated Mo Kα radiation. A total of 7370 independent reflections were collected up to $2\theta = 58.0°$ 2914 of which were observed with $I > 2\sigma(I)$. Correction for Lorentz−polarization and φ-scan absorption was applied. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares (on F^2) with anisotropic thermal parameters for all non-hydrogen atoms. The H atoms were not refined but included at calculated positions in the final refinement. Crystal, collection, and refinement data are given in Table 1. The programs used are given in refs 8 and 9. Selected bond lengths and angles are listed in Table 2.

Cobalt−Carbon Bond Cleavage Induced by Acids. In typical experiments, solutions of **3** in water-methanol of the following composition were used: 5×10^{-4} M complex, 30% methanol, 1×10^{-3} M $HClO_4$. For anaerobic conditions the solution was first rigorously deareated with nitrogen. After completion of the reactions the organic products (benzaldehyde or dibenzyl) were analyzed by HPLC. The identities and yields of the products were determined by comparison with standards.

In an alternative procedure, the alkylation was carried out in aqueous solutions having concentrations of complex and $HClO_4$ as indicated above. The organic products were extracted into *n*-hexane, identified, and quantitatively analyzed by means of UV spectrophotometry using standard solutions of benzaldehyde and dibenzyl in *n*-hexane.

Kinetic Measurements. The decomposition of the complex **3** was followed spectrophotometrically at 370 nm and 25 °C. The reaction was started by addition of appropriate amounts of 1 M $HClO_4$ to a solution of the following composition: 5×10^{-5} M complex, 1.0 M $NaClO_4$, and 10% methanol. The proton concentration, ranging from 3×10^{-4} to 5×10^{-2} M, was taken as the analytical concentration of the acid, being in excess with respect to the complex concentration.

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Supporting Information Available: Tables of crystal data and collection and refinement parameters, positional parameters, bond distances and angles, hydrogen atom coordinates, and anisotropic thermal factors (6 pages). Ordering information is given on any current masthead page.

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