Photolysis Secondary Products of Cobaloximes and Imino/Oxime Compounds Controlled by Steric Hindrance Imposed by the Lewis Base

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Anaerobic photolysis of alkylpyridinecobaloximes and alkylpyridine and alkylphosphine imino/oxime compounds with visible light was studied by electron paramagnetic resonance spectroscopy in aprotic solvents, in frozen (77 K) and in fluid solution (250 K and 300 K). Irradiation of samples in a frozen matrix allows identification of photolysis primary products, which are, for all the compounds studied, a Co(II) five-coordinate species and an organic radical, thus implying homolytic cleavage of the cobalt−carbon bond. The behavior of imino/oxime compounds is identical for all the alkyl radicals, contrasting with that observed for methyl and benzyl pyridine cobaloximes, for which no cleavage of the Co−C bond was observed when irradiation was performed with visible light at 250 and 77 K. Relaxation of the frozen samples to room temperature, 300 K, results in the formation of Co(II) secondary products, namely, six-coordinate species containing two molecules of base, with the exception of *ortho*-substituted pyridines or triphenylphosphine, for which the five-coordinate cobalt(II) species is not involved in further reactions. These results are rationalized in terms of structural deformations induced by the Lewis base in the equatorial moiety. The results obtained for imino/oxime compounds constitute spectroscopic evidence that formation of six-coordinate species with two axially bound bases results from abstraction of base molecules from the five-coordinate Co(II) species as a Co(II) four-coordinate species is observed simultaneously, and its EPR signal is lost if photolysis is performed in the presence of an excess of base. The results suggest that formation of diamagnetic entities after abstraction of base molecules occurs for cobaloximes but not for imino/oxime compounds. The results observed for samples irradiated at 250 and 300 K are identical to those obtained for samples irradiated at 77 K after relaxation to room temperature, thus indicating that the same mechanism is operative at both irradiation temperatures.

Introduction

Structural characterization of B_{12} systems has revealed the existence of a cobalt−carbon bond, and subsequent studies demonstrated that cleavage of this bond is a key step in the enzymatic mechanisms in which coenzyme B_{12} and methylB_{12} are involved.[1−3] It is well recognized that for coenzyme B_{12} homolysis of the cobalt−carbon bond is the only role identified in all enzymatic processes dependent on this cofactor.[4,5] As a consequence, the understanding of the mechanism and factors that influence the cleavage of the cobalt−carbon is crucial for the knowledge of B_{12} coenzymes and its role.[4−14]

As it became relevant to B_{12} biochemistry, the chemistry of organocobalt compounds has gained a special interest and several classes of model compounds have been synthesized and studied along the years.[4,5,15−22] Although it has not been possible to find a class of model compounds that mimics the physical properties of cobalamines, they have been widely used and have provided decisive information in the development of methods for understanding B_{12} properties, especially the factors that stabilize/labilize the Co−C bond.

The relevance of electronic and steric effects in Co−C bond cleavage mechanisms has been clearly demonstrated in model compounds by investigations concerning the influence of the ligand *trans* to the alkyl group

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[1] Banerjee, R. *Chemistry and Biochemistry of B_{12}*; Wiley-Interscience: New York, 1999.

[2] Krautler, B.; Arigoni, D.; Golding, B. T. *Vitamin B_{12}* and B_{12}−*Proteins*; Wiley-VCH: Chichester, 1998.

[3] (a) Dolphin, D. *B_{12}*; Wiley: New York, 1982. (b) Halpern, J. *Science* **1985**, *227*, 869. (c) Finke, R. G.; Schiraldi, D. A.; Mayer, B. J. *Coord. Chem. Rev.* **1984**, *54*, 1. (d) Pratt, J. M. *Chem. Soc. Rev.* **1985**, *14*, 161.

[4] (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, (d) Randaccio, L. *Comments Inorg. Chem.* **1999**, *21*, 327.

[5] (a) Hay, B. P.; Finke, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 8012. (b) Hay, B. P.; Finke, R. G. *Polyhedron* **1988**, *7*, 1469, and references therein.

[6] (a) Pett, V. B.; Liebman, M. N.; Murray-Rust, P.; Prasad, K.; Glusker, J. P. *J. Am. Chem. Soc.* **1987**, *109*, 3207. (b) Rossi, M.; Glusker, J. P. In *Environmental Influences and Recognition in Enzyme Chemistry*; Liebman, J. F., Greenberg, A., Eds.; VCH: New York, 1988.

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in a series of alkylcobaloximes and imino/oxime compounds, with nitrogen[4,17] and phosphorus donor ligands.[4b,18] Most of this work has been performed with cobalt(III) compounds, and much less information exists on the structure and reactivity of the cobalt(II) species formed upon homolysis of the cobalt−carbon bond, a fact that can be traced to (a) the lability of cobalt(II) compounds, which renders greater complexity to their chemistry, and (b) the great difficulty in obtaining crystals of diffractometric quality for cobalt(II) compounds with relevance to model systems in B_{12} chemistry.

An X-ray structure of Co(II) B_{12} coenzyme has been reported,[25] and XAFS solution studies have provided chemical and structural information on Co(II) and Co(I) intermediates of cyanocobalamin and adenosylcobalamin observed during catalysis. EPR and UV/vis spectroscopies have been used to get information on the electronic structure of cobalt(II) intermediates.[26]

Homolysis of the cobalt−carbon bond in naturally occurring cobalamines and in model compounds is induced by photolysis and thermolysis, and it is believed that the products of these reactions are identical to those found during the enzymatic processes in which cobalamines are present.[3,4a] Accordingly, information on the structure and reactions in which the cobalt(II) species are involved may be achieved by studying photolysis and thermolysis of B_{12} compounds and related models.[21,27−33]

For B_{12} model compounds several studies concerning anaerobic photolysis in protic and aprotic solvents of alkylcobaloximes with nitrogen[18−32] and phosphorus[33] donor bases have appeared in the literature and more recently a study of photolysis of methylaquacobinamide in the presence of N-donor ligands, which impose variable electronic and steric effects,[21] although no work on photolysis of imino/oxime compounds has been reported.

The results obtained point, in general, to light-induced homolytic cleavage of the cobalt−carbon bond, although exceptions have been found for some methyl and benzyl cobaloxime derivatives for which homolysis of the cobalt−carbon bond does not occur at all irradiation temperatures, reflecting the stronger Co−C bonds present in those componds.[31] Photolysis products of alkylcobaloximes with symmetric phosphorus donor bases have been shown to be independent of the alkyl group and of the temperature of irradiation. Photolysis induces in all cases homolytic cleavage of the cobalt−carbon bond and originates as products alkyl radicals and cobalt(II) five-coordinate species, which are not involved in subsequent reactions in the temperature range 77−300 K.[33] For alkylcobaloximes with nitrogen bases, the same is not true, and it has been shown that the products that are observed after photolysis depend both on the alkyl group and on the Lewis base.[28,30−32]

The purpose of this work is to characterize the products of anaerobic photolysis in aprotic solvents of alkylpyridinecobaloximes and similar imino/oxime compounds (Figure 1). We have included imino/oxime compounds with triphenylphosphine to be compared with previous work on cobaloximes and also to confirm deformations induced by bulky ligands.

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(7) (a) Summers, M. F.; Marzilli, L. G.; Bresciani-Pahor, N.; Randaccio, L. *J. Am. Chem. Soc.* **1984**, *106*, 4478. (b) Randaccio, L.; Bresciani-Pahor, N.; Toscano, P. J.; Marzilli, L. G. *J. Am. Chem. Soc.* **1981**, *103*, 6347.

(8) Nie, S.; Marzilli, P. A.; Marzilli, L. G.; Yu, N. T. *J. Am. Chem. Soc.* **1990**, *112*, 6084.

(9) Marzilli, L. G. In *Bioinorganic Catalysis*; Reedijk, J., Bauman, E., Ed.; Marcel Dekker: New York, 1999.

(10) (a) Buckel, W.; Golding, B. T. *Chem. Soc. Rev.* **1996**, 329. (b) Golding, B. T.; Buckel, W. In *Comprehensie Biochemical Catalysis*; Sinnott, M. L., Ed.; Academic Press: London, 1997.

(11) (a) Padmakumar, R.; Taoke, S.; Padmakumar, R.; Banerjee, R. *J. Am. Chem. Soc.* **1995**, *117*, 7033. (b) Zelder, O.; Beatrix, B.; Kroll, F.; Buckel, W. *FEBS Lett.* **1995**, *369*, 252. (c) Mancia, F.; Keep, N. H.; Nakagawa, A.; Leadley, P. F.; McSweeney, S.; Rasmussen, B.; Bosecke, P.; Diat, O.; Evans, P. R. *Structure* (*London*) **1996**, *4*, 339. (d) Thomas, N. H.; Meier, T. W.; Evans, P. R.; Leadley, P. F. *Biochemistry* **1998**, *37*, 14386. (e) Mancia, F.; Evans, P. R. *Structure (London)* **1998**, *6*, 711. (f) Reitzer, R.; Gruber, K.; Jogl, G.; Wagner, U. G.; Bothe, H.; Buckel, W.; Kratky, C. *Structure (London)* **1999**, *7*, 891.

(12) (a) Chang, C. H.; Frey, P. A. *J. Biol. Chem.* **2000**, *275*, 106. (b) Chen, H. P.; Wu, S. H.; Lin, Y. L.; Chen, C. M.; Tsay, S. S. *J. Biol. Chem.* **2001**, *276*, 44744.

(13) (a) Yamanishi, M.; Yamada, S.; Muguruma, H.; Murakami, Y.; Tobimatsu, T.; Ishida, A.; Yamauchi, J.; Toraya, T. *Biochemistry* **1998**, *37*, 4799. (b) Abend, A.; Nitsche, R.; Bandarian, V.; Stupperich, E.; Retey, J. *Angew. Chem., Int. Ed.* **1998**, *37*, 625. (c) Abend, A.; Bandarian, V.; Nitsche, R.; Stupperich, E.; Retey, J.; Reed, G. H. *Arch. Biochem. Biophys.* **1999**, *370*, 138. (d) Ke, S. C.; Torrent, M.; Museav, D. G.; Morokuma, K.; Warncke, K. *Biochemistry* **1999**, *38*, 12681. (e) Shibata, N.; Masuda, J.; Tobimatsu, T.; Toraya, T.; Suto, K.; Morimoto, Y.; Yasuoka, N. *Structure (London)* **1999**, *7*, 997. (f) Masude, J.; Shibata, N.; Morimoto, Y.; Toraya, T.; Yasuoka, N. *Structure (London)* **2000**, *8*, 775. (g) Bandarian, V. P.; Reed, G. H. *Biochemistry* **2002**, *41*, 8580.

(14) (a) Lawrence, C. C.; Gerfen, G. J.; Samano, V.; Nitsche, R.; Robins, M. J.; Retey, J.; Stubbe, J. *J. Biol. Chem.* **1999**, *274*, 7039. (b) Sintchak, M. D.; Arjara, G.; Kellogg, B. A.; Stubbe, J.; Drennan, C. L. *Nat. Struct. Biol*. **2002**, *9*, 293.

(15) (a) Finke, R. G.; Smith, B. L.; McKenna, W. A.; Christian, P. A. *Inorg. Chem.* **1981**, *20*, 687. (b) Elliot, C. M.; Hershenhart, E.; Finke, R. G.; Smith, B. L. *J. Am. Chem. Soc.* **1981**, *103*, 5558. (c) Finke, R. G.; McKenna, W. A.; Schiraldi, D. A.; Smith, B. L.; Pierpont, C. *J. Am. Chem. Soc.* **1983**, *105*, 7592. (d) Finke, R. G.; Smith, B. L.; Meyer, B. J.; Molinero, A. A. *Inorg. Chem*. **1983**, *22*, 3679.

(16) (a) Polson, S. M.; Hansen, L.; Marzilli, L. G. *J. Am. Chem. Soc.* **1996**, *118*, 4804. (b) Hirota, S.; Polson, S. M.; Puckett, J. M., Jr.; Moore, S. J.; Mitchell, M. B.; Marzilli, L. G. *Inorg. Chem.***1996**, *35*, 5646. (c) Marzilli, L. G.; Polson, S. M.; Hansen, L.; Moore, S. J.; Marzilli, P. A. *Inorg. Chem.* **1997**, *36*, 3854.

(17) (a) Parker, W. O., Jr.; Zangrando, E.; Bresciani-Pahor, N.; Marzilli, P. A.; Randaccio, L.; Marzilli, L. G. *Inorg. Chem.* **1988**, *27*, 2170. (b) Seeber, R.; Parker, W. O., Jr.; Marzilli, P. A.; Marzilli L. G. *Organometallics* **1989**, *8*, 2377.

(18) Parker, W. O., Jr.; Bresciani-Pahor, N.; Zangrando, E.; Marzilli, P. A.; Randaccio, L.; Marzilli, L. G. *Inorg. Chem.* **1986**, *25*, 1303.

(19) Toscano, P. J.; Seligson, A. L.; Currain, M. T.; Skrobutt, A. T.; Sonnemberger, D. C. *Inorg. Chem.* **1989**, *28*, 166; **1989**, *28*, 1610.

(20) Geremia, S.; Calligaris, M.; Randaccio, L. *Eur. J. Inorg. Chem.* **1999**, 981.

(21) Trommel, J. S.; Warncke, K.; Marzilli, L. G. *J. Am. Chem. Soc*. **2001**, *123*, 3358.

(22) Song, X.; Chen, Y.; Chen, H. *New J. Chem.* **2001**, *25*, 985.

(23) Yao, K.; Zhang, X.; Chen, H. *J. Chem. Soc., Dalton Trans.* **2004**, *21*, 3642.

(24) Alzoubi, B. M.; Hamza, M. S. A.; Felluga, A.; Randaccio, L.; Tauzher, G.; Van Eldik, R. *Eur. J. Inorg. Chem.* **2004**, *3*, 53.

(25) Kratky, C.; Farber, G.; Gruber, K.; Wilson, K.; Dauter, Z.; Nolting, F.; Konrat, R.; Krautler, B. *J. Am. Chem. Soc.* **1995**, *117*, 4654.

(26) (a) Sagi, I.; Chance, M. R. *J. Am. Chem. Soc.* **1992**, *114*, 8061−8066. (b) Wirt, M. D.; Sagi, I.; Chen, E.; Frisbie, S. M.; Lee, R.; Chance, M. R. *J. Am. Chem. Soc.* **1991**, *113*, 5299. (c) Sagi, M. D.; Wirt, E.; Chen, E.; Frisbie, S. M.; Chance, M. R. *J. Am. Chem. Soc*. **1990**, *112*, 8639. (d) Wirt, M. D.; Kumar, M.; Ragsdale, S. W.; Chance, M. R. *J. Am. Chem. Soc*. **1993**, *115*, 2146.

(27) Brown, K. L.; Zou, X.; Banka, R. R.; Perry, C. B.; Marques, H. M. *Inorg. Chem*. **2004**, *43*, 8130.

(28) (a) Giannotti, C.; Bolton, J. R. *J. Organomet. Chem.* **1974**, *80*, 379. (b) Giannotti, C.; Merle, G.; Bolton, J. R. *J. Organomet. Chem.* **1975**, *99*, 1456.

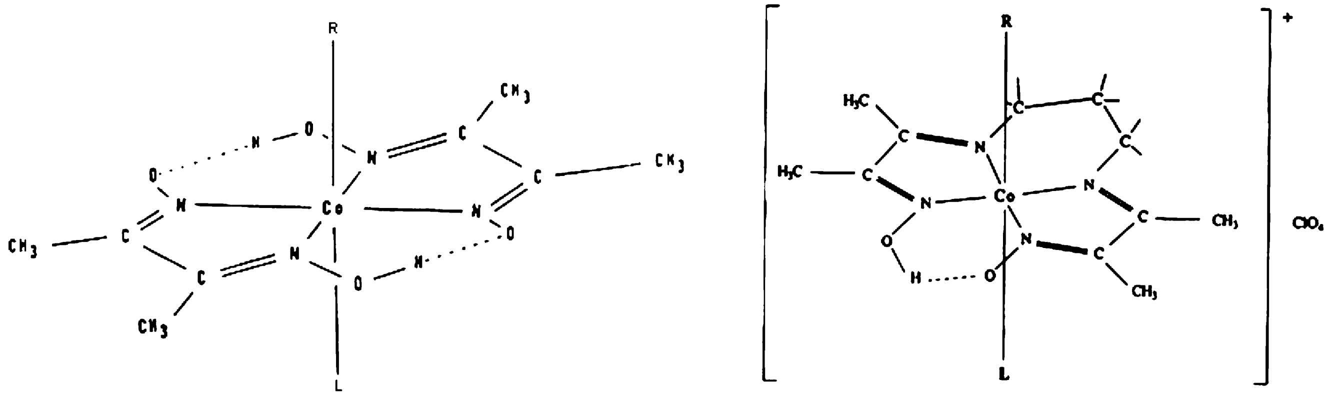
(29) (a) Rao, D. N. R.; Symons, M. C. R. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 423. (b) Rao, D. N. R.; Symons, M. C. R. *J. Chem. Soc*., *Perkin Trans. 2* **1983**, 187.

(30) Arcos, T.; de Castro, B.; Ferreira, M. J.; Rangel, M.; Raynor, J. B. *J. Chem. Soc*., *Dalton Trans*. **1994**, 369.

(31) Rangel, M.; Arcos, T.; de Castro, B. *Organometallics* **1999**, *18*, 3451.

(32) Rangel, M.; Pereira, E.; Oliveira, C.; de Castro, B. *J. Organomet. Chem*. **2001**, *632*, 85.

(33) de Castro, B.; Pereira, J.; Rangel, M. *Organometallics* **1991**, *10*, 3848.



Cobaloximes

1 $sec\text{-}C_4H_9Co(DH)_2$ py
2 $i\text{-}C_3H_7Co(DH)_2$ py
3 $i\text{-}C_3H_7Co(DH)_2$ (3-pic)
4 $i\text{-}C_3H_7Co(DH)_2$ (3,5-lut)
5 $i\text{-}C_3H_7Co(DH)_2$ $(2NH_2)$
6 $i\text{-}C_3H_7Co(DH)_2$ (2-pic)

"Costa" type compounds

a CH_3 (Co(DO)(DOH)pn) py
b $C_6H_5CH_2$ (Co(DO)(DOH)pn) py
c $i\text{-}C_3H_7$ (Co(DO)(DOH)pn) py
d CH_3 (Co(DO)(DOH)pn) PPh_3
e $C_6H_5CH_2$ (Co(DO)(DOH)pn) PPh_3
f $i\text{-}C_3H_7$ (Co(DO)(DOH)pn) PPh_3

Figure 1. Formulas of cobaloximes and imino/oxime compounds studied.

Comparison of the results obtained for cobaloxime and imino/oxime analogous compounds is useful to get insight on structural factors imposed by the equatorial moiety that may influence the nature of photolysis primary products and their involvement in further reactions, since the two equatorials moieties are different in terms of flexibility or ability to bend under the influence of bulky axial ligands.

To distinguish between primary and secondary photolysis products, solutions were irradiated and characterized at 77 K, then allowed to warm to room temperature and frozen again to analyze new species that have resulted from the involvement of the primary products in further reactions. The reactivity of photolysis products is deeply related with their structure, and this knowledge is important to the use of these cobalt(II) species in other fields such as catalysis and synthesis of new organocobalt compounds.[34]

EPR spectroscopy was used and, as in previous studies, proved to be the method of choice to monitor the photolysis process,[28−33] to identify the paramagnetic species formed, and to get relevant information about the structure of the cobalt(II) complexes.[32−38] The characterization of the products was achieved by analysis of the EPR spectra exhibited by the corresponding solutions after irradiation at different temperatures.

Experimental Section

Reagents. The solvents, obtained from Merck, were dried and distilled from P_2O_5 according to standard procedures[39] and kept over 4 Å molecular sieves prior to use. All other chemicals were from Aldrich and used without purification.

Instrumentation. EPR measurements were made on a Varian E-109 and on a Bruker ESP 300E spectrometer, both operating at 9 GHz and equipped with a variable-temperature unit (Varian E-257 and Bruker B-VT2000). The spectra were calibrated with diphenylpicrylhydrazyl (dpph), and the magnetic field was calibrated using Mn^{2+} in MgO.

Sample irradiation was performed under anaerobic conditions in EPR quartz tubes using a 250W Philips HP/T Hg lamp, $\lambda_{max} = 560-580$ nm, and irradiation times of about 60 min for samples at 77 K and 30 min for samples at 250 and 300 K, with the exception of the methyl and benzyl derivatives of the imino/oxime compounds, for which irradiation at 77 K was performed for 120 min.

Synthesis. alkylcobaloximes, compounds of general formula $RCo(DH)_2L$, were prepared by the procedure described by Toscano et al;[40] imino/oxime complexes, $[RCo\{(DO)(DOH)pn\}L)]ClO_4$, by that of Parker et al.[41] For all prepared compounds the expected stoichiometry was confirmed by elemental analysis and ^1H and ^{13}C NMR.

Sample Preparation. All manipulations were carried out under nitrogen; solvents were deoxygenated by reflux/distillation under nitrogen and all solids degassed under vacuum prior to use. Samples for photolysis were prepared by making $10^{-2}-10^{-3}$ solutions of the desired compounds in toluene/dichloromethane (1:1 or 1:2); these solutions were then irradiated in EPR sample tubes.

Results

Freshly prepared toluene/dichloromethane solutions of all reported cobaloximes and imino/oxime compounds are EPR silent and remain so for a few days when kept in the dark, as expected for low-spin Co(III) compounds. After being exposed to visible light these solutions exhibit EPR signals, thus implying the formation of paramagnetic species. Analysis of the EPR spectra exhibited by irradiated frozen solutions allows identification and characterization of the photolysis primary

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(34) Lohr, G. J.; Welker, M. E. *Inorg. Chim. Acta* **1999**, *296*, 13.

(35) Pezeshk, A.; Coffman, R. E. *J. Chem. Soc., Dalton Trans.* **1985**, 891.

(36) Pilbrow, J. R. In B_{12}; Dolphin, D., Ed.; Wiley: New York, 1982.

(37) Daul, C.; Schapfer, C. W.; von Zelewsky, A. *Struct. Bonding* **1979**, *36*, 130.

(38) de Castro, B.; Rangel, M.; Raynor, J. B. *J. Chem. Soc., Dalton Trans.* **1990**, 3311, and references therein.

(39) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; Pergamon: Oxford, 1988.

(40) Toscano, P. J.; Swiden, F. F.; Marzilli, L. G.; Bresciani-Pahor, N.; Randaccio, L. *Inorg. Chem.* **1983**, *18*, 3416.

(41) (a) Parker, W. O., Jr.; Bresciani-Pahor, N.; Zangrando, E.; Randaccio, L.; Marzilli, L. G. *Inorg. Chem.* **1985**, *24*, 3908. (b) Parker, W. O., Jr.; Bresciani-Pahor, N.; Zangrando, E.; Randaccio, L.; Marzilli, L. G. *Inorg.* Chem. **1986**, *25*, 3489.

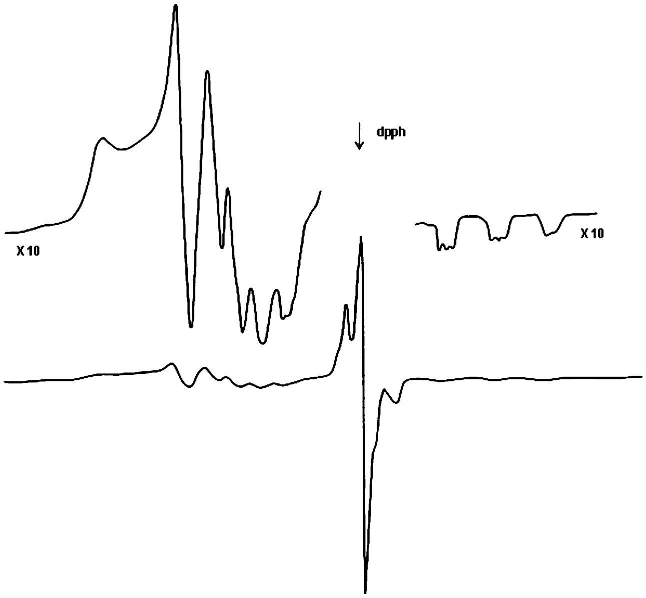

Figure 2. Frozen solution EPR spectrum of a toluene/dichloromethane solution of i-$C_3H_7Co(DH)_2py$ irradiated at 77 K and recorded at 100 K.

products and consequently determines if photolysis induced homolytic cleavage of the cobalt−carbon bond. Analysis of EPR spectra exhibited by irradiated frozen solutions that were warmed to room temperature or photolyzed at RT provides information about further reactions in which the primary products may have been involved.

Photolysis of Alkylcobaloximes, RCo(DH)$_2$L, at 77 K. Solutions of isopropyl- and *sec*-butylpyridinecobaloximes (1−6) irradiated and observed at 77 K yield EPR spectra that show a narrow signal at $g = 2.00$, a broad band at $g = 2.14$, and a signal that is spread over a wider range of magnetic field values and with substantial g tensor anisotropy ($g_{av} = 2.15$). The latter is assigned to a paramagnetic metal center, as can be inferred from the observed hyperfine splitting lines in the high-field region due to interaction of the unpaired electron with the cobalt atom. On warming this solution to 100 K, the band at $g = 2.14$ vanishes, but the other two remain detectable (Figure 2) and are assigned to an organic radical (R) and to a five-coordinate Co(II) species, [Co(DH)$_2$L], as the spectrum shows interaction of the unpaired electron with the cobalt atom (^{59}Co, I = 7/2) and with one axially bound nitrogen atom (^{14}N, I = 1) (Figure 2). The broad band observed at $g = 2.14$ and that vanishes when the matrix is relaxed to 100 K must be due to the strongly exchanged coupled system {[R$^{\bullet}$$\cdot$$\cdot$CoII(DH)$_2$L]}, which is kept immobilized by the lattice.[29b]

When the sample is further warmed, the radical signal loses intensity and vanishes and the cobalt(II) signal starts to broaden and converges into a single line at 300 K. If this solution is recooled to 100 K, two types of EPR spectra (A and B) are observed depending on the N-donor base: (a) spectra of type A for compounds with *ortho*-substituted pyridines bases (5 and 6) and (b) spectra of type B for compounds with pyridine or *meta*-substituted pyridines (1−4). Both types of spectra exhibit g tensor anisotropy and are typical of metal complexes with a d^7 (S = 1/2) electron configuration, thus implying a +2 formal oxidation state for the cobalt atom and providing evidence for reduction of the metal center.

Spectra of type A (Figure 3a), with larger g tensor anisotropy and for which three g features are discernible, exhibit in the high-field region hyperfine coupling of the unpaired electron with the cobalt (^{59}Co, I = 7/2) and nitrogen (^{14}N, I = 1) atoms. Each of the eight lines arising from coupling to cobalt is further split into three with relative intensities 1:1:1, due to superhyperfine coupling with one axially bound nitrogen atom. This spectrum is assigned to a low-spin cobalt(II) compound with one axially bound pyridine or substituted pyridine molecule, [Co(DH)$_2$ L].

Spectra of type B (Figure 3b) exhibit two well-separated g features, and in the high-field region it is possible to identify lines due to hyperfine coupling of the unpaired electron with the cobalt (^{59}Co, I = 7/2) and nitrogen (^{14}N, I = 1) atoms. Each of the eight lines arising from coupling to cobalt is further split into five, with relative intensities 1:2:3:2:1, due to superhyperfine coupling with two equivalent axially bound nitrogen atoms. This spectrum is assigned to a low-spin cobalt(II) compound with two axially bound pyridine or substituted pyridine molecules, [Co(DH)$_2$L$_2$].

Photolysis of Imino/Oxime Compounds, [RCo{(DO)(DOH)pn}L]ClO$_4$, at 77 K. EPR spectra of solutions of imino/oxime compounds a−f irradiated and observed at 77 K are similar to those observed for cobaloximes and also show bands due to three para-

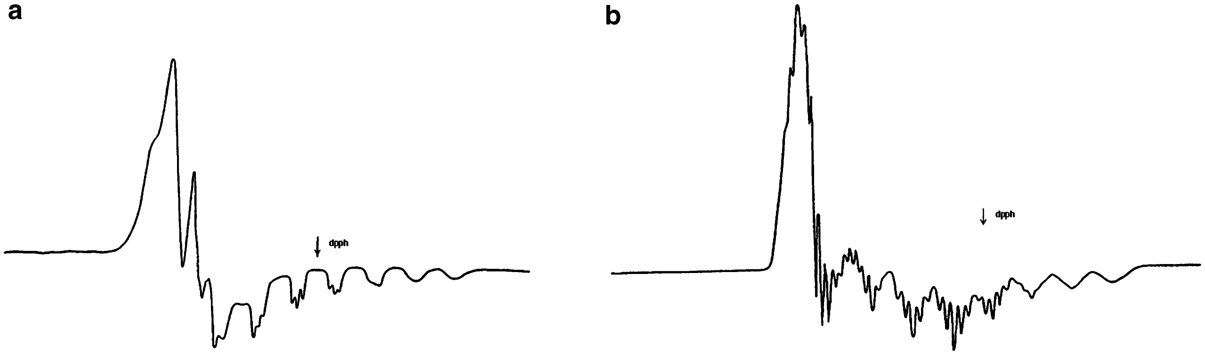

Figure 3. (a) Frozen solution EPR spectrum of a toluene/dichloromethane solution of i-$C_3H_7Co(DH)_2$2-NH$_2$py, irradiated at 77 K and recorded at 100 K, after being warmed to room temperature and frozen to 100 K. Spectrum of type A. (b) Frozen solution EPR spectrum of a toluene/dichloromethane solution of i-$C_3H_7Co(DH)_2py$, irradiated at 77 K and recorded at 100 K, after being warmed to room temperature and frozen to 100 K. Spectrum of type B.

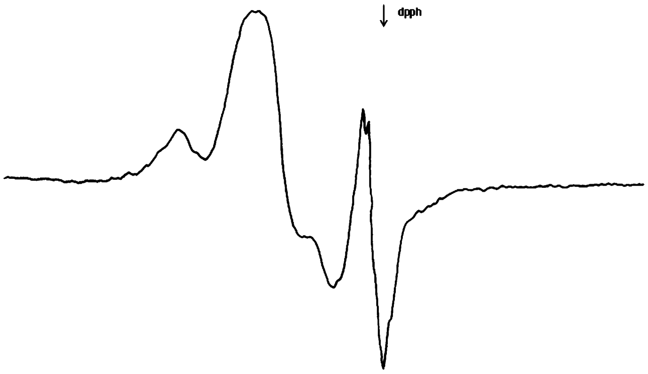

Figure 4. Frozen solution EPR spectrum of a toluene/dichloromethane solution of i-$C_3H_7(Co\{(DO)(DOH)pn\})py$, irradiated at 77 K and recorded at 77 K. $(Co\{(DO)(DOH)pn\})L_2$.

magnetic species: (a) a strong and narrow band at $g = 2.00$ due to a radical; (b) a broad band at $g_{av} = 2.14$ due to a coupled system; and (c) a third at $g_{av} = 2.15$ that shows substantial g tensor anisotropy. In Figure 4 the spectrum obtained for compound "a" is shown.

When the temperature is raised to 100 K, the signal at $g = 2.14$ disappears, and bands indicative of the presence of an organic radical (R) and of a five-coordinate cobalt(II) compound are observed. In Figure 5a is depicted the spectrum observed for the compound f with triphenylphosphine clearly exhibiting hyperfine coupling of the unpaired electron to the cobalt and phosphorus atoms.

On further warming the solution to 300 K, the signal due to the organic radical is lost and that of the cobalt(II) broadens and converges to one band, pyridine compounds a−c, or two bands, triphenylphosphine compounds d−f.

After being warmed at 300 K, the solutions were recooled to 100 K and their EPR spectra recorded.

Solutions of imino/oxime triphenylphospine compounds exhibit EPR spectra characteristic of a single species with well-separated g features. In the high-field region the signals show splitting due to hyperfine coupling of the unpaired electron with the cobalt atom (^{59}Co, $I = 7/2$) and with one phosphorus atom (^{31}P, $I = 1/2$), as each of the eight bands arising from coupling to cobalt is further split into two lines with equal intensity. This result is indicative of the existence in solution of the five-coordinate species $[Co\{(DO)(DOH)pn\}PPh_3]^+$ and also that this species does not undergo further reactions. The spectrum of the species $[Co\{(DO)(DOH)pn\}PPh_3]^+$ (Figure 5b) is the only signal observed for irradiated solutions of the imino/oxime triphenylphospine compounds even in the presence of an excess of triphenylphosphine.

Solutions of compounds, in which the base is pyridine (compounds a−c), after being irradiated at 77 K, warmed to 300 K, and recooled at 100 K exhibit identical spectra, and the one recorded for compound $[i$-$C_3H_7Co\{(DO)(DOH)pn\}py]^+$ is depicted in Figure 6a. This spectrum is clearly not due to just one cobalt(II) species, as can be inferred by observation of the unequally separated bands in the high-field region as well as the features in the low-field region, but appears as a superposition of two signals. One signal is very similar to the one observed for cobaloximes, exhibiting hyperfine splitting

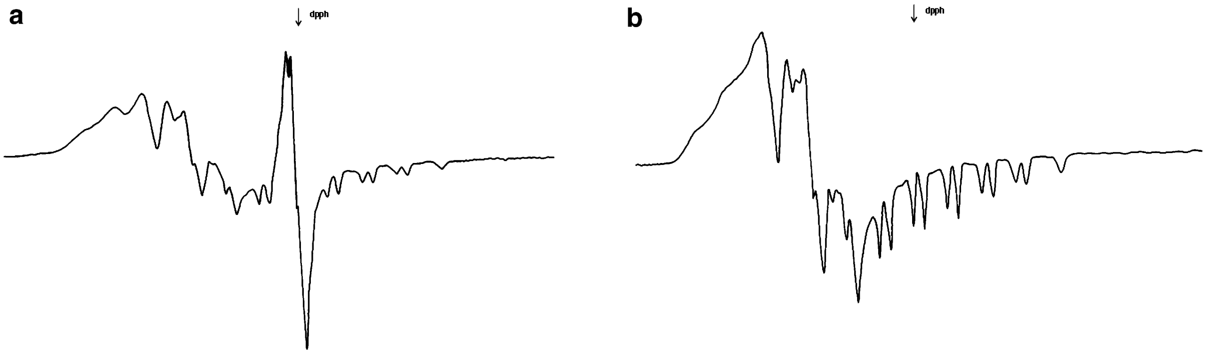

Figure 5. (a) Frozen solution EPR spectrum of a toluene/dichloromethane solution of i-$C_3H_7(Co\{(DO)(DOH)pn\})PPh_3$, irradiated at 77 K and recorded at 100 K. (b) Frozen solution EPR spectrum of a toluene/dichloromethane solution of i-$C_3H_7(Co\{(DO)(DOH)pn\})PPh_3$, irradiated at 300 K and recorded at 100 K.

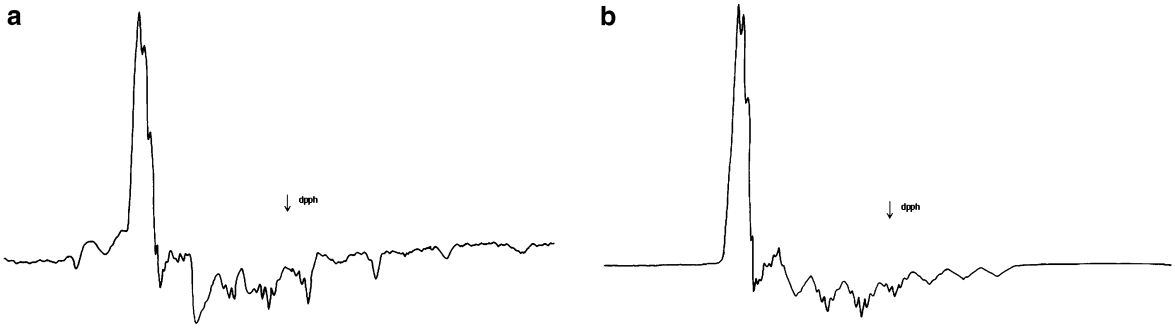

Figure 6. (a) Frozen solution EPR spectrum of a toluene/dichloromethane solution of i-$C_3H_7(Co\{(DO)(DOH)pn\})py$, irradiated at 77 K and warmed to 300 K, recorded at 100 K. (b) Frozen solution EPR spectrum of a toluene/dichloromethane solution of i-$C_3H_7(Co\{(DO)(DOH)pn\})py$, irradiated at room temperature in the presence of excess pyridine and recorded at 100 K.

Table 1. EPR Parameters of the Paramagnetic Species Formed after Photolysis of the Organocobalt Compounds[a]

compound	cobalt hyperfine interaction						N or P hyperfine interaction		
	g_x	g_y	g_z	A_x	A_y	A_z	A_x	A_y	A_z
$Co^{II}(DH)_2$ compounds									
$[Co^{II}(DH)_2py_2]$[b]	2.197	2.181	2.016	25	42	83	13	13	16
$[Co^{II}(DH)_2(3\text{-pic})_2]$[b]	2.195	2.176	2.012	26	35	84	12	12	16
$[Co^{II}(DH)_2(3,5\text{-lut})_2]$[b]	2.194	2.178	2.016	26	35	84	12	12	16
$[Co^{II}(DH)_2py]$	2.395	2.180	2.006	20	5	105	11	11	14
$[Co^{II}(DH)_2(2\text{-NH}_2)]$[b]	2.277	2.191	2.017	5	5	96	11	11	13
$[Co^{II}(DH)_2(2\text{-pic})]$[b]	2.280	2.188	2.016	8	5	110	12	9	13
$[Co^{II}(DH)_2(3\text{-pic})]$	2.393	2.182	2.006	20	5	106	10	10	13
$[Co^{II}(DH)_2(3,5\text{-lut})]$	2.393	2.182	2.006	20	5	106	10	10	13
"imine/oxime" compounds									
$[Co^{II}\{(DO)(DOHpn)\}py_2]$	2.207	1.176	2.016	27	25	86	13	13	14
$[Co^{II}\{(DO)(DOHpn)\}py]$	2.382	2.182	2.007	30	4	99	11	7	12
$[Co^{II}\{(DO)(DOHpn)\}PPh_3]$	2.353	2.164	2.004	25	12	86	90	104	114

[a] The units of A_x, A_y, A_z, and A_{iso} are 10^{-4} cm^{-1}. [b] Values coincident with those reported for solutions of aqua-(*sec*-butyl)bis(dimethylglyoximato)cobalt(III) in the presence of the corresponding base.[19]

due to the interaction of the unpaired electron with the cobalt atom (^{59}Co, $I = 7/2$) and with two equivalent axially coordinated nitrogen atoms (^{14}N, $I = 1$), and the other shows in the high-field region a splitting pattern ascribed to hyperfine interaction of the unpaired electron with a cobalt atom (^{59}Co, $I = 7/2$) but with no further splitting due to axial ligands.

The observation of the two latter signals seems to provide evidence for formation in solution of $[Co\{(DO)(DOH)pn\}]^+$ and of $[Co\{(DO)(DOH)pn\}py_2]^+$, and to clarify this result, the photolysis of solutions of compounds a−c was also performed in the presence of an excess of pyridine. The EPR spectrum obtained in these conditions is depicted in Figure 6b and is undoubtedly due to the species $[Co\{(DO)(DOH)pn\}py_2]^+$.

Photolysis at 250 and 300 K. The EPR spectra obtained for solutions of both cobaloximes and imino/oxime compounds irradiated at 250 and 300 K and recorded at 100 K are identical to those obtained for solutions irradiated at 77 K that were further warmed to 300 K and recooled to 100 K, thus indicating that the photolytic mechanism is operative for both temperatures of irradiation.

EPR Spectra Analysis. Cobalt(II) spectra were obtained at 100 K. The results reported above for EPR spectra of frozen solution of cobalt(II) complexes show that these can be grouped in two sets, based on the number of axial ligands bound (one or two) to the $[Co(DH)_2]$ and $[Co(DO)(DOH)pn]$ equatorial moieties. All spectra show large *g* tensor anisotropy and are typical of low-spin d^7 ($S = 1/2$) electron configuration species, thus implying a formal oxidation state of +2 for the cobalt center. Interactions of the unpaired electron with the cobalt atom (^{59}Co, $I = 7/2$) and with the nitrogen (^{14}N, $I = 1$) or phosphorus (^{31}P, $I = 1/2$) atoms of the axial ligands are clearly seen in the high-field region of the spectra. No hyperfine interaction with the nitrogen atoms of the equatorial ligands was ever observed in the spectra.

The components of the spin-Hamiltonian parameters (Table 1) were obtained by computer simulation of the experimental spectra, and the results confirm that the spectra must be interpreted in terms of three different *g* values.[42] In the analysis, an $^2A_1$ ground state was assumed for the complex comprising a mixture of the d_{z^2} and $d_{x^2-y^2}$ metal orbitals of the form $\Phi = a d_{z^2} + b d_{x^2-y^2}$ (taking the point-group symmetry to be C_{2v}).[36,42−44] The EPR parameters are quite similar for compounds with the same number and type (P or N donor) of axial ligands, but the degree of anisotropy, measured as $\Delta_{xy} = g_x - g_y$, is significantly higher for five-coordinate compounds; these also show the largest values for the A_z component of the cobalt hyperfine tensor and the smallest values of the A_x and A_y components.

Data Analysis. Computer Simulation. EPR spectra of cobalt(II) compounds were simulated using a program based on Pilbrow's formalism,[44] which uses a spin-Hamiltonian of the type $H = H(\text{Zeeman}) + H(\text{hyperfine}) + H(\text{ligand})$. The hyperfine term was deduced assuming a C_{2v} point-group symmetry at the cobalt center and the noncoincidence of the *g* and *A*(Co) tensor axes in the *xy* plane. As no interaction of the unpaired electron with the nitrogen atoms of the equatorial plane was observed, the ligand term includes only the nitrogen axial interaction, and it was assumed that the nitrogen tensor has the same principal axis as that of the *g* tensor. For the simulation of the spectra of the compounds reported, the best fit was obtained for collinear *g* and *A* tensors in the *x* and *y* plane (rhombic symmetry) with neglect of any quadrupolar contribution to the spin-Hamiltonian

Cobalt Spin Density. Analysis of the *g* and cobalt hyperfine tensors allows deduction of the unpaired spin density in the metal 3d and 4s orbitals. The procedures for this have been fully described by us[19] and are based on those of McGarvey.[42] The results obtained are shown in Table 2.

Ligand Spin Density. No hyperfine coupling was observed with the equatorial nitrogen atoms, but from the observed hyperfine coupling to the axial donor nitrogen and phosphorus atoms, spin density on base nitrogen 2s and 2p orbitals and on base phosphorus 3s and 3p orbitals could be determined. The procedures for this have already been described,[32,38] and the results are shown in Table 2.

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(42) McGarvey, B. R. *Can. J. Chem.* **1975**, *53*, 249.

(43) For the $Co(DMG)_2$ species with one bound pyridine the symmetry point group is $C_{2v}(z)$, but for the imino/oxime compounds the symmetry point group is C_s. For the compounds with none or two bound pyridine molecules the symmetry point group is $C_{2v}(x)$. This difference is solely reflected in the symmetry labeling of two states that in our case are excited states, which are not discussed in this work.

(44) Pilbrow, J. R.; Winfield, M. E. *Mol. Phys.* **1973**, *25*, 1073.

Table 2. ESR Parameters of the Cobalt(II) Species Formed

compound	a^2	b^2	$-kP$	P	ρ_{3d}	ρ_{4s}	ρ_{Co}	ρ_{2p}	ρ_{2s}	ρ_L	$2_{\rho L}$	ρ_{total}
[$Co^{II}(DH)_2py_2$]	0.9892	0.0108	0.0040	89	0.35	0.06	0.41	0.070	0.026	0.096	0.192	0.599
[$Co^{II}(DH)_2$(3-pic)$_2$]	0.9967	0.0033	0.0038	93	0.37	0.06	0.42	0.075	0.025	0.100	0.200	0.622
[$Co^{II}(DH)_2$(3,5-lut)$_2$]	0.9969	0.0031	0.0038	94	0.37	0.06	0.43	0.075	0.025	0.100	0.200	0.626
[$Co^{II}(DH)_2py$]	0.9962	0.0038	0.0006	205	0.81	0.06	0.87	0.043	0.022	0.065		0.935
[$Co^{II}(DH)_2(2\text{-}NH_2)$]	0.9984	0.0016	0.0006	177	0.70	0.06	0.76	0.041	0.019	0.060		0.820
[$Co^{II}(DH)_2$(2-pic)]	0.9988	0.0011	0.0013	201	0.79	0.06	0.85	0.040	0.020	0.060		0.910
[$Co^{II}(DH)_2$(3-pic)]	0.9963	0.0037	0.006	208	0.82	0.06	0.88	0.060	0.030	0.090		0.970
[$Co^{II}(DH)_2$(3,5-lut)]	0.9963	0.0037	0.006	208	0.82	0.06	0.88	0.060	0.030	0.090		0.970
[Co^{II}{(DO)(DOH)pn}py]	0.9997	0.0003	0.0013	178	0.70	0.06	0.76	0.062	0.019	0.081	0.081	0.840
[Co^{II}{(DO)(DOH)pn}py_2]	1	0	0.0034	105	0.41	0.06	0.47	0.030	0.025	0.055	0.110	0.579

compound								ρ_{3p}	ρ_{3s}	ρ_L	ρ_{total}
[Co^{II}{(DO)(DOH)pn}PPh_3]	0.9858	0.0142	−0.002	218	0.86	0.04	0.90	7	3	10	100

Discussion

In the present study we observed that photolysis induces homolytic cleavage of the cobalt−carbon bond, as can be gathered by the unambiguous identification of cobalt(II) species and of organic radicals in solution for all the compounds studied (cobaloximes and imino/oxime) and in both fluid and frozen solution.

Homolysis of the cobalt−carbon bond is interpreted according to the mechanism proposed by Symons[29a] that assumes that on light absorption an electron from the equatorial plane moves into the Co(d_{z^2}) σ^* orbital. The antibonding character of this orbital is then relieved by bond fission, following the sequence

$$R{-}Co(DH)_2L \rightarrow [R^{\bullet}] + [Co^{II}(DH)_2L]$$

$$[R^{\bullet}] + H_{solvent} \rightarrow RH + [solvent^{\bullet}]$$

$$[R^{\bullet}] \rightarrow R^{\bullet}$$

where the brackets represent cage trapping.

A comparative analysis of photolysis primary and secondary products is done below, for the different compounds studied, taking into account the different equatorial and axial ligands.

For isopropylpyridinecobaloximes cobalt−carbon bond homolysis was for all the compounds induced with visible light, in fluid and frozen solution, in contrast with the result observed by us[31] for methyl and benzyl pyridinecobaloximes, for which homolytic cleavage of the bond was only achieved at 300 K or with UV light, as a consequence of the stronger bonds present in the methyl and benzyl organocobalt(III) compounds. The reported values for bond dissociation energies for the bonds Co−C(CH_3), Co−C(C_6H_5), and Co−C(i-C_3H_7) in pyridinecobaloximes[19] are respectively 35, 31, and 21 kcal mol^{-1}, and it is important to point out that these differences are reflected in the photolytic behavior. In contrast to cobaloximes, the photolysis results observed for the imino/oxime isopropyl and methyl derivatives are identical: cleavage of the Co−C bond is induced by visible light for both compounds. The result suggests that in imino/oxime compounds the Co−C(CH_3) and Co−C(C_6H_5) bonds must be weaker than those of the parent cobaloximes. The reported values for the Co−C(CH_3) bond distances are 1.998 Å for pyridinecobaloxime and 2.003 Å for the pyridineimino/oxime compound, and the values of the stretching frequencies in solution of Co−C(Me) are 504 cm^{-1} in the cobaloxime compound and 497 cm^{-1} in the imino/oxime compounds. The observed values of the Co−N bond lengths are 2.068 Å for the cobaloxime compound and 2.106 Å for the imino/oxime compound, suggesting that the different photolytic behavior must be due to the electronic effect of the *trans* ligand.

Moreover, for pyridineimino/oxime compounds the Co−C bond suffers homolytic cleavage at 250 K, in contrast with the methyl and benzyl pyridine cobaloximes, for which homolysis does not occur.[31]

The results obtained for cobaloximes with *ortho*-substituted pyridines are in close agreement with those reported by us for *sec*-butylpyridinecobaloximes[30] and by Marzilli et al. for cobinamide models[21] and show the effect of the steric hindrance imposed by the base on the equatorial moiety on the reactivity of the photolysis primary product. For these compounds the Co(II) five-coordinate species, $Co(DH)_2L$, does not undergo further reaction to form a six-coordinate species with two axial base molecules $Co(DH)_2L_2$, as bending of the equatorial dimethylglyoxime units away from the base makes the sixth coordination position less accessible. This same effect has already been observed for cobaloximes with symmetric phosphines[33] and also in the present work for the imino/oxime compounds with triphenylphosphine.

For cobaloximes and imino/oxime compounds in which the base is pyridine or a *meta*- or *para*-substituted pyridine we observed, as previously for solutions of aquocobaloxime and added bases,[30] that the photolysis primary product, $Co(DH)_2L$, is observable only in frozen solution. As soon as the matrix is relaxed to room temperature, the Co(II) five-coordinate species is involved in a further reaction, giving rise to the Co(II) six-coordinate species with two axially bound pyridine molecules, $Co(DH)_2L_2$.

Considering the results obtained for cobaloximes and imino/oxime compounds with the same axial ligands, it is evident that its photolytic behavior is the same, equivalent primary and secondary products are detected, and in both cases the predisposition of the five-coordinate Co(II) species to bind a second base molecule is dictated by the steric hindrance imposed by the Lewis base on the equatorial ligand.

An interesting result that emerges from these results is the one that concerns formation of the six-coordinate Co(II) species with two axially bound pyridine molecules. Formation of such a species upon photolysis of the organocobalt(III) compounds implies that the five-coordinate Co(II) complex must be able to abstract pyridine molecules from other species present in solution, which had to be either another $Co(DH)_2L$ molecule or a cobalt(III) species still present in solution, as the photolysis quantum yield is less than 100%.

The results obtained in this work and previously by us for other pyridinecobaloximes[30] were not conclusive, as the only signal observed in the EPR spectrum is the one characteristic of the $Co(DH)_2L_2$ species, but insight into this matter was obtained from the results obtained for the imino/oxime parent compounds. EPR spectra of the latter exhibit two superimposed signals attributable respectively to the six-coordinate cobalt(II) species, (Co{(DO)(DOH)pn})L_2, with two bound pyridine molecules and to the four-coordinate compound, Co{(DO)(DOH)pn}, weakly solvated.[45] The observation of both signals indicates that the pyridine molecules must be abstracted from Co(II) five-coordinate species and rules out the possibility of pyridine abstraction from cobalt(III) species[46,47] still present in solution. This explanation gains support by noting that when photolysis of the imino/oxime compound is performed in the presence of excess pyridine, only the six-coordinate species with two bound pyridine molecules is detected.

The above results are indicative that the four-coordinate Co(II) units with the two ligands behave differently, and on the basis of preliminary magnetic susceptibility measurements in solution we propose that formation of diamagnetic species such as dimers or aggregates must occur for the dimethylglyoxime compound, as has been observed in the case of $[Ni(DH)_2]$ in the solid state.[48] Such an interesting behavior is being explored in a different study that involves Co(II) compounds synthesized with various ligands of the glyoxime type.[49]

The values obtained from spectra simulation for the spin-Hamiltonian g and A tensor components (Table 1) are consistent with those obtained for other cobaloximes and clearly indicate a larger rhombic distortion ($\Delta_{x,y} = g_x - g_y$) and larger values of the A_z component of the cobalt hyperfine tensor for five-coordinate Co(II) species compared to the six-coordinate ones. No significant differences are observable for the two classes of compounds. For all the Co(II) compounds the EPR parameters are characteristic of a $^2A_1$ ground state (with a 99% contribution of the d_{z^2} orbital). The positive values of the Fermi contact term indicate strong admixture of the 4s and $3d_{z^2}$ orbitals, and the amount of 4s character depends on coordination geometry. The values of spin densities clearly indicate spin delocalization to the axial ligand and equatorial ligands.

In conclusion we may infer that the different equatorial moieties are not determinant in terms of the nature of the photolysis primary products, and the only difference observed so far resides in the fact that for cobaloximes the spectrum of the species with no bound pyridines was never observed, but in the case of imino/oxime compounds the EPR spectrum of this species is observed superimposed with the one corresponding to the six-coordinate compound. This result seems to be more related with the fact that the dimethylglyoxime square planar compound has an ability to form dimers or pack in diamagnetic arrays, while its parent imino/oxime compound does not. Maybe the presence of the imino bridge prevents the necessary planarity or minimal distance for metal−metal interactions.

Finally it is important to stress that for both classes of B_{12} model compounds the cobalt(II) species resulting from homolysis of the cobalt−carbon bond have a considerable tendency to coordinate a sixth ligand and so like cobalamin(II) a considerable reactivity toward available substrates present in solution media.

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(45) Gomes, J. Ph.D. Thesis, University of Porto, 1996.

(46) Hill, H. O.; Morallee, K. J. *J. Chem. Soc. (A)* **1969**, 554.

(47) Costa, G.; Mestroni, G.; Tauzher, G.; Stefani, L. *J. Organomet. Chem.* **1966**, *6*, 181. Costa, G.; Mestroni, G.; Tauzher, G.; Stefani, L. *J. Organomet. Chem.* **1967**, *7*, 493.

(48) Godyki, L. E.; Rundle, R. E. *Acta Crystallogr.* **1953**, *6*, 487. Williams, D. E.; Wohlaeur, G.; Rundle, R. E. *J. Am. Chem. Soc.* **1959**, *81*, 755.

(49) Rangel, M.; de Castro, B. Unpublished results.