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New Alkyl–Cobalt(III) Complexes Containing Chiral Centers in the Chelating System

Renata Dreos, Alessandro Felluga, Giorgio Nardin, Lucio Randaccio,* Mauro Sandri, and Giovanni Tauzher*

Dipartimento di Scienze Chimiche, Università di Trieste, via Giorgieri 1, 34127 Trieste, Italy

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The complex *mer*-$[Co^{III}(L_1Npy)_2]^+$ (**1′**) where the L_1Npy^- is the tridentate 3-[(2-pyridyl)methylimino]butan-2-one oximate ligand, gives alkyl–cobalt derivatives after reduction with $NaBH_4/Pd^{2+}$ to the Co^I and alkylation. The formation of the cobalt–carbon bond is accompanied by the reduction to the amino form of one or both imino ligands (depending on the experimental conditions) initially present in **1′**. In one series of experiments, complexes of the type *fac*-$[RCo^{III}(L_1Npy)(H\text{-}L_1NHpy)]^+$ (R = Me, *i*-Pr, CH_2Cl, CH_2Br, CH_2CF_3, and Bz) were obtained, in which only one of the two ligands was reduced to the amino form (H-L_1NHpy). The saturation of one azomethine group causes the products to assume a *fac* configuration and induces the formation of one asymmetric carbon and one asymmetric nitrogen center in the chelating system. When an excess of reducing agent is used, both azomethine groups may be saturated, causing the introduction of one pair of chiral carbons and one pair of chiral nitrogens. Two isomers of the methyl derivative $[MeCo^{III}(L_1NHpy)(H\text{-}L_1NHpy)]^+$ were isolated. The X-ray analysis reveals that these isomers differ from one another in configuration of the C and N chiral centers. Possible reaction mechanisms leading to these different types of complexes are proposed.

Introduction

In previous works we have shown that the cobalt(III) complexes containing tridentate amino−oxime and imino−oxime ligands can be used as precursors in the synthesis of alkyl−cobalt derivatives with stable Co−C bonds. The ligands mentioned in this paper are depicted in Figure 1.

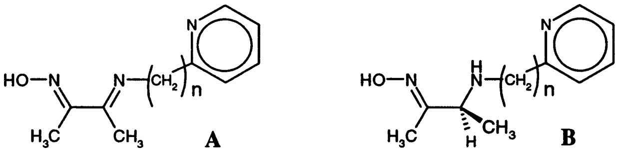
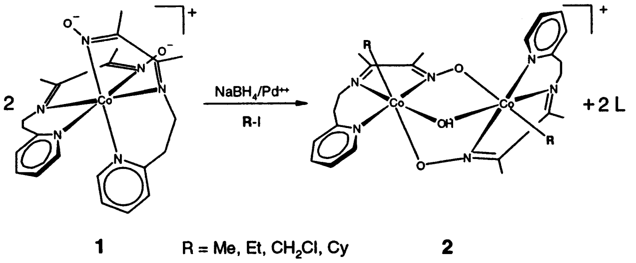


Figure 1. **A**: (*n* = 1) 3-[(2-pyridyl)methylimino]butan-2-one oxime (H-L_1Npy); (*n* = 2) 3-[2-(2-pyridyl)ethylimino]-butan-2-one oxime (H-L_2Npy). **B** (*n* = 1) 3-[(2-pyridyl)methylamino]-butan-2-one oxime (H-L_1NHpy); (*n* = 2) 3-[2-(2-pyridyl)ethylamino]-butan-2-one oxime (H-L_2NHpy). Italic *H* indicates the acidic hydrogen of the oxime group. The ligands may be coordinated also in the form of oximate, i.e.: L_1Npy^-, L_2Npy^-, L_1NHpy^-, L_2NHpy^-.

More specifically, we reported that the *mer*-$[Co^{III}(L_2Npy)_2]^+$ (**1**), after reduction to Co^I and alkylation with several alkyl halides, gives dinuclear organometallic species of the type $[\mu\text{-}OH(RCo^{III}L_2Npy)_2]^+$ (**2**), (R = Me, Et, CH_2Cl, CH_2CF_3, and Cy)[1,2] (Scheme 1). When ClBz and ICy were used as alkylating agents, the products were a mononuclear benzyl derivative[3] and a mixture of separable mono- and dinuclear cyclohexyl derivatives,[2] respectively.

Scheme 1



Under the same treatment the *fac*-$[Co^{III}(L_2NHpy)(H\text{-}L_2NHpy)]^{2+}$ dication (**3**) gives the mononuclear alkyl−cobalt derivatives[4,5] $[RCo^{III}(L_2NHpy)(H\text{-}L_2NHpy)]^+$ (**4**). As illustrated in Scheme 2, cations **4** may be formally derived from **3** by replacement of one of the two pyridyl groups with

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* Authors to whom correspondence should be addressed. E-mail: tauzher@dsch.univ.trieste.it (G.T.); randaccio@univ.trieste.it (L.R.).

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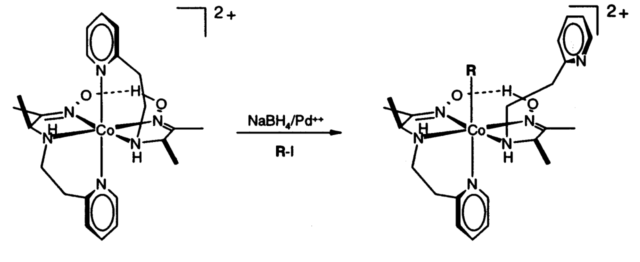
Scheme 2



3 **4**

R = Me, Et, CH_2Cl, CH_2Br, CH_2I, CH_2CF_3, n-Bu

the alkyl R group. The species **4**, reminiscent of the "lariat" type complexes described by Marzilli et al.,[6,7] have been shown to be a better structural model for cobalamins than those previously reported.[4]

In order to obtain further insight into the influence of the nature of the tridentate ligand on the alkylation reactions, we synthesized and characterized a new series of alkyl−cobalt complexes. They derive from the *mer*-$[Co^{III}(L_1Npy)_2]^+$ cation (**1′**)[8] containing the L_1Npy^- which differs from L_2Npy^- (present in **1**) only for having a shorter "arm" ($-CH_2-$ vs $-CH_2CH_2-$) which links the pyridyl group to the equatorial moiety. The L numeral subscript indicates the number of CH_2 groups of the "arm". In view of the similarities between complexes **1** and **1′**, it is expected that the latter one, under reduction and alkylation, may give dinuclear alkyl derivatives closely related to those deriving from **1**. On the contrary, the results obtained show that complex **1**, under the same treatment applied to **1′**, gives mononuclear alkyl derivatives. In addition, the reaction of **1′** involves a *mer* → *fac* configurational change and at the same time the reduction of one of the two imino tridentate ligands to the amino form (compounds **6′a**−**6′f**). When an excess of reducing agent is used, both of the tridentate ligands may be reduced. Two isomers of the methyl derivative with both of the ligands in the amino form were obtained (compounds **4′** and **5′**). They differ from one another in the configuration of the C and N chiral centers located over the plane of the chelating system.

Results and Discussion

Syntheses. The reactions that were studied are summarized in Scheme 3. The experimental conditions of reactions 1−3 in Scheme 3 are reported in the text.

Reaction 1 leads to alkyl compounds of the type $[RCo^{III}(L_1Npy)(H\text{-}L_1NHpy)]^+$ (R = Me (**6′a**), *i*-Pr (**6′b**), CH_2Cl (**6′c**), CH_2Br (**6′d**), CH_2CF_3 (**6′e**), and Bz (**6′f**)), where only one of the two imino ligands is reduced to the amino form, and the unmodified imino ligand acts as a bidentate ligand.

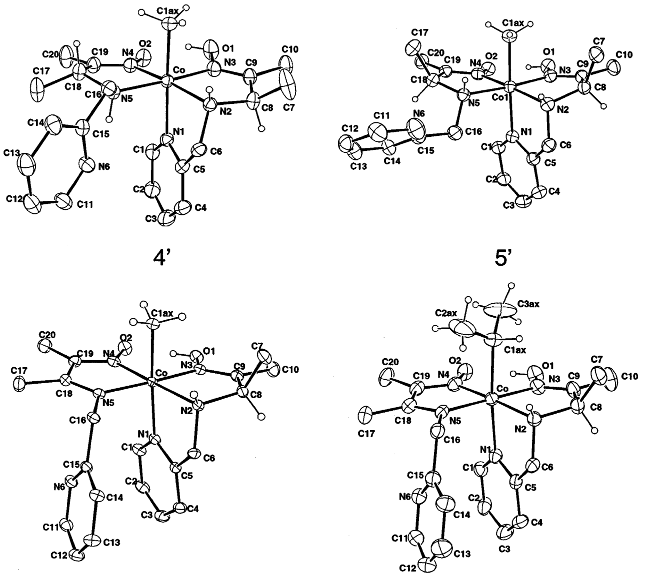

4′ 5′ 6′a 6′b

Figure 2. ORTEP diagram of the cations $[MeCo^{III}(L_1Npy)(H\text{-}L_1NHpy)]ClO_4$ (isomer *a*) (**4′**), $[MeCo^{III}(L_1Npy)(H\text{-}L_1NHpy)]ClO_4$ (isomer *b*) (**5′**), $[MeCo^{III}(L_1Npy)(H\text{-}L_1NHpy)]^+$ (**6′a**), and $[i\text{-Pr}\ Co^{III}(L_1Npy)(H\text{-}L_1NHpy)]^+$ (**6′b**).

Reaction 1 was performed in an alkaline (NaOH) water/methanol solution, at room temperature, under inert atmosphere (N_2) and with the reaction vessel protected from direct exposure to the light. Reduction of **1′** to Co^I was achieved by addition of a $NaBH_4/PdCl_2$ solution, and the appropriate alkyl halide was then added. Excess $NaBH_4$ was subsequently destroyed by addition of concentrated CH_3COOH. The nonorganometallic complex *fac*-$[Co^{III}(L_1NHpy)(H\text{-}L_1NHpy)]^+$ (**3′**) (previously described[8]) in an approximate 1:1 molar ratio with the alkyl−cobalt complex is also formed.

Reaction 2 (CH_3I was the only alkylating agent used in this instance) gives the complex $[MeCo^{III}(L_1NHpy)(H\text{-}L_1NHpy)]^+$ (isomer *a*) (**4′**), with both of the ligands in the amino form and two chiral carbons and two chiral nitrogens present in the chelating system. Reaction 2 requires some modifications of the above procedure; i.e., the temperature was raised to 40 °C, and the quenching with CH_3COOH was avoided. As found in reaction 1, **3′** was recovered from the reaction mixture together with the organocobalt complex.

Further reduction of **6′a** with $NaBH_4$ in methanol (reaction 3) in the presence of air gave $[MeCo^{III}(L_1NHpy)(H\text{-}L_1NHpy)]^+$ (isomer *b*) (**5′**), with both of the ligands in the amino form. Isomer *b* differs from isomer *a* for the opposite configuration of the C and N centers located on the ligand acting as bidentate. The configuration of the two isomers *a* and *b* is assigned on the basis of the X-ray analysis. In Scheme 3 the aerobic photolysis of **4′** to give **3′** is also illustrated. All of the above-mentioned complexes were obtained as perchlorate salts. Isolation procedures and other details of the syntheses are given in the Experimental Section.

Structures. The ORTEP drawings of **4′**, **5′**, **6′a**, and **6′b** are depicted in Figure 2. The corresponding crystallographic data are reported in Table 1.

For **5′**, only the ORTEP drawing of one of the two crystallographically independent molecules is shown. Se-

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(4) Dreos, R.; Felluga, A.; Nardin, G.; Randaccio, L.; Siega, P.; Tauzher, G. *Eur. J. Inorg. Chem.* **2001**, 267.

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(8) Catalano, L.; Dreos, R.; Nardin, G.; Randaccio, L.; Tauzher, G.; Vuano, S. *J. Chem. Soc., Dalton Trans.* **1996**, 4267.

Scheme 3

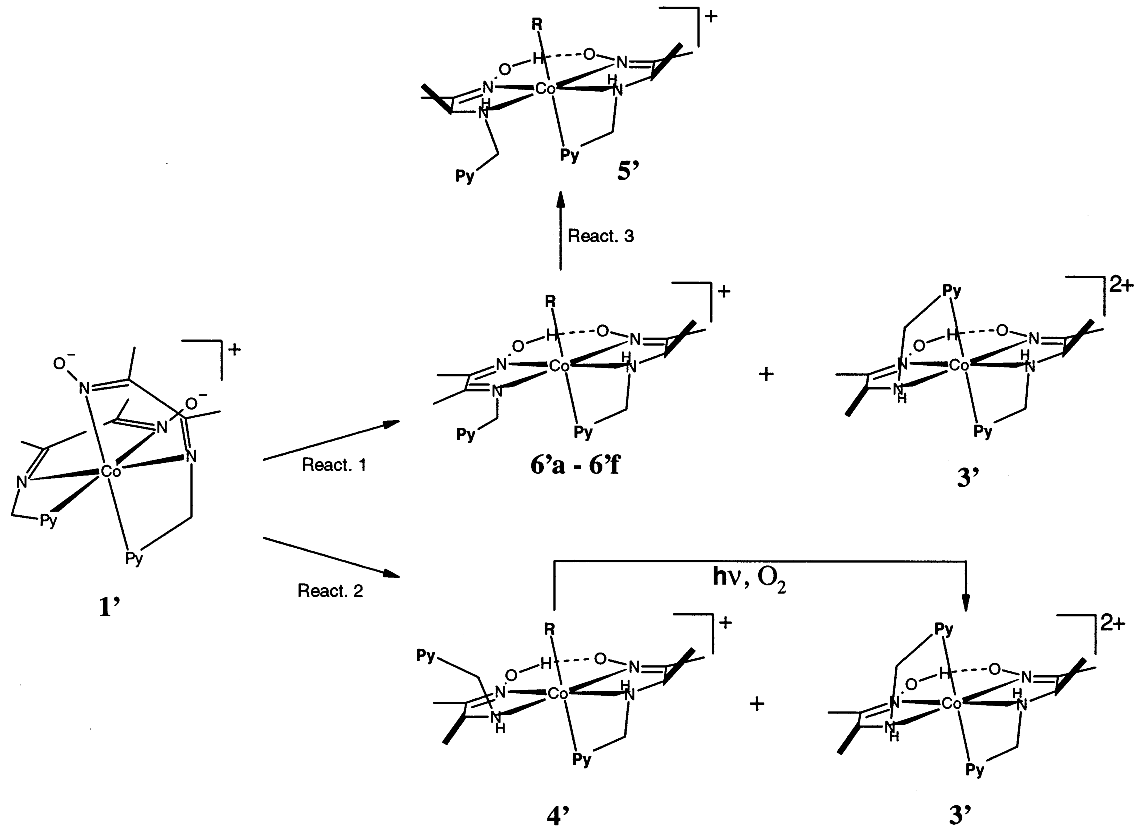

Table 1. Coordination Bond Lengths and Angles in the Five- and Six-Membered Rings Involving the N_{py} Donor

	1	1′	3	3′	4	4′	5′	6′a	6′b
Co−N_{py}	**2.038(4)**[a]	**1.954(4)**	**2.020(5)**	**1.924(4)**	2.160(5)	2.072(3)	2.032(4)	2.018(3)	2.047(7)
Co−C					1.972(7)	1.980(3)	1.994(5)	1.987(3)	2.063(8)
N1−Co−N2	**93.7(2)**	**83.9(2)**	**93.0(2)**	**83.5(2)**	92.7(2)	80.9(1)	82.7(2)	82.3(1)	82.2(2)
Co−N1−C5	**123.8(2)**	**113.8(3)**	**125.9(2)**	**114.3(2)**	125.7(4)	112.4(2)	114.4(3)	114.8(2)	113.1(5)
Co−N1−C1	**119.0(3)**	**125.7(3)**	**116.9(2)**	**126.0(2)**	117.8(4)	128.2(2)	127.0(4)	126.5(3)	127.1(6)
N3−O1	1.268(5)	1.279(7)	1.349(6)	1.341(4)	1.362(7)	1.354(4)	1.353(5)	1.367(4)	1.364(8)
N4−O2	1.265(5)	1.277(6)	1.344(6)	1.346(5)	1.363(7)	1.355(3)	1.350(5)	1.330(4)	1.325(9)
O···O			2.408(6)	2.386(4)	2.402(7)	2.427(3)	2.423(5)	2.440(4)	2.494(8)

[a] Figures in bold are the mean values of chemically equivalent distances or angles.

lected bond lengths and angles are given in Table 1. The complexes **4′** and **5′** have opposite configurations of the N5 and C18 chiral centers. Furthermore, the pendant pyridyl is arranged to form a N5−H···N6 bond (N5···N6 = 2.731(4) Å) in **4′**, whereas no hydrogen bond is present in **5′** (N5···N6 = 3.317 (3.351) Å) (Figure 1). The complex **4′** can be formally described as derived from the parent compound **3′**, by substitution of one axial pyridyl residue with the methyl group. The complex **4′** closely resembles the analogous methyl derivative **4**, (R = Me in Scheme 2), having the same configuration of the N and C chiral centers.

In **6′a** and **6′b** (Figure 2 and Supporting Information) the tridentate ligand is the amino−oxime *H*-L_1NHpy and the bidentate is the imino−oximate L_1Npy^-. Comparison of the N−O distances in both complexes **6′a** and **6′b** and the inspection of the Fourier difference maps strongly suggest that the H atom of the oxime bridge is bonded to O1. In both **6′a** and **6′b** the noncoordinated pyridyl residue is approximately parallel to that coordinated to Co (Figure 2). The configuration of the chiral N2 and C8 centers is the same as that found in **4′** and **5′**. The lengthening of both Co−C and Co−N_{py} axial distances in **6′b** with respect to **6′a** (Table 1) can be attributed to the increased trans influence (Co−N_{py} lengthening) and bulk (Co−C lengthening) of *i*-Pr compared with Me. The same trend is usually found in B_{12} models.[9]

The coordination bond lengths and angles of a series of organocobalt complexes with tridentate ligands and their respective parent compounds **1**, **3** and **1′**, **3′** are summarized in Table 1. The following points appear to be noteworthy. The Co−C (C = Me) bond length does not substantially vary along the series and appears to be very close to that reported for the methyl derivatives of many other B_{12} models.[9] The Co−N_{py} bond length trans to the Me group varies from 2.018(3) Å in **6′a** to 2.072(3) Å in **4′**. Both of these derivatives contain the L_1NHpy ligand. The corre-

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(9) Bresciani-Pahor, N.; Forcolin, M.; Marzilli, L. G.; Randaccio, L.; Summers, M. F.; Toscano, P. J. *Coord. Chem. Rev.* **1985**, *63*, 1.

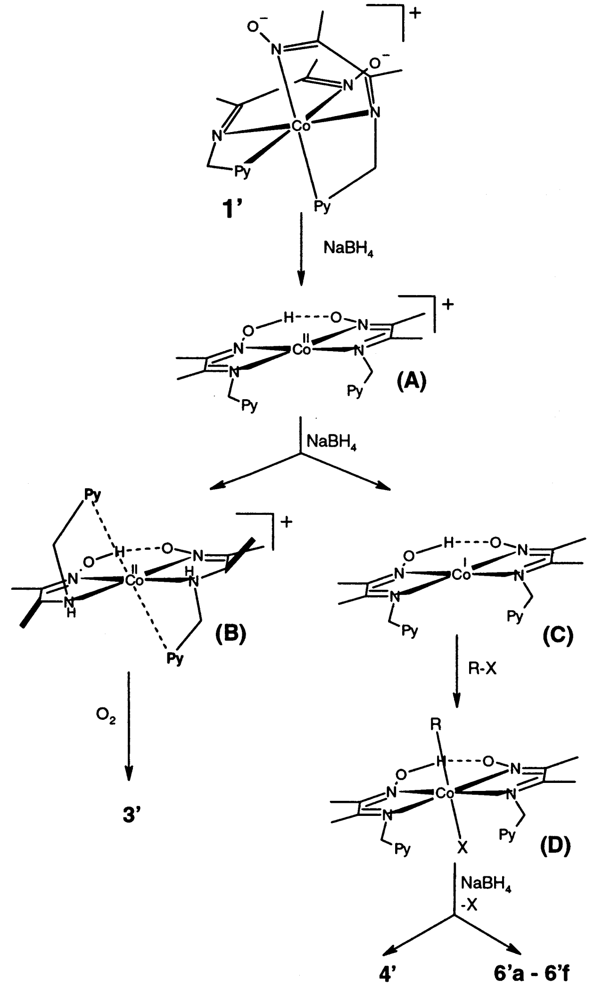
sponding Co−N_{py} bond distance is significantly higher (2.134(5) Å) in cation **4**, which contains the L_2NHpy ligand. This difference in the Co−N_{py} distances is also found when the Co−N_{py} distances are compared in the parent coordination complexes, that is, **1** versus **1′** and **3** versus **3′**. As expected, the N1−Co−N2 and Co−N1−C5 angles are smaller by about 10° for the L_1NHpy derivatives compared with the L_2NHpy derivatives. These differences in geometry are due to the different constraints required for the five-membered metallocycle closure with respect to those required for the six-membered cycle closure.

The trend observed for the Co−N_{py} distances, increasing in the order **6′a** (2.018(3) Å) < **5′** (2.032(4) Å) < **4′** (2.072(3) Å) (Table 1), clearly shows the cis influence of the equatorial moiety in complexes containing L_1NHpy ligands. Noteworthily, the Co−N_{py} found in **6′a** is shorter than any other Co−N(axial) distance so far reported in the vitamin B_{12} models.[9]

Photolysis of the Complex 4′. It is well-known that alkyl−cobalt compounds are light sensitive.[10] In particular, the methyl derivatives under exposure to light, in the presence of oxygen, undergo homolytic cleavage of the Co−C bond. The products of the photodecomposition are a Co^{II} complex and formaldehyde, the latter resulting from the reaction of dioxygen with the Me radical. After the aerobic photolysis of **4′** in methanol solution (Scheme 3), **3′** was recovered from the reaction mixture, suggesting that the initially formed Co^{II} complex has been oxidized in air. The formation of **3′** from **4′** is favored by the configuration of the chiral nitrogen bearing the pendent pyridyl. Similar behavior[4] is exhibited by the methyl derivative **4**, which has chiral centers with the same configuration of **4′**. No analogous reaction could be given by **5′** as an obvious consequence of its stereochemical properties (Figure 2). Only unidentified materials could be recovered after exposure of the latter complex to light.

Formation of the Nonorganometallic Complex 3′. Reactions 1 and 2 in Scheme 3 show that the nonorganometallic amino compound **3′** is also formed. This should be explained on the basis of some hypotheses as illustrated in Scheme 4.

Scheme 4



It is assumed that the Co^{II} complex[11−14] (intermediate **A**) could be the initial product of the reduction of **1′** and that two competitive pathways arise from it. One involves the Co^{II}−Co^{I} reduction to give intermediate **C**, followed by alkylation (intermediate **D**). Excess $NaBH_4$, still present in the reaction mixture, induces reduction of one or both tridentate ligands of intermediate **D** to give **6′a**−**6′f** or **4′**, respectively. The sp^3 character assumed by the N donors after reduction allows the folding of the pyridyl group toward the axial position.

The other pathway, which leaves unchanged the +2 oxidation state of the metal, involves the reduction of both of the ligands of intermediate **A** to the amino form. As above, this allows the approaching of the pyridyls to the axial positions[15] (intermediate **B**). When the reaction mixture is exposed to air, oxidation of **B** to **3′** occurs. Since **B** gives **3′**, it implies that **B** is not capable of affording alkyl−cobalt derivatives, despite the presence in solution of an excess of both reducing and alkylating agents. This hypothesis is supported by the observation that when **3′** is treated with $NaBH_4$ and alkyl halides, instead of the expected alkyl derivatives, a Co^{II} species is formed.[8] This Co^{II} species has been characterized in solution by means of UV/vis spectra and corresponds to intermediate **B** of Scheme 4. Thus, in the absence of the nucleophilic Co^{I} the oxidative alkylation

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(10) Toscano, P. J.; Marzilli, L. G. *Prog. Inorg. Chem.* **1984**, *31*, 105 and references therein.

(11) To the intermediate **A** in Scheme 4 is assigned a square planar configuration with the ligands occupying the equatorial positions. This structure is favored by the presence of the O−H···O bridge and probably is the most appropriate one to account for the *mer* → *fac* configurational change passing from the reactant **1′** to the products. Similar arrangement of the two ligands has been observed by us to be present in the neutral *trans*-[$(Bz)_2Co^{III}$(*H*-L_2Npy)(L_2Npy)] bis-organometallic complex and in other related compounds derived from imino−oxime ligands (to be published). The axial positions of intermediate **A** may be occupied or not by solvent molecules. It is well-known that Co^{II} complexes containing equatorial chelating systems include four-, five-, and six-coordinate species. Significant examples for each of these categories are Co^{II}(salen),[12] Co^{II}(salen)-py,[13] and $Co^{II}(DH)_2(py)_2$.[14] Axial ligands, when present, were recognized to be weakly linked.

(12) Schaeffer, W. P.; Marsch, R. E. *Acta Crystallogr., Sect. B* **1969**, 1675.

(13) Calligaris, M.; Minichelli, D.; Nardin, G.; Randaccio, L. *J. Chem. Soc.* **1970**, 2411.

(14) Schrauzer, G. N.; Windgassen, R. J. *Chem. Ber.* **1966**, *99*, 602.

(15) In this species an interaction with the two pyridyls is possible with the formation of a pseudo-octahedral species. As an example for a six-coordination in a Co^{II} complex see $Co^{II}(DH)_2(Py)_2$.[14]

does not occur. This experiment shows also that **B** cannot give alkyl derivatives via a radical process.[16−22] In conclusion, it can be said that the reduction of **1′** to Co^I (and successively the alkylation) takes places only when both or at least one of the two ligands are still in the imino form. Reduction of the ligand occurs successively to the alkylation. It can be also observed that $Co^{II} \rightarrow Co^I$ reduction is easily accomplished in the imino intermediate **A**, whereas it fails in the amino intermediate **B**, at least under the same experimental conditions. This behavior is consistent with the observation that, in certain cobalt complexes containing macrocyclic ligands, the stabilization of the +1 oxidation state of the cobalt increases with increasing unsaturation extent of the ligand.[23]

Formation of Isomers *a* (4′) and *b* (5′). The major products isolated from reactions 2 and 3 were **4′** and **5′**, respectively. However, taking into account the small quantities of material employed in the syntheses, it cannot be ruled out that other minor isomers were formed.

Noteworthy, since the reduction of **6′a** affords **5′**, it is unlikely that **6′a** is the precursor of **4′**. It is also demonstrated (see the above paragraph) that **4′** cannot be formed from **3′**. Consequently, a different (unknown) intermediate precursor of **4′** must be inferred to be present in the reaction mixture. At present, the available data do not allow one to advance a reasonable hypothesis on the nature of this species.

Differences in the Reactivity between 1 and 1′. The different reactivity exhibited by **1′** (Scheme 3) with respect to the previously studied **1**[1,2] (Scheme 1) arises mainly from the fact that the L_1Npy^- ligand present in **1′** can be more easily reduced to the amino form than the L_2Npy^- ligand present in **1**. This might appear surprising, because of the close analogy of these two chelating systems. It is difficult to give an unambiguous interpretation of this behavior, since the kinetic aspects of the processes and the properties of the lowest cobalt oxidation states are unknown. Only the properties of the starting Co^{III} species are well-defined. Structural data indicate that the $Co-N_{imine}$ and $Co-N_{py}$ distances (Table 1) found in **1′** are shorter than those in **1** by 0.04 Å (mean value) and 0.08 Å (mean value), respectively. In addition, molecular mechanics calculations[24] indicate that there is a significant increase in the strain energy passing from **1** (with the "longer" L_2Npy^- ligand) to **1′** (with the "shorter" L_1Mpy^- ligand). Interestingly, when the complexes **3** and **3′** (both containing an amino ligand) are considered, an inverse trend is observed. The above findings show that significant difference in the ground state properties of **1** and **1′** (and **3** and **3′**) is apparent. It is expected that these differences will be found also in the reactivity. Since it is generally assumed that the more strained the structure, the more reactive the compound, it may be supposed that the imino complex **1′** will tend to assume the more stable amino form, whereas **1** will prefer to maintain its imino form.

Concluding Remarks

Many of the alkylcobalt complexes prepared so far include tetradentate equatorial ligands[10] such as bis-oximes, Schiff bases, corrins, porphyrins, and other tetranitrogen macrocycles. These complexes may be formally derived from the corresponding nonorganometallic compounds by substitution of one axial Lewis base, generally a monoanion, for an alkyl group. Thus the formation of a stable Co−C bond, which involves a transient Co^I species and its successive alkylation, does not alter the chemical nature of the equatorial ligand. Conversely, the production of alkyl−cobalt from **1′** is accompanied by modifications and rearrangements of the whole ligand system surrounding the metal ion. The observed products can be explained by two reaction pathways. The first is the saturation of one or two imino ligands causing the *mer* → *fac* configurational change in concomitance with the sp^3 character assumed by the N donors. The second is the formation of a stable Co−C bond, which forces one of the two tridentate ligands to act as a bidentate ligand. This introduces in the alkyl−cobalt elements of asymmetry not present in **1′**. It is also of interest that, at least in the case of the methyl derivative, two isomers (*a* and *b*) could be obtained as pure products using different synthetic procedures. Thus, additional interest in these compounds is found in their stereochemical properties. However, the stereochemistry of the reduction reaction needs further investigation, especially with respect to understanding the role played by the alkyl group.

Experimental Section

Instruments and Material. ^1H NMR spectra were recorded with a JEOL EX-400 at 400 MHz from DMSO-d_6 solutions with TMS as the internal standard. Commercially available chemicals were purchased from Aldrich and used without further purification.

Syntheses. The complexes of the type $[RCo^{III}(L_1Npy)(H\text{-}L_1\text{-}NHpy)]^+$ with R = Me (**6′a**), *i*-Pr (**6′b**), CH_2Cl (**6′c**), CH_2Br (**6′d**), CH_2CF_3 (**6′e**), and Bz (**6′f**) have been prepared following the general method of synthesis described below. All of the operations were performed at room temperature and in indirect light. The complexes were obtained as perchlorate salts (yield 30−40%). **CAUTION:** *Although no problems were encountered in the present study,*

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[16] Cobalt(II) complexes are odd electron, and as such they react with free radical pathways. The reactions with alkyl halides (RX) were found have the following stoichiometry: $2LCo^{II} + RX \rightarrow LCo^{III}R + LCo^{III}X$. This reaction has been studied in detail for several systems, including $[Co^{II}(CN)_5]^{3-}$,[17] $LCo^{II}(DH)_2$,[18] LCo^{II}(saloph),[19] and vitamin B_{12r}.[20] This synthetic method is usually employed when no other methods are available. In addition to the alkyl halides, some other sources of radicals have been used. For instance, $[Co^{II}(NH_3)_5O_2CR]^{2+}$ (R = Me, vinyl) has been used in the synthesis of organocobalt complexes of saturated four-nitrogen donor macrocycles;[21] methylhydrazine has been used in the synthesis of $[Co^{III}(NH_3)_5(CH_3)]^{2+}$ from pentamine cobalt(II).[22] Attempts to alkylate the Co^{II} complex derived from **3′** with MeI were unsuccessful. The Co^{II} complex derived from **3** has been found to exhibit analogous behavior.[17]

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perchlorate salts are potentially explosive and should be handled in small quantities. A solution of NaOH (0.78 g, 19.5 mmol) in 2 mL of water was added to a suspension of **1′** (1 g, 1.84 mmol) in 150 mL of methanol under a nitrogen atmosphere with stirring. The resulting solution was treated with $NaBH_4$ (0.5 g, 13.5 mmol) dissolved in a minimum volume of water, followed by two drops of $PdCl_2$ solution, which was prepared by addition of concentrated HCl to a suspension of 1 g of $PdCl_2$ in 20 mL of water until complete dissolution. When the reaction mixture assumed a dark brown color (after about 5 min), the alkyl halide was added in a molar ratio 10:1 with respect to the complex. As soon as the dark brown solution turned to bright orange (15−30 min after the addition of the alkyl halide), the flow of nitrogen was suspended and the alkaline reaction mixture was neutralized with concentrated CH_3COOH. Methanol was removed by a rotary evaporator at 40 °C and the resulting aqueous solution extracted three times with 20 mL of CH_2Cl_2. The organic phase was concentrated to about 10 mL and passed through a chromatographic column of silica. Elution with $CH_2Cl_2/(CH_3)_2CO$ in a 5:1 volume ratio gave about 50 mL of solution containing the product. The elute was treated with *n*-pentane dropwise until turbid and allowed to stand overnight. Crystals of the product were recovered by filtration and air-dried.

[MeCo^{III}(L$_1$Npy)(*H*-L$_1$NHpy)]ClO$_4$ (6′a): orange crystals. Anal. Calcd for $C_{21}H_{30}ClCoN_6O_6$: C, 45.3; H, 5.43; N, 15.1. Found: C, 45.5; H, 5.49; N, 15.1. ^{1}H NMR: d 1.38 (3H, d, CH_3−CH); 1.43 (3H, s, CH_3−Co); 1.74, 2.10, 2.26 (9H, s, 3CH$_3$−C═N); 3.54 (1H, q, C*H*−CH$_3$); 4.04, 4.20 (4H, 2CH$_2$); 5.81 (1H, s, NH); 6.67, 7.17, 7.29, 7.52, 7.62, 7.94, 8.19 (8H, 2C$_5$H$_4$N).

[*i*-PrCo^{III}(L$_1$Npy)(*H*-L$_1$NHpy)]ClO$_4$ (6′b): red dark crystals. Anal. Calcd for $C_{23}H_{34}ClCoN_6O_6$: C, 47.2; H, 5.86; N, 14.3. Found: C, 47.1; H, 5.83; N, 14.2. ^{1}H NMR: d 0.60 (6H, d, 2CH_3−CH (axial)); 1.44 (3H, d, CH_3−CH(ligand)); 1.75, 2.04, 2.28 (9H, s, 3CH$_3$−C═N); 3.51 (2H, 2CH); 3.94, 4.99 (4H, 2CH$_2$); 5.32 (1H, s, NH); 6.43, 7.10, 7.17, 7.42, 7.61, 7.88, 8.10, 8.23 (8H, 2C$_5$H$_4$N).

[ClCH$_2$Co^{III}(L$_1$Npy)(*H*-L$_1$NHpy)]ClO$_4$ (6′c): yellow crystals. Anal. Calcd for $C_{21}H_{29}Cl_2CoN_6O_6$: C, 42.6; H, 4.94; N, 14.2. Found: C, 42.5; H, 4.98; N, 13.9. ^{1}H NMR: d 1.50 (3H, d, CH_3−CH); 1.82, 2.14, 2.35 (9H, s, CH$_3$−C═N); 3.67 (1H, q, C*H*−CH$_3$); 4.05, 4.65 (4H, 2CH$_2$); 5.05 (2H, s, CH$_2$Cl); 5.82 (1H, s, NH); 6.74, 7.15, 7.28, 7.56, 7.64, 7.96, 8.10, 8.16 (8 H, 2C$_5$H$_4$N).

[BrCH$_2$Co^{III}(L$_1$Npy)(*H*-L$_1$NHpy)]ClO$_4$ (6′d): yellow crystals. Anal. Calcd for $C_{21}H_{29}BrClCoN_6O_6$: C, 39.7; H, 4.60; N, 13.2. Found: C, 39.3; H, 4.56; N, 12.9. ^{1}H NMR: d 1.50 (3H, d, CH_3−CH); 1.82, 2.14, 2.35 (9H, s, CH$_3$−C═N); 3.68 (1H, q, C*H*−CH$_3$); 4.06, 4.51 (4H, 2CH$_2$); 5.45 (2H, s, CH$_2$Br); 5.96 (1H, s, NH); 6.76, 7.17, 7.28, 7.56, 7.64, 7.97, 8.11, 8.16 (8 H, 2C$_5$H$_4$N).

[CF$_3$CH$_2$Co^{III}(L$_1$Npy)(*H*-L$_1$NHpy)]ClO$_4$ (6′e): yellow crystals. Anal. Calcd for $C_{22}H_{29}ClCoF_3N_6O_6$: C, 42.3; H, 4.68; N, 13.4. Found: C, 42.2; H, 4.70; N, 13.3. ^{1}H NMR: d 1.40 (3H, d, CH_3−CH); 1.82, 2.10, 2.50 (9H, s, CH$_3$−C═N); 3.65 (1H, q, C*H*−CH$_3$); 3.90, 4.15 (4H, 2CH$_2$); 5.15 (2H, s, CH$_2$CF$_3$); 6.15 (1H, s, NH); 6.75, 7.15, 7.25, 7.55, 7.65, 7.95, 8.05, 8.10 (8 H, 2C$_5$H$_4$N).

[BzCH$_2$Co^{III}(L$_1$Npy)(*H*-L$_1$NHpy)]ClO$_4$·CH$_2$Cl$_2$ (6′f): red crystals. Anal. Calcd for $C_{28}H_{36}Cl_3CoN_6O_6$: C, 46.8; H, 5.05; N, 11.7. Found: C, 46.9; H, 5.05; N, 11.7. ^{1}H NMR: d 1.50 (3H, d, CH_3−CH); 1.62, 1.78, 1.85 (3H, s, 3CH$_3$−C═N); 3.59 (1H, q, C*H*−CH$_3$); 3.76, 4.09 (4H, 2CH$_2$); 5.10 (2H, d, CH$_2$Bz); 5.75 (2H, s, CH$_2$Cl$_2$); 5.87 (1H, s, NH); 6.41−8.18 (8 H, 2C$_5$H$_4$N, and 5H, C$_6$H$_5$).

Formation of [Co^{III}(L$_1$Npy)(*H*-L$_1$NHpy)](ClO$_4$)$_2$·H$_2$O (3′). From the aqueous phase remaining after extraction of the organometallic type **5** complexes (see the general method of synthesis), the nonorganometallic complex **3′** was precipitated by addition of a concentrated solution of $NaClO_4$, collected by filtration, and air-dried. An equimolar quantity (with respect to the organometallic compound) of the pure product was recovered (as monohydrate) and characterized by elemental analysis and ^{1}H NMR spectra. Anal. Calcd for $C_{20}H_{31}Cl_2CoN_6O_{11}$: C, 36.3; H, 4.70; N, 12.7. Found: C, 36.4; H, 4.40; N, 12.7. ^{1}H NMR: d 0.90 (6H, d, 2CH_3−CH); 2.13 (6H, s, 2CH$_3$−C═N); 4.07 (1H, m, C*H*−CH$_3$); 4.60, 5.44 (4H, d, 2CH$_2$); 6.98 (2H, s, NH); 7.66, 7.84, 7.97, 8.21 (8 H, 2C$_5$H$_4$N).

[MeCo^{III}(L$_1$Npy)(*H*-L$_1$NHpy)]ClO$_4$ (Isomer *a*) (4′). This complex was obtained by three modifications of the procedure followed for the synthesis of complex **6′a** (see above), i.e.: the reaction temperature was raised to 40 °C; the quenching of the reaction with concentrated CH_3COOH was omitted, and a Al_2O_3 chromatographic column instead of a silica column was used for the purification of the product. Anal. Calcd for $C_{21}H_{32}ClCoN_6O_6$: C, 45.1; H, 5.77; N, 15.0. Found: C, 45.2; H, 5.70; N, 14.9. From the extracted water solution, the nonorganometallic **3′** was isolated and identified as above.

[MeCo^{III}(L$_1$Npy)(*H*-L$_1$NHpy)]ClO$_4$ (Isomer *b*) (5′). To 0.2 g (0.36 mmol) of **6′a** dissolved in 50 mL of methanol and in the presence of air was added 0.3 g (8.02 mmol) of $NaBH_4$ dissolved in a minimum amount of water. After 30 min, methanol was removed by a rotary evaporator (40 °C). The residue was treated with 10 mL of water and extracted with CH_2Cl_2 (3 × 20 mL). The organic phase was concentrated to about 10 mL, passed through on a chromatographic column, and eluted with a 5:1 (volume) mixture of CH_2Cl_2 and $(CH_3)_2CO$. To the eluate, concentrated to 5 mL, was added *n*-pentane until the mixture became turbid. After 12 h, the orange precipitate which was formed was collected by filtration and air-dried. Anal. Calcd for $C_{21}H_{32}ClCoN_6O_6$: C, 45.1; H, 5.77; N, 15.0. Found: C, 45.0; H, 5.82; N, 14.9.

Photochemical Decomposition of 4′. To a solution of **4′** (0.10 g, 0.17 mmol) dissolved in a minimum amount of methanol was added 50 mL of water. Then the solution was exposed to sunlight for 1 h. After addition of a few drops of a saturated $NaClO_4$ solution, the solution was left to evaporate in the presence of air. Red crystals of **3′** were collected by filtration and identified by ^{1}H NMR spectroscopy.

Structure Determination of 4′, 5′, 6′a, and 6′b. Crystal and refinement data are given in Table 2. Single crystals, suitable for X-ray data collection, were obtained as reported in Syntheses. X-ray diffraction data for **4′**, **5′**, and **6′a** were collected at room temperature and those for **6′b** at 150 K, with a Nonius DIP 1030 H System, using graphite-monochromated Mo Kα radiation. For all compounds a total of 36 frames were collected, using the Xpress program,[25] over a half of reciprocal space with rotation of 5° about the φ axis. A Mac Science Image Plate (diameter = 300 mm) was used, and the crystal-to-plate distance was fixed at 90 mm. The determination of unit-cell parameters, integration of reflection intensities, and data scaling were performed using MOSFLM and SCALA from the CCP4 program suite.[26] Reflections, which were measured on previous and following frames, were used to scale the frames on each other, a procedure that partially eliminated absorption effects, taking into account also any crystal decay. The structures were solved with direct methods,[27] followed by Fourier syntheses, and refined by full-matrix least-squares (on F^2) cycles.[28] Compound **5′**

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Table 2. Summary of Crystallographic Details for **4′**, **5′**, **6′a**, and **6′b**

	4′	**5′**	**6′a**	**6′b**
formula	$C_{21}H_{32}ClCoN_6O_6$	$C_{42}H_{64}Cl_2Co_2N_{12}O_{12}$	$C_{22}H_{32}Cl_3CoN_6O_6$	$C_{23}H_{34}ClCoN_6O_6$
fw	558.91	1117.81	641.82	584.94
space group	Cc	$P2_1/c$	$P\bar{1}$	$P2_12_12_1$
a, Å	17.321(4)	12.131(3)	10.896(3)	11.430(4)
b, Å	11.195(2)	26.305(5)	11.370(4)	11.710(4)
c, Å	14.124(3)	15.790(3)	12.229(4)	19.882(6)
α, deg	90	90	108.44(8)	90
β, deg	108.34(7)	95.27	97.12(7)	90
γ, deg	90	90	99.06(7)	90
V, Å^3	2599.7(6)	5017.4(8)	1394.6(9)	2661.1(10)
Z	4	4	2	4
ρ_{calcd}, g cm^{-3}	1.43	1.48	1.53	1.46
T, K	293	293	293	150
μ(Mo Kα), mm^{-1}	0.810	0.839	0.951	0.795
R1 [$I > 2\sigma(I)$][a]	0.044	0.086	0.060	0.076
wR2 (all data)[b]	0.123	0.271	0.182	0.217

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

crystallized with two crystallographically nonequivalent molecules, while **6′a** cocrystallized with a molecule of CH_2Cl_2. The solvent molecule was fully ordered and refined anisotropically without restraint. The H atoms were not refined but included at calculated positions, in the final refinements. A suite of programs[29] was also used in the geometrical and final calculation.

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Supporting Information Available: Crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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