

EPR characterization of the photolysis and thermolysis products of alkylcobaloximes with symmetric phosphines and phosphites. Factors that stabilize the cobalt homolysis fragments

Baltazar. De Castro, Jose. Pereira, and Maria. Rangel

Organometallics, 1991, 10 (11), 3848-3855 • DOI: 10.1021/om00057a014 • Publication Date (Web): 01 May 2002

Downloaded from <http://pubs.acs.org> on March 8, 2009

More About This Article

The permalink <http://dx.doi.org/10.1021/om00057a014> provides access to:

- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article



85.1 (C≡CH), 115.7 (FeC≡CC), 124.5 (CC≡CH), 130.7 (CH), 133.0 (FeC≡C), 135.4 (CH), 146.9 (FeC≡C); λ_{\max} (THF, log ϵ) 250 (4.10), 405 (3.72) nm; $\nu_{\text{C}\equiv\text{C}}$ (Nujol) 2033 cm^{-1} . Anal. Calcd for $\text{FeC}_{36}\text{H}_{42}\text{P}_4$: C, 66.06; H, 6.42. Found: C, 66.5; H, 6.7.

trans-Fe(C≡CC(CH₃)₂(DMPE)₂ (7a). A solution of $\text{FeH}_2(\text{DMPE})_2$ (1a) (40 mg, 0.11 mmol) in methanol (3 mL) was added to a solution of *tert*-butylacetylene (91 mg, 1.11 mmol) in methanol (3 mL) with vigorous stirring. The crude product precipitated from solution over a period of 30 min. The solution was filtered, and the residue was washed with methanol and recrystallized from benzene to afford $\text{Fe}(\text{C}\equiv\text{CC}(\text{CH}_3)_2)(\text{DMPE})_2$ (7a) as a pale yellow crystalline solid (41 mg, 71%): decomposed without melting at $T > 300$ °C; $^{31}\text{P}\{^1\text{H}\}$ NMR (THF-*d*₆) δ 69.4; ^1H NMR (THF-*d*₆) δ 1.12 (s, 18 H, CCH₃), 1.58 (bs, 24 H, PCH₃), 1.84 (bs, 8 H, CH₂); $^{13}\text{C}\{^1\text{H}, ^{31}\text{P}\}$ NMR (THF-*d*₆) δ 17.7 (PCH₃), 31.7 (CCH₃), 32.9 (CH₂), 35.0 (CCH₃), 111.9 (FeC≡C), 121.9 (FeC≡C); λ_{\max} (THF, log ϵ) 350 (3.91); $\nu_{\text{C}\equiv\text{C}}$ (Nujol) 2059 cm^{-1} . Anal. Calcd for $\text{FeC}_{24}\text{H}_{50}\text{P}_4$: C, 55.60; H, 9.65. Found: C, 56.0; H, 10.0.

trans-Fe(C≡CCH₃)₂(DMPE)₂ (3a). A solution of $\text{FeH}_2(\text{DMPE})_2$ (1a) (20 mg, 56 μmol) in methanol (3 mL) was added, with vigorous stirring, to a methanol solution of propyne (2 mL, 0.22 M) in which sodium (5 mg) had been dissolved. The crude product precipitated from solution over a period of 30 min. The solution was filtered, and the residue was washed with pentane and recrystallized from pentane to afford $\text{Fe}(\text{C}\equiv\text{CCH}_3)_2(\text{DMPE})_2$ (3a) as a pale yellow crystalline solid (14 mg, 57%): decomposed without melting at $T > 300$ °C; $^{31}\text{P}\{^1\text{H}\}$ NMR (THF-*d*₆) δ 69.5; ^1H NMR (THF-*d*₆) δ 1.30 (bs, 24 H, PCH₃), 1.53 (s, 6 H, CCH₃), 1.57 (bs, 8 H, CH₂); $^{13}\text{C}\{^1\text{H}, ^{31}\text{P}\}$ NMR (THF-*d*₆) δ 8.0 (CH₃), 17.7

(PCH₃), 32.8 (CH₂), 104.7 (FeC≡C), 112.8 (FeC≡C); λ_{\max} (THF) 232, 400 nm; $\nu_{\text{C}\equiv\text{C}}$ (Nujol) 2075 cm^{-1} . Anal. Calcd for $\text{FeC}_{18}\text{H}_{38}\text{P}_4$: C, 49.77; H, 8.76. Found: C, 50.0; H, 8.9.

trans-Fe(C≡CPh)₂(DEPE)₂ (4b). A solution of $\text{FeH}_2(\text{DEPE})_2$ (1b) (5 mg, 10 μmol) in methanol (3 mL) was added, with vigorous stirring, to a solution of phenylacetylene (500 mg, 5 mmol) in methanol. The crude product precipitated from solution over a period of 30 min. The solution was filtered, and the residue was washed with methanol and recrystallized from benzene to afford $\text{Fe}(\text{C}\equiv\text{CPh})_2(\text{DEPE})_2$ (4b) as an orange-yellow crystalline solid: decomposed at $T > 250$ °C; $^{31}\text{P}\{^1\text{H}\}$ NMR (THF-*d*₆) δ 76.0; ^1H NMR (THF-*d*₆) δ 1.20 (bs, 24 H, CH₃), 1.61 (bs, 16 H, CH₂), 2.39 (bs, 8 H, CH₂), 6.75 (m, 2 H, CH), 6.87 (m, 4 H, CH), 6.94 (m, 4 H, CH); $^{13}\text{C}\{^1\text{H}, ^{31}\text{P}\}$ NMR (dichloromethane-*d*₂) δ 10.2 (CH₃), 21.8 (CH₂CH₃), 30.5 (CH₂), 117.8 (C≡CC), 122.6 (CH), 128.5 (CH), 130.4 (CH), 131.7 (FeC≡C), 142.0 (FeC≡C); λ_{\max} (THF, log ϵ) 258 (4.52), 374 (4.54) nm; $\nu_{\text{C}\equiv\text{C}}$ (Nujol) 2035 cm^{-1} . Anal. Calcd for $\text{FeC}_{36}\text{H}_{58}\text{P}_4$: C, 64.49; H, 8.66. Found: C, 64.2; H, 8.6.

Acknowledgment. We gratefully acknowledge financial support from the Australian Research Grants Scheme.

Supplementary Material Available: Tables of crystal data, bond lengths and angles, thermal parameters, and hydrogen atom positional and thermal parameters for 3a, 4b, and 5a and tables of least-squares calculations for 4b and 5a (11 pages); tables of observed and calculated structure factors for 3a, 4b, and 5a (30 pages). Ordering information is given on any current masthead page.

EPR Characterization of the Photolysis and Thermolysis Products of Alkylcobaloximes with Symmetric Phosphines and Phosphites. Factors That Stabilize the Cobalt Homolysis Fragments

Baltazar de Castro,*† José Pereira,† and Maria Rangel†

Departamento de Química, Faculdade de Ciências do Porto, 4000 Porto, Portugal,
and Instituto de Ciências Biomédicas de Abel Salazar, 4000 Porto, Portugal

Received January 2, 1991

The products of anaerobic photolysis of several alkylcobaloximes with symmetric phosphines and phosphites were studied by electron paramagnetic resonance spectroscopy in nonaqueous solutions and at several temperatures. Evidence is provided for photochemically induced homolytic cleavage of the cobalt-carbon bond and for the formation of stable cobalt(II) five-coordinated species and of organic radicals as homolysis products. The resulting cobalt(II) species are independent of the alkyl group of the cobaloxime, as the EPR spectra of the different alkylcobaloximes with the same phosphorus ligand are identical. A rationale for the lack of reactivity of the cobalt(II) five-coordinated species is provided by an analysis of the EPR parameters and the use of extended Hückel calculations that show the cobalt atom to lie well above the equatorial coordination plane defined by the glyoximes, thus rendering the sixth position not easily available for coordination.

Introduction

The recognition that homolysis of the Co-C bond in coenzyme B₁₂ (5'-deoxyadenosylcobalamin) dependent rearrangements is the only role identified thus far for this cofactor has spurred a new interest in the aspects that promote cleavage of this bond.¹⁻³ Conformational changes in both coenzyme B₁₂ and the protein upon addition of the substrate to the holoenzyme have been widely accepted to be responsible for enzyme-accelerated Co-C bond

cleavage. An enzyme-induced distortion of the corrin ring toward the adenosyl moiety reminiscent of the butterfly conformation observed in the corrin,²⁻⁵ a lengthening of

* Faculdade de Ciências do Porto.

† Instituto de Ciências Biomédicas de Abel Salazar.

(1) (a) Dolphin, D., Ed. *B₁₂*; 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.

(2) (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.

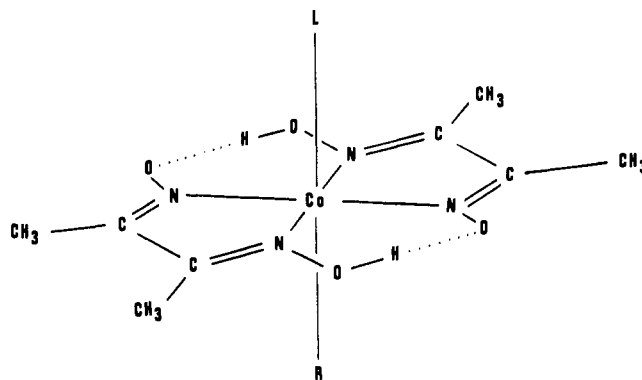
(3) (a) Hay, B. P.; Finke, R. G. *J. Am. Chem. Soc.* 1987, 109, 8012. (b) Hay, B. P.; Finke, R. G. *Polyhedron* 1988, 7, 1469 and references therein.

the Co-C bond induced by strong binding to the protein,^{1d} an alteration in the position of the axial 5,6-dimethylbenzimidazole ligand,^{5a} and angular distortion of the Co-C group^{5b} have been postulated as possible contributions to the conformationally induced Co-C bond cleavage.

All these mechanisms have been proposed by assuming that Co-C homolysis acceleration is mainly due to a ground-state effect: the weakening of the Co-C bond. Recently, however, an alternate explanation, forwarded by Marzilli et al.⁶ and derived from their Raman spectroscopy studies on organocobalt B₁₂ and model compounds, assumes the transition state to resemble the Co^{II}B₁₂/Ado[•] intermediate state, and thus a stabilization of this state will accelerate Co-C bond cleavage. Additional support for this suggestion is provided by the observation that the corrin moiety conformations in coenzyme B₁₂ and in methyl B₁₂ are strikingly similar to that of cob(II)alamin, the five-coordinate Co(II) compound formed by Co-C bond cleavage, and the main differences lie in a displacement of the cobalt atom toward the benzimidazole with concomitant conformational changes of the nucleotide loop. Kräutler et al.⁷ concluded from the structural information presented in their X-ray study that the interaction apoenzyme/coenzyme at the corrin moiety of coenzyme B₁₂ appear insufficient to provide the major means for a protein-induced activation of bound coenzyme B₁₂ toward homolysis of its Co-C bond, and they argued for a labilization of this bond through an apoenzyme induced separation of the homolysis fragments.

Nevertheless, the relevance of steric interactions 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 in a series of alkylcobaloximes⁸ and other organocobalt compounds with nitrogen^{2,9} and phosphorous donor ligands.^{2b,10} Despite the inadequacy of these model compounds to mimic the physical properties of cobalamins, they have provided decisive information in the development of methods for understanding B₁₂ properties, especially the factors that influence the Co-C bond.

Homolytic cleavage of the cobalt-carbon bond in B₁₂ systems and in model compounds can also be induced by photolysis and thermolysis, and it is believed that the products of these reactions are identical with those found during the enzymatic processes in which cobalamins are present.^{1,2a} Thermolysis of the Co-C bond has been extensively studied in coenzyme B₁₂³ and in model compounds,¹¹ and the first decomposition temperature in the differential scanning calorimetry of these latter compounds was used to probe electronic and stereochemical effects of



- | | |
|-----------------------------------------------------------------|-----------------------------------------------------------------|
| 1. L = PPh ₃ ; R = CH ₃ | 5. L = PBu ₃ ; R = C ₂ H ₅ |
| 2. L = PPh ₃ ; R = C ₂ H ₅ | 6. L = PBu ₃ ; R = C ₂ H ₅ |
| 3. L = PPh ₃ ; R = C ₂ H ₅ | 7. L = PEt ₃ ; R = C ₂ H ₅ |
| 4. L = PBu ₃ ; R = CH ₃ | 8. L = PcHx ₃ ; R = C ₂ H ₅ |
| 9. L = P(OPh) ₃ ; R = CH ₃ | 13. L = P(OMe) ₃ ; R = C ₂ H ₅ |
| 10. L = P(OPh) ₃ ; R = C ₂ H ₅ | 14. L = P(OMe) ₃ ; R = C ₂ H ₅ |
| 11. L = P(OPh) ₃ ; R = C ₂ H ₅ | 15. L = P(OEt) ₃ ; R = C ₂ H ₅ |
| 12. L = P(OMe) ₃ ; R = CH ₃ | 16. L = P(OBu) ₃ ; R = C ₂ H ₅ |

Figure 1. Alkylcobaloximes, LCo(Hdmg)₂R, studied.

the axial substituents on the strength of the organocobalt bond. Finke and co-workers³ were able to demonstrate the reversible thermal homolysis of the Co-C bond in coenzyme B₁₂ in the absence of the enzyme and to characterize the homolysis products as cob(II)alamin and 5'-deoxyadenosyl radical, with the latter radical being trapped with the nitroxide radical TEMPO. Spin-trap techniques¹² were also widely used in photolysis studies of these systems mainly to characterize the radical species formed after homolytic cleavage of the organocobalt bond^{13,14} and to get insight into the mechanisms of electron transfer to the Co(d_{z²}) σ* orbital prior to subsequent homolysis of the Co-C bond. Several studies on the photolysis products of some pyridine alkylcobaloximes, pyCo(DH)₂R, have appeared in the literature and point to a dependence of the photolysis products on the alkyl ligand and on the temperature of irradiation.¹² These factors also seem to control the reactivity of the cobalt fragment formed, although much less attention has been devoted to the characterization of these species.

Electron paramagnetic resonance (EPR) spectroscopy has proved to be the method of choice to identify the photolysis products of the Co(III) species¹²⁻¹⁴ and to get relevant information about the structure of the cobalt(II) complexes formed.^{15,16} As an example, we note that the first definitive identification of the reduced form of the coenzyme, cob(II)alamin, was provided by the observation of an EPR spectrum typical of a low-spin cobalt(II) complex after anaerobic photolysis of coenzyme B₁₂.¹⁷

(4) (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.

(5) (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.

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

(7) Kräutler, B.; Keller, W.; Kratky, C. *J. Am. Chem. Soc.* **1989**, *111*, 8936.

(8) Cobaloximes are compounds of general formula LCo(DH)₂X, where L and X are neutral and mononegative monodentate axial ligands and DH is the monoanion of dimethylglyoxime.

(9) (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.

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

(11) Brown, K. L.; Young, G. W.; Segal, R.; Rajeshwar, K. *Inorg. Chim. Acta* **1987**, *128*, 197.

(12) (a) Giannotti, C.; Bolton, J. R. *J. Organomet. Chem.* **1976**, *110*, 383. (b) Maillard, P.; Giannotti, C. *Can. J. Chem.* **1982**, *60*, 1402.

(13) (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*, 145.

(14) (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.

(15) (a) Pilbrow, J. R. In *B₁₂*; Dolphin, D., Ed.; Wiley: New York, 1982; Chapter 12. (b) Pilbrow, J. R.; Winfield, M. E. *Mol. Phys.* **1973**, *25*, 1073.

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

(17) Hogenkamp, H. P. C.; Barker, H. A.; Mason, H. S. *Arch. Biochem. Biophys.* **1963**, *100*, 353.

The purpose of the present work is to use EPR spectroscopy to characterize the cobalt products of the anaerobic photolysis and thermolysis, in aprotic solvents, of several alkylcobaloximes with phosphorus donor ligands trans to the alkyl radical (Figure 1) and to assess the influence of steric interactions on the stability and the structure of the resulting photolysis products of these B_{12} model compounds. The choice of these alkylcobaloximes was dictated by the observation, in their known crystallographic structures, that these P-donor ligands have a marked effect on the Co-C bond length through a trans effect that is due to a cis stereochemical pressure on the equatorial ligands that are folded away from the P-donor ligand. These ligands provide B_{12} models in which the position of the cobalt atom relative to the four-coordinated nitrogen atoms of the equatorial plane can be controlled by changing the bulkiness of the P-donor ligand and thus changing the stability of the Co(II)/R^{*} intermediate state.

Qualitative molecular orbital theory calculations (extended Hückel type) were also performed in order to get some insight into the stability of the cobalt fragments resulting from homolysis of phosphine and phosphite alkylcobaloximes, specifically on the dependence of the total one-electron energy of the five-coordinated complex with the position of the cobalt atom relative to the equatorial plane.

Experimental Section

Reagents. The solvents were from Merck, and the other chemicals were from Aldrich. All solvents were purified by standard methods¹⁸ and kept over 4-Å molecular sieves prior to use. Triphenylphosphine was recrystallized twice from ethanol, and all other chemicals were used without further purification.

Instrumentation. The X-band EPR spectral measurements were made on a Varian E-109 instrument with a Varian E-257 VT unit, and Q-band spectra were obtained on a Bruker ER 200 instrument with an ER 053 QRD bridge. The EPR spectra were calibrated with diphenylpicrylhydrazyl (dpph), and the X-band magnetic field was calibrated by using Mn²⁺ in MgO. Photolysis of the alkylcobaloxime solutions were performed with a Hg lamp (250-W Philips HP/T; $\lambda = 560\text{--}580$ nm) in anaerobic conditions at three different temperatures (77, 240, 300 K). Samples were irradiated for up to 1 h, and the results were independent of irradiation time.

Synthesis. The cobaloximes were prepared by the method described by Marzilli et al.¹⁹ Co(DH)₂ and LCo(DH)₂ were prepared by the method described by Schrauzer and Lee.²⁰

Sample Preparation. All manipulations were carried out under nitrogen; the solvents were deoxygenated with nitrogen, and all the solids were degassed under vacuum. The samples to be irradiated were prepared by making solutions of the alkylcobaloximes in toluene/dichloromethane (1:1) or by adding the phosphorus ligands to solutions of the aquocobaloximes in toluene/dichloromethane.

Extended Hückel Calculations. All calculations were of the extended Hückel type,²¹ with the tight-binding approach.²² The parameters used are collected in Table I. The atomic coordinates of the Co(DH)₂ fragment are the average of known structures of cobaloximes,^{4a} with the further assumption that it is planar, in the absence of axial coordination. The total energy of the adduct was calculated as a function of (i) the bending angle between the two dimethylglyoxime units (α), assuming the four-coordinated

Table I. Parameters Used in the Extended Hückel Calculations

atom	orbital	H_{ii}/eV	ζ_i
Co	4s	-9.21	2.0
	4p	-5.29	2.0
	3d	-13.18	5.55 ^a
P	3s	-18.6	1.75
	3p	-14.0	1.30
O	2s	-32.3	2.275
	2p	-14.8	2.275
N	2s	-26.0	1.950
	2p	-13.4	1.950
C	2p	-21.4	1.625
	2s	-11.4	1.625
H	1s	-13.6	1.3

^a The coefficients used in the double- ζ expansions of the cobalt d orbitals were $c_1^a = 0.5680$ and $c_2^a = 0.6060$. The value of ζ_2 was 2.10.

nitrogen atoms to be planar, and (ii) the distance between the cobalt atom and the plane defined by the four-coordinated nitrogen atoms (d). The coordinates of the phosphine atoms are those observed in ClCo(DH)₂(PPh₃),²³ the phosphine was assumed to behave rigidly in all calculations. The cobalt-phosphorus distance was allowed to change between 231.8 and 251.8 pm, a 20-pm interval centered on the value observed for Co-P in methyl(phosphine)cobaloxime, 241.8 pm.

Results

The solutions of the alkylcobaloximes studied, RCo(DH)₂PX₃ (see Figure 1), in toluene/dichloromethane are EPR silent and remain so for a few days when kept in the dark, as expected for low-spin Co(III) compounds. Solutions of these compounds exposed to light show room-temperature EPR spectra with $g_{\text{iso}} \sim 2.15$, significantly higher than the free electron value.

Irradiation of Alkylcobaloximes at Room Temperature or above the Solution Freezing Point. Alkylcobaloxime solutions irradiated at room temperature or above the solution freezing point exhibit frozen-solution EPR spectra with large g -tensor anisotropy and are typical of low-spin d^7 ($S = 1/2$) electron configuration species, implying a formal oxidation state of +2 for the cobalt center. These spectra exhibit hyperfine coupling to the cobalt and to one phosphorus atom and no hyperfine coupling to the equatorial nitrogens.

The X-band EPR spectra of the $i\text{-C}_3\text{H}_7\text{Co}(\text{DH})_2\text{P}(\text{Ph})_3$ and $i\text{-C}_3\text{H}_7\text{Co}(\text{DH})_2\text{P}(\text{OPh})_3$ compounds after anaerobic photolysis at room temperature are presented in Figures 2b and 3b, and identical spectra are observed for the other alkyl substituents studied. *The key result is that all irradiated alkylcobaloximes with the same phosphorus ligand originate identical EPR spectra, regardless of the cobaloxime alkyl group.*

The X-band EPR spectra show two separate g features, whereas Q-band spectra of the same solutions (Figure 4) exhibit three well-spaced g features, thus clearly implying a C_{2v} symmetry for the cobaloximes and not an effective C_{4v} symmetry as was claimed in earlier studies.²⁴ At both frequencies, the higher field region exhibits well-resolved cobalt hyperfine coupling (^{59}Co ; $I = 7/2$) and phosphorus superhyperfine coupling (^{31}P ; $I = 1/2$).

Irradiation of Alkylcobaloximes at Liquid-Nitrogen Temperature. The EPR spectra, recorded at 77 or 100 K, of the irradiated solutions at liquid-nitrogen temperature show one signal identical with that ascribed to the

(18) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: Oxford, England, 1988.

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

(20) Schrauzer, G. N.; Lee, L. P. *J. Am. Chem. Soc.* **1970**, *92*, 1551.

(21) (a) Hoffmann, R. J. *J. Chem. Phys.* **1963**, *39*, 1397. (b) Hoffmann, R. J.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 2179, 3489; **1962**, *37*, 2872.

(22) (a) Whangbo, M.-H.; Hoffmann, R. J. *J. Am. Chem. Soc.* **1978**, *100*, 6093. (b) Whangbo, M.-H.; Hoffmann, R. J.; Woodward, R. B. *Proc. R. Soc. London* **1979**, *A366*, 23.

(23) Brückner, S.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* **1974**, 1017.

(24) Rockenbauer, A.; Zahonyi, E. B.; Simandi, L. I. *J. Chem. Soc., Dalton Trans.* **1975**, 1729.

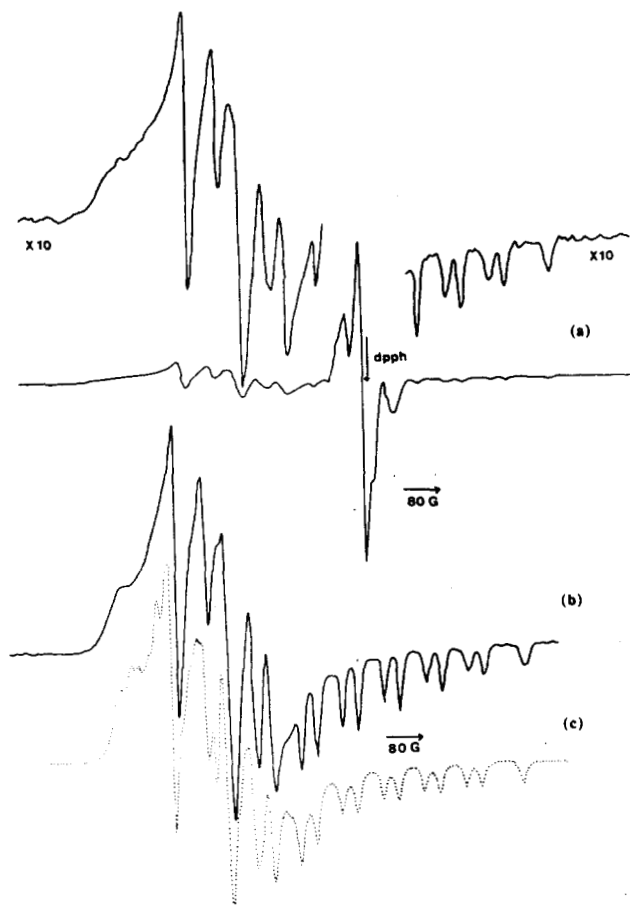


Figure 2. Frozen-matrix (100 K) X-band (8.9 GHz) EPR spectra of (a) solutions of $\text{PPh}_3\text{Co}(\text{Hdmg})_2\text{R}$ irradiated at 77 K and (b) the same solutions after being warmed to room temperature and recooled to 100 K. The simulated spectrum of (b) is presented in (c).

cobalt(II) species formed in the irradiation at room temperature and a strong and much narrower signal centered at $g \approx 2.00$ (Figures 2a and 3a).

The EPR spectra of these solutions change smoothly with an increase in the temperature of observation: the cobalt bands start to broaden and the intensity of the radical signal decreases. Near the softening point of the glass the radical signal disappears, and above this temperature the cobalt spectra converge into two broad bands for the phosphite derivatives whereas three bands are observed with phosphines. After recooling of these solutions to 100 K, their EPR spectra show the original cobalt(II) features, but no signal at $g \approx 2.00$ is observed.

Although no systematic study was undertaken to complete the identification of the band at $g \approx 2.00$, it must be attributed to an alkyl radical or to a reaction product of the "hot" alkyl radicals with solvent molecules,¹⁴ since (a) identical EPR radical signals are observed for all cobaloximes with the same alkyl group and (b) no EPR spectra were observed for the pure solvents, after irradiation under the same experimental conditions used for the cobaloxime solutions.

Thermolysis of Alkylcobaloximes. Alkylcobaloxime solutions incubated in sealed tubes in the dark at 40 °C for several hours produce EPR spectra identical with those obtained by room-temperature photolysis of the same solutions. This observation implies that the results presented for photolysis of cobaloximes at room temperature apply to the thermolysis of the same compounds and the information gathered from the analysis of the cobalt spectra is also valid for the characterization of these thermolysis

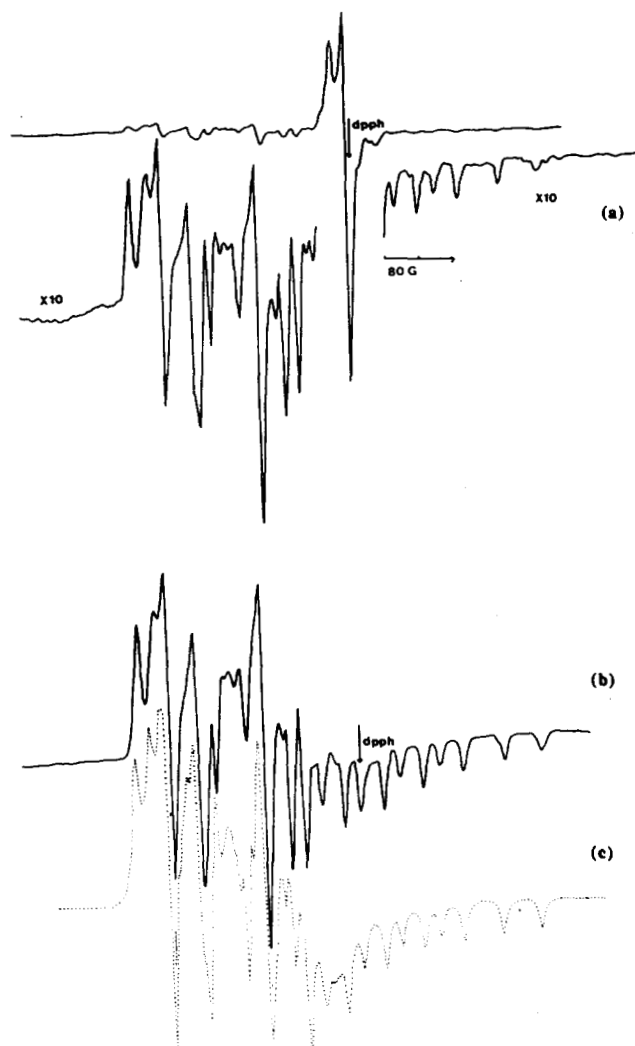


Figure 3. Frozen-matrix (100 K) X-band (8.9 GHz) EPR spectra of (a) solutions of $\text{P}(\text{OPh})_3\text{Co}(\text{Hdmg})_2\text{R}$ irradiated at 77 K and (b) the same solutions after being warmed to room temperature and recooled to 100 K. The simulated spectrum of (b) is presented in (c).

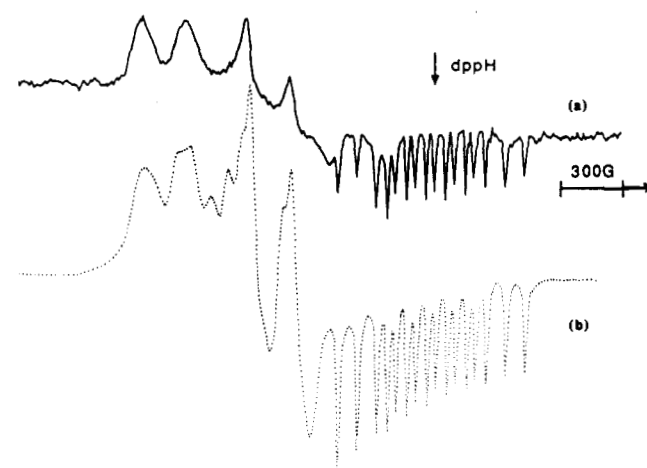


Figure 4. Frozen-matrix (100 K) Q-band (34.1 GHz) EPR spectra of a solution of $\text{P}(\text{OPh})_3\text{Co}(\text{Hdmg})_2\text{R}$ irradiated at 77 K after being warmed to room temperature and recooled to 100 K. The simulated spectrum is presented in (b).

products of the phosphorus-containing alkylcobaloximes.

Cobalt EPR Spectra. Frozen-solution Co(II) EPR spectra recorded at 77 or at 100 K after photolysis were usually well resolved although, in most cases, the three g

Table II. EPR Parameters for the Fragments $\text{LCo}(\text{Hdmg})_2$ Obtained after Photolysis of the Corresponding Alkylcobaloximes^a

ligand (L)	g_x	g_y	g_z	$-A_x(\text{Co})$	$-A_y(\text{Co})$	$A_z(\text{Co})$	$A_x(\text{P})$	$A_y(\text{P})$	$A_z(\text{P})$	$A_{\text{iso}}(\text{P})$	TCA ^b
P(Cy) ₃	2.347	2.172	2.004	10	10	75	89	100	116	102	172
PPh ₃	2.326	2.152	2.011	10	10	90	92	105	124	107	156
PBu ₃	2.268	2.191	2.017	10	10	81	105	141	155	134	136
PEt ₃	2.258	2.181	2.009	10	10	75	106	143	157	136	132
P(OPh) ₃	2.251	2.139	2.016	15	10	86	196	207	226	209	128
P(OBu) ₃	2.230	2.152	2.011	15	10	82	167	178	202	182	
P(OEt) ₃	2.233	2.153	2.016	13	10	83	170	180	203	184	107
P(OMe) ₃	2.230	2.139	2.010	15	10	84	178	188	208	192	109

^a Extracted from ref 25; the units of the hyperfine coupling tensors are 10^{-4} cm^{-1} . ^b Tolman's cone angle; see refs 36 and 37.

features could not be clearly observed at X-band frequencies. All spectra clearly showed an interaction of the unpaired electron with the cobalt atom (d^7 , $S = 1/2$) and with the axial ligands. The high-field region (g_z) exhibits cobalt hyperfine coupling and superhyperfine coupling to only *one* axially coordinated phosphorus atom (^{31}P ; $I = 1/2$), thus making it possible to obtain values of g_z and of the cobalt and phosphorus hyperfine couplings directly from the spectra. At lower fields, the X-band spectral lines also exhibit hyperfine coupling to cobalt and phosphorus atoms but it is not possible to directly get good values of the g tensor or of the hyperfine couplings (Figures 2 and 3), whereas at Q-band frequencies (Figure 4a) the middle g feature yields the g_y value and the hyperfine coupling to phosphorus and the lower field region gives the g_x value but resolved hyperfine coupling to phosphorus being only observed for the phosphite species. Analysis of the Q-band spectra revealed unambiguously a rhombic symmetry for all the compounds studied. The components of the spin Hamiltonian parameters were obtained by computer simulation of the X- and Q-band spectra (vide infra), and the results obtained confirmed that the spectra must be interpreted in terms of three g values. The spin Hamiltonian parameters were analyzed by assuming a 2A_1 ground state comprising a mixture of the d_{z^2} and $d_{x^2-y^2}$ metal orbitals of the form $\Psi = ad_{z^2} + bd_{x^2-y^2}$ (taking the point group symmetry to be C_{2v}), and the EPR parameters relevant for this work are presented in Table II. Finally, we note that the Q- and X-band Co(II) EPR spectra are identical with those of solutions of the authentic five-coordinate complexes $[\text{LCo}(\text{DH})_2]$, where L is the same phosphine or phosphite present in the irradiated cobaloxime. A full analysis of the EPR data for the latter compounds was published elsewhere.²⁵

To confirm the stability of the five-coordinated cobalt(II) complexes in solution, we have performed a titration of $[\text{Co}(\text{DH})_2]$ with triphenylphosphine. The spectra of the resulting solutions can be accounted for in terms of a mixture of $[\text{Co}(\text{DH})_2]$ and of $[\text{LCo}(\text{DH})_2]$ up to a molar ratio for triphenylphosphine/ $[\text{Co}(\text{DH})_2]$ of 1:1. For higher concentrations of triphenylphosphine (at least up to a molar ratio of 4:1), only the spectrum of $[\text{PPh}_3\text{Co}(\text{DH})_2]$ is observed.

Computer Simulation and Data Analysis. The simulations of the EPR spectra were carried out by using a program based on Pilbrow's formalism,^{15b} which uses a spin Hamiltonian of the type (1), where the hyperfine term was

$$\mathcal{H} = \mathcal{H}(\text{Zeeman}) + \mathcal{H}(\text{hyperfine}) + \mathcal{H}(\text{ligand}) \quad (1)$$

deduced by assuming C_2 point-group symmetry at the cobalt center and noncoincidence of the g and A (cobalt) tensor axis in the xy plane. Since no unpaired electron interaction with the equatorial nitrogen atoms was observed, the $\mathcal{H}(\text{ligand})$ term in the spin Hamiltonian in-

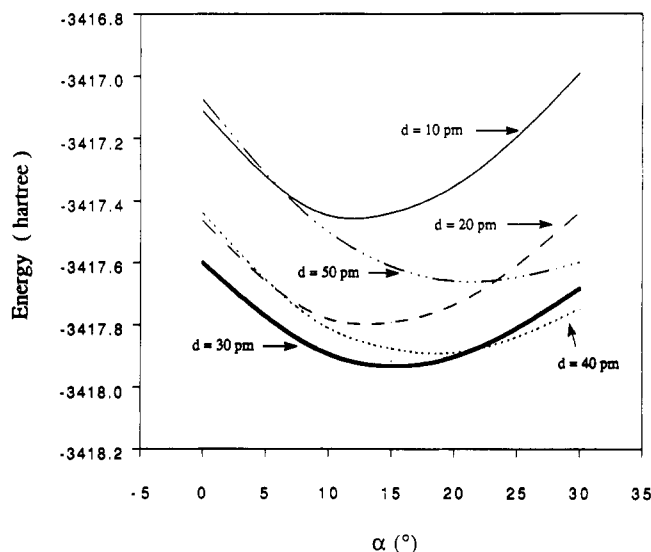


Figure 5. One-electron energy of $\text{Co}^{\text{II}}(\text{Hdmg})_2\text{PPh}_3$ as function of the parameters α and d (see text).

cludes only the phosphorus axial interaction, and it was further assumed that $A(\text{P})$ and g have the same principal axis^{15b} (which is required for C_{2v} symmetry). For the compounds studied, the best fit was observed for colinear g and $A(\text{Co})$ tensors (i.e., $\alpha = 0$). Contributions from quadrupolar interactions were found to be negligible, as different line spacings were observed at X-band frequencies but not in the Q-band spectra. The computer-simulated spectra are shown with the experimental ones.

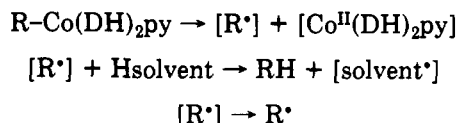
Extended Hückel Calculations. To rationalize the stability of $\text{LCo}(\text{DH})_2$ in solution when L is a phosphorus donor, extended Hückel molecular orbital calculations were performed to assess the effect of two geometric parameters on the one-electron energy of these species: (a) the angle between the two dimethylglyoxime units; (b) the distance of the cobalt atom above the coordinated plane. Under the constraints imposed by keeping fixed the geometry of the equatorial DH subunit, the cobalt-phosphorus bond length, (241.8 pm) and the phosphine geometry, the energy minimum takes place at values of $\alpha = 15^\circ$ and $d = 31$ pm (Figure 5). The energy minimum was also calculated for other values of the Co-P bond length. A reduction of the Co-P bond length (231.8 pm) increases the value of α to 16° and of d to ≈ 35 pm, at which the energy minimum occurs; the corresponding values for an increase in bond length (251.8 pm) are $\alpha = 14^\circ$ and $d = 29$ pm. These results imply a large displacement of the cobalt atom out of the plane of the four-coordinated nitrogens and a folding of the dimethylglyoxime units away from the phosphine ligand.

Discussion

Homolysis of the Cobalt-Carbon Bond. Anaerobic photolysis of alkyl(pyridine)cobaloximes and of alkyl-

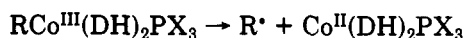
(25) de Castro, B.; Rangel, M.; Raynor, J. B. *J. Chem. Soc., Dalton Trans.* 1990, 3311.

cobalamins has been extensively studied in protic^{13b,14} and aprotic solvents.^{12a} The results obtained were interpreted by assuming that on light absorption an electron from the equatorial ligand system moves into the Co(d_{z²}) σ* orbital. The antibonding character of this orbital is then relieved by bond fission, following the proposed sequence



where the brackets represent cage trapping.^{14a}

Our results for alkylcobaloximes with symmetric phosphorus donor ligands irradiated and observed at 77 K in toluene/dichloromethane should conform to this mechanism, as the EPR spectra of the photolyzed solutions show bands that are identical with those of samples of the authentic five-coordinated Co^{II}(DH)₂PX₃ complexes and a strong and narrow signal at *g* = 2 superimposed on that of the cobalt(II) species. These results are interpreted to provide conclusive evidence that photolysis of cobaloximes with P-donor ligands cleaves homolytically the Co–C bond and produces a radical and a cobalt(II) complex.



Additional support for this mechanism can be gained by noting (a) that all irradiated alkylcobaloximes with the same ligand PX₃ originate identical Co^{II}(DH)₂PX₃ spectra, regardless of the alkyl group and of the temperature of irradiation, (b) that alkylcobaloximes with the same alkyl group yield, in toluene/dichloromethane and for the bases studied, identical signals at *g* = 2, irrespective of the P-donor ligand, and (c) that there is similarity of the radical bands of samples irradiated and observed at 77 K with those of samples irradiated at 77 K, annealed to 140 K, and observed at 100 K.

These latter observations also suggest that the fragments resulting from the homolysis of cobaloximes do not spin interact strongly (if at all) with each other, even when kept in a solid matrix, since the small matrix relaxation that accompanies this thermal cycle would allow for a separation of the fragments and a change of their intermolecular coupling that would then induce changes in the EPR spectra. Furthermore, the organic radicals formed do not react with the equatorial dimethylglyoxime, as solutions irradiated at 77 K, heated above the solution freezing point, and cooled down to 100 K produce cobalt(II) spectra identical with and with intensity similar to those observed prior to the thermal cycle.²⁶

The same mechanism for Co–C bond homolysis must be operative at room temperature, since the cobalt fragments produce the same EPR spectra when irradiated at room or at liquid-nitrogen temperature.

For the homolytic cleavage of the organocobalt bond of some alkyl(pyridine)cobaloximes induced photolytically at 113 K in chloroform solutions, a similar mechanism was proposed as frozen-solution EPR spectra of their photolysis products show bands due to an alkyl radical and to a Co(II) complex coordinated to the axial pyridine.^{12a} However, for (pyridine)cobaloximes the photolysis products depend markedly on the temperature of irradiation and on the alkyl substituent.

Methyl- and benzyl(pyridine)cobaloximes irradiated at 253 K in chloroform show EPR spectra that do not exhibit

bands typical of low-spin Co(II) species;¹² furthermore, toluene/dichloromethane solutions of the methyl derivative irradiated at 77 K yield only a narrow band that disappears on warming.²⁷ For other alkyl(pyridine)cobaloximes, samples irradiated at 77 K, warmed to room temperature, and recooled to 100 K show only bands due to a cobalt complex but with *two* coordinated pyridine molecules, the same result that is observed for room-temperature photolysis.²⁷

Contrasting with these results, photolysis of RCo(DH)₂PX₃ in toluene/dichloromethane, even for R = CH₃, yields always five-coordinated Co^{II}(DH)₂PX₃ complexes that do not react with excess base present in solution.

A rationalization for the different photochemical behavior of the pyridine- and phosphine-containing alkylcobaloximes can be provided by the strength of the Co–C bond in these compounds. Halpern and co-workers found weak Co–C bonds in complexes of the type LCo(DH)₂CHMePh₂, when L = bulky phosphine ligands, with bond dissociation energies (BDE) ranging from 17 to 24 kcal mol⁻¹.²⁸ Toscano and co-workers determined the BDE for the same alkyl(pyridine)cobaloximes by a calorimetric method and obtained values of 34.6 ± 1.4 kcal mol⁻¹ for the methyl and 31.1 ± 2.2 kcal mol⁻¹ for the benzyl derivatives, in contrast with the isopropyl analogue, which has a BDE of only 21.3 ± 2.0 kcal mol⁻¹.²⁹ No values for the Co–C bond in methyl- or in isopropyl(phosphine)cobaloximes are reported in the literature, but assuming the Co–C bond lengths to correlate with the strength of the bond,^{2b} we note that values of 199.8 and 208.5 pm are reported for L = py and R = CH₃,³⁰ and *i*-C₃H₇,³¹ respectively, whereas for L = PPh₃ the corresponding values are 202.6³² and 222 pm.³³ Thus, it can be assumed that the photochemically induced Co–C bond cleavage with visible light at temperatures below –20 °C can only take place in aprotic solvents if the BDE of the Co–C bond is smaller than ~30 kcal mol⁻¹. For the methyl- and benzyl(pyridine)cobaloximes the EPR spectra of samples irradiated at –20 °C do not reveal the presence of cobalt(II) species; instead the photolysis products must have an unpaired electron σ* to the alkyl substituent. All cobaloximes in our study must have BDE smaller than the threshold value and so always yield the cobalt(II) species and the organic radical regardless of the irradiation temperature.

Structure of Co(DH)₂PX₃. The stability of the five-coordinate cobalt(II) species when the fifth ligand is a symmetric phosphine or phosphite, even in the presence of high molar ratios of phosphorous ligand/cobalt complex, deserves further explanation, mainly since the corresponding five-coordinate cobalt(II) pyridine complexes are highly reactive at room temperature.

Marzilli and co-workers have demonstrated by crystallographic and NMR methods that bulky phosphine ligands distort the Co(DH)₂ moiety of cobaloximes toward the R group due to an increase in the steric repulsion between the equatorial moiety and the phosphines.³⁴ In methyl-

(27) Rangel, M. Ph.D. Thesis, University of Porto, Porto, Portugal, 1988.

(28) Geno, M. K.; Halpern, J. *J. Am. Chem. Soc.* **1987**, *109*, 1238.

(29) Toscano, P. J.; Seligson, A. L.; Currain, M. T.; Skrobitt, A. T.; Sonnenberger, D. C. *Inorg. Chem.* **1989**, *28*, 166; **1989**, *28*, 1610.

(30) Bigotto, A.; Zangrando, E.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* **1976**, 96.

(31) Marzilli, L. G.; Toscano, P. J.; Randaccio, L.; Bresciani-Pahor, N.; Calligaris, M. *J. Am. Chem. Soc.* **1979**, *101*, 6754.

(32) Bresciani-Pahor, N.; Calligaris, M.; Randaccio, L.; Marzilli, L. G. *Inorg. Chim. Acta* **1979**, *32*, 181.

(33) Randaccio, L.; Bresciani-Pahor, N.; Toscano, P. J.; Marzilli, L. G. *J. Am. Chem. Soc.* **1980**, *102*, 7372.

(26) The stabilities of the photolysis species obtained in our work are different from those reported in Symons's elegant study of photolysis of alkyl(pyridine)cobaloximes,^{14a} where it is claimed that upon annealing all EPR are rapidly lost.

cobaloximes the values of the angle between the two dimethylglyoxime planes are 14° for triphenylphosphine, 10° for triphenyl phosphite, and $\approx 0^\circ$ for pyridine. For alkylcobaloximes with the same R group, the position of the cobalt atom with respect to the plane of the four equatorial coordinated nitrogen atoms depends largely on the axial base; for methylcobaloximes the d values are 10 pm for triphenylphosphine, 17 pm for triphenyl phosphite, and 2 pm for pyridine.³⁵

It is conceivable that, in the five-coordinate complex $\text{Co}(\text{DH})_2\text{PX}_3$, the symmetrical phosphines and phosphites will pull the cobalt atom well above the equatorial plane and will fold the $\text{Co}(\text{DH})_2$ moiety away from the axial ligand, thus rendering the other axial position less likely to be involved in bonding. In the absence of X-ray structural data for these compounds no direct evidence to support this explanation for the stability of $\text{Co}(\text{DH})_2\text{PX}_3$ in solution is available.

EPR spectra analysis does not provide directly such information; however, some indirect evidence for the displacement of the cobalt atom from the equatorial plane can be obtained by analyzing the dependence of the values of the g -tensor components and of the unpaired spin densities with the Tolman's cone angle (TCA) and electronic parameter (χ).^{36,37} First, we note that the g_x values show a much greater variation than the other components of the g tensor and all the ensuing analysis will be centered on the dependence of the g_x values with the Tolman parameters.

For a $^2A_1(d_{z^2})$ ground state, the application of the model developed by McGarvey,³⁸ in conjunction with the approximation suggested by Raynor³⁹ that uses a single (average) value for the energy of the quartet states, furnishes the following equations for the g -tensor components:

$$g_z = 2.0023 + 2C_3^2 + 2C_1C_3 - 3C_2^2 - 3C_1^2$$

$$g_y = 2.0023 + 2C_3^2 - 3C_1C_2 - 3C_2^2 + 6C_1$$

$$g_x = 2.0023 + 2C_3^2 - 3C_1C_2 - 3C_1^2 + 6C_2$$

Here $C_1 = \xi/\Delta(^2B_1)$, $C_2 = \xi/\Delta(^2B_2)$, $C_3 = \xi/\Delta(^4B_2)$, and $\Delta(^4\Gamma_1)$ is the energy difference between the state $^4\Gamma_1$ and the ground state (2A_1) and ξ is the one-electron spin-orbit coupling constant. Neglecting second-order terms, g_x is then given by

$$g_x \approx 2.0023 + 6C_2$$

and $\Delta(^2B_2)$ can be taken to be an approximation of the energy difference between d_{z^2} and d_{yz} . An increase in g_x ⁴⁰

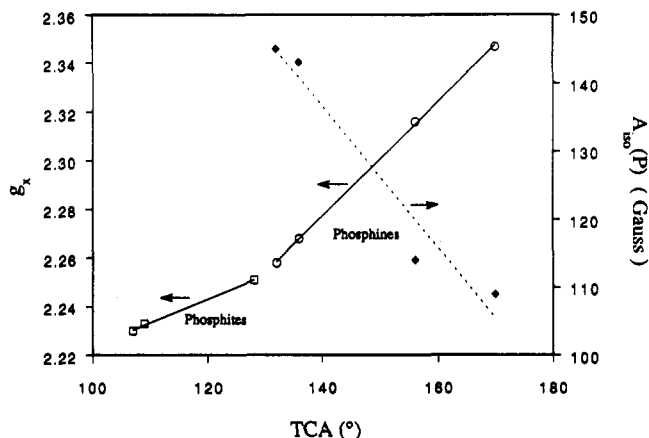


Figure 6. Values of (a) g_x of $\text{PR}_3\text{Co}^{\text{II}}(\text{DH})_2$ and of $\text{P}(\text{OR})_3\text{Co}^{\text{II}}(\text{DH})_2$ and (b) $A_{\text{iso}}(\text{P})$ of $\text{PR}_3\text{Co}^{\text{II}}(\text{DH})_2$ versus Tolman's cone angle.

would then be ascribed to an increase in C_2 and a decrease in this energy difference.

A plot of g_x against the Tolman χ parameter and the Tolman cone angle (TCA) (Figure 6) for the phosphorus ligands studied shows no correlation with χ , whereas two good linear relations with TCA are observed, one for the phosphines and the other for the phosphites. This implies that steric effects will be dominant in bonding of these ligands to the $\text{Co}(\text{DH})_2$ moiety. As the range of g_x values is larger for phosphines (0.089) than for phosphites (0.021), the dependence for these latter ligands will not be pursued further, since the g values reported may be in error by as much as 0.005.

Phosphines with large TCA values show large g_x values and consequently must have smaller energy differences between d_{z^2} and d_{yz} . This result can be interpreted as to imply a longer P-Co bond length for the bulkier ligands, as an increase in axial bond length must imply a decrease of the energy of the antibonding d_{z^2} orbital.⁴¹ Additional support for this interpretation can be provided by noting that the values of $A_{\text{iso}}(\text{P})$ also correlate with TCA values, being larger for the smaller phosphines (Figure 6). As $A_{\text{iso}}(\text{P})$ diminishes, so does the unpaired spin density on the phosphorus s orbital. As the unpaired electron interacts directly with the phosphorus atom, this also suggests larger Co-P bond length for the bulkier phosphines.⁴² This lengthening of the Co-P bond with the bulkiness of the phosphines is also observed in cobaloximes^{2b} and follows the order $\text{PcHx}_3 > \text{PPh}_3 > \text{PBU}_3$. For chlorocobaloximes the corresponding bond lengths are 236.9, 232.7, and 227.1 pm, and for the methyl cobaloximes they are 246.3, 241.8, and 229.5 pm.^{2b}

We also note that the unpaired spin density on the cobalt atom and on the axial ligand does not add up to 100%. The remaining spin density is usually assumed to lie on the equatorial ligand, since it not much spin density straying is expected beyond the phosphorus atom.³⁹ As no superhyperfine structure coupling due to the equatorial

(34) (a) Randaccio, L.; Bresciani-Pahor, N.; Orbell, J. D.; Calligaris, M.; Summers, M. F.; Snyder, B.; Toscano, P. J.; Marzilli, L. G. *Organometallics* 1985, 4, 469. (b) Bresciani-Pahor, N.; Randaccio, L.; Toscano, P. J.; Sandercock, A. C.; Marzilli, L. G. *J. Chem. Soc., Dalton Trans.* 1982, 129.

(35) It is noteworthy to point out that cobaloximes with di- and tri-substituted phosphines and phosphites have a much smaller effect in the displacement of the cobalt out of the plane of the four nitrogens (<9 pm),^{3b} and accordingly, we were not able to prepare five-coordinate complexes with these phosphorus ligands.^{2b}

(36) Values are taken from or calculated with the data from: Tolman, C. A. *Chem. Rev.* 1977, 77, 313.

(37) A value of 156° was used for the TCA of PPh_3 , as reported by: Bresciani-Pahor, N.; Randaccio, L.; Toscano, P. J. *J. Chem. Soc., Dalton Trans.* 1982, 1559.

(38) McGarvey, B. R. *Can. J. Chem.* 1975, 53, 2498.

(39) (a) Labauze, G.; Raynor, J. B. *J. Chem. Soc., Dalton Trans.* 1980, 2388. (b) Labauze, G.; Raynor, J. B. *J. Chem. Soc., Dalton Trans.* 1981, 590.

(40) In the absence of EPR crystal data, the assignment of labels to the g -tensor components follows the standard convention for low-spin Co(II) complexes.^{3b} As the z axis is defined along the Co-P bond, there is good reason to believe g_z is the lowest g value. Although, the choice of the x and y labels is arbitrary, the conclusions of the ensuing analysis are valid even if the labels are incorrectly assigned, since the labels (xy) and (xz) for the states would then be exchanged.

(41) No similar correlation was observed for g_y , as should be expected from increased d_{z^2} stabilization with increase bulk of the phosphines. However, it must be pointed out that the d_{yz} and d_{zx} energies may also be slightly affected by deformations on the equatorial ligands, and coupling of this observation with the smaller observed changes in the g_y values and with the larger errors associated with their determination can provide an explanation for the lack of g_y correlation with TCA.

(42) It is interesting to note that, for the phosphites, the values of $A_{\text{iso}}(\text{P})$ correlate with the Tolman electronic parameter, being larger for the more electron-withdrawing phosphites, in accordance with the suggestion that electronic factors are important in phosphites.⁴³

(43) Kargol, J. A.; Crecey, R. W.; Burmeister, J. L.; Toscano, P. J.; Marzilli, L. G. *Inorg. Chim. Acta* 1980, 40, 79.

nitrogen atoms is observed, very little spin delocalization through σ bonding from the x and y components of the d_{z^2} orbital must take place. Delocalization of spin density into the equatorial ligand must occur by π bonding, and this is only possible if the cobalt and the equatorial ligating atoms are not coplanar.³⁹ Similar observations have been reported for similar square-pyramidal cobalt(II) complexes with the axial ligand coordinated by a nitrogen atom, where deviations of the cobalt atom from the equatorial plane and toward the axial ligating atom take place for the stronger and shorter axial bonds. In our case, it is possible to occur simultaneously a displacement of the cobalt atom from the equatorial plane and also a folding of the two DH units away from the axial ligand. It is difficult to separate these two effects, but nevertheless it appears that the cobalt atom is not in the plane of the equatorial coordinating atoms.

The EHMO calculations provide further support for this assumption, since the energy minimum for the $\text{Co}(\text{DH})_2\text{PPh}_3$ fragment is obtained with values of $\alpha \approx 15^\circ$ and $d \approx 30$ pm (Figure 4). Notwithstanding the crudity of the model, the calculated angular distortion is similar to the value observed for alkyl(phosphine)cobaloximes. The larger value of d is to be expected for five-coordinate species, as compared with the values of the alkylcobaloximes, but resembles the value reported for $\text{Co}(\text{salen})\text{py}$.⁴⁴

Despite the limitations of the previous analysis, the combination of our EPR data with the EHMO calculations, the crystallographic^{2b} and NMR^{34a,45} data for alkylcobaloximes with P-donor ligands, and the observed lack of further coordination for $\text{Co}(\text{DH})_2\text{PX}_3$ complexes present a strong case to postulate a square-pyramid structure for $\text{Co}(\text{DH})_2\text{PX}_3$ with a large displacement of the cobalt atom from the equatorial coordination plane in the direction of the axial ligating atom and a folding of the $\text{Co}(\text{DH})_2$ moiety away from the P-donor ligands.

Implications for Co–C Bond Cleavage. Kräutler et al.⁷ observed that "the structure of the cobalt(II) corrin" in the X-ray structure determination they have performed of cob(II)alamin "is strikingly similar to that of the corrin moiety of coenzyme B_{12} " and thus it seems that the 5'-

deoxyadenosyl ligand does not influence corrin ring pucker significantly. The same authors have proposed that the Co–C bond must be labilized largely by apoenzyme-induced separation of the homolysis fragments. Similarly, the recent proposal of Marzilli et al.⁶ that the transition state resembles the $\text{Co}^{\text{II}}\text{B}_{12}/\text{Ado}^\bullet$ intermediate state points toward the importance of stabilizing the Co(II) state in accelerating Co–C bond homolysis.

Our results provide evidence that supports the viability of promoting Co–C bond cleavage in cobaloximes by increased steric repulsion between the equatorial moiety and the alkyl ligand and also demonstrates that the reactivity of the homolysis fragments depend largely on their structure. A displacement of the cobalt atom away from the equatorial plane stabilizes the homolysis fragments and hinders coordination in the sixth position. It is feasible that the downward movement of the cobalt atom (12 pm) from the plane of the coordinated corrin nitrogens and toward the axial base, observed in the structure of cob(II)alamin,⁷ may play an important role in stabilizing the Co(II) state as has been claimed⁶ and also that this displacement of the cobalt atom would make it less reactive toward the Ado^\bullet radical or other species formed during the enzymatic process. A role for the benzimidazole nucleotide would then be to pull the cobalt atom away from the equatorial ligand, since in the crystal structure of a cob(II) corrin lacking the benzimidazole group the displacement of the cobalt atom is only 4.8 pm. The ease of transformation of base-on/base-off forms of cob(II)-alamin can be thought to be related with the release of the cobalt atom back to the equatorial plane to trap the Ado^\bullet radical when the enzymatic cycle is terminated.

Acknowledgment. We are indebted to Dr. M. J. Calhorda (Centro de Tecnologia Química e Bioquímica, Lisboa) for her help with the EHMO calculations and to Dr. J. B. Raynor for helpful discussions and for allowing us to use the Q-band EPR facilities at the University of Leicester. This work was supported by Instituto Nacional de Investigação Científica (Lisboa) Contract No. 89/EXA/3. J.P. thanks the Junta Nacional de Investigação Científica (Lisboa) for a fellowship.

Supplementary Material Available: Text describing computer spectral simulation procedures and the McGarvey formalism (6 pages). Ordering information is given on any current masthead page.

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

(45) Bresciani-Pahor, N.; Randaccio, L.; Zangrando, E.; Summers, M. F.; Ramsden, J. H.; Marzilli, P. A.; Marzilli, L. G. *Organometallics* 1985, 4, 2086.