the nonrigid nature of $Ru(R_2dtc)_3Cl$.[5]

The reaction chemistry of the $Ru(R_2dtc)_3I \cdot I_2$ complexes is essentially identical with that of $Ru(Et_2dtc)_3Cl$[5] and will not be discussed in detail here. Several important reactions are the formation of $[Ru_2(R_2dtc)_5]BF_4$[30] upon addition of $AgBF_4$ and the formation of $Ru(R_2dtc)_3$ upon addition of NaR_2dtc both in acetone solution. These reactions illustrate the labile nature of the Ru–I bond.

The addition of I_2 to $Fe(Me_2dtc)_3$ in CH_2Cl_2 solution yielded a black crystalline compound which was identified to be $Fe(Me_2dtc)_2I$.[31] The analogous compound (R = Et) has been prepared by reaction of $Fe(Et_2dtc)_3$ with aqueous HI.[8] These novel square-pyramidal, paramagnetic ($S = {}^3/_2$) complexes do not have analogues with ruthenium, presumably because of the greater tendency of ruthenium toward diamagnetism.

Acknowledgment. This research was supported by Grant CHE-19560 from the National Science Foundation. The help of Professor D. Britton on the x-ray determination is also gratefully acknowledged.

Registry No. $Ru(Me_2dtc)_3I_3$, 60949-75-9; $Ru(Et_2dtc)_3I_3$, 60949-76-0; $Ru((Me)(Ph)dtc)_3I_3$, 60949-77-1; $Ru(Bzl_2dtc)_3I_3$, 60949-78-2; $Fe(Me_2dtc)_2I$, 23672-38-0; $Ru(Me_2dtc)_3$, 31656-15-2.

Supplementary Material Available: Table SI, physical and spectroscopic data for $Ru(R_2dtc)_3I \cdot I_2$ complexes, and Table SII, observed and calculated structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

References and Notes

(1) H. C. Brinkhoff, J. A. Cras, J. J. Steggerda, and J. Willemse, *Recl. Trav. Chim. Pays-Bas*, **88**, 633 (1969).

(2) H. C. Brinkhoff, *Recl. Trav. Chim. Pays-Bas*, **90**, 377 (1971).

(3) J. Willemse, Ph.D. Thesis, Nijmegen, 1974, p 51; J. Willemse, J. A. Cras, J. G. Wijnhoven, and P. T. Beurskens, *Recl. Trav. Chim. Pays-Bas*, **92**, 1199 (1973).

(4) J. G. Wijnhoven, Th. E. M. van den Hark, and P. T. Beurskens, *J. Cryst. Mol. Struct.*, **2**, 189 (1972).

(5) K. W. Given, B. M. Mattson, and L. H. Pignolet, *Inorg. Chem.*, **15**, 3152 (1976).

(6) B. F. G. Johnson, K. H. Al-Obaidi, and J. A. McCleverty, *J. Chem. Soc. A*, 1668 (1969); T. F. Brennan and I. Bernal, *Inorg. Chim. Acta*, **7**, 283 (1973).

(7) S. R. Fletcher and A. C. Skapski, *J. Chem. Soc., Dalton Trans.*, 486 (1974).

(8) R. L. Martin and A. H. White, *Inorg. Chem.*, **6**, 712 (1967).

(9) D. J. Duffy and L. H. Pignolet, *Inorg. Chem.*, **13**, 2045 (1974).

(10) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(11) Three local programs by Dr. L. W. Finger were used to solve and refine the structure: UMPREL for statistics and Patterson map, UMLSTSQ for full-matrix least-squares refinement, and BADTEA for bond distances, angles, and errors. All data processing was done with the Control Data 6600 computer at the University of Minnesota Computer Center.

(12) $R = \sum||F_o| - |F_c||/\sum|F_o|$, $r = \sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o|^4$; the numerator of r was the function minimized; the weights were $1/(\sigma(F^2))^2$ where $\sigma(F_o^2) = \sigma(I)/Lp$. Atomic scattering factors were taken from "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1962, Table 3.3.1A (S, C, N, I) and Table 3.3.1B (Ru). Anomalous dispersion corrections from the same source (Table 3.3.2C) were used for Ru, I, and S.

(13) R_4tds ($R_2NC(S)SSC(S)NR_2$) is the two-electron oxidation product obtained upon reacting R_2dtc^- with I_2.

(14) The reaction of Cl_2 with $Ru(R_2dtc)_3$ in benzene yields $RuCl_3$ and R_4tds rather than $Ru(R_2dtc)_3Cl$.

(15) Even though the data suggested that $Ru(Me_2dtc)_3I_3$ and $Ru(Et_2dtc)_3Cl$ are structurally similar, an x-ray investigation of the former was carried out due to the different preparative procedures employed[5] and in order to elucidate the nature of the three iodine atoms. In addition, the structural determination of $Ru(Me_2dtc)_3I_3$ was begun before the structure of $Ru(Et_2dtc)_3Cl$ was solved.

(16) A. I. Kitaigorodskii, T. L. Khotsyanova, and Y. T. Struchkov. *Zh. Fiz. Khim.*, **27**, 780 (1953).

(17) H. A. Tasman and K. H. Boswijk, *Acta Crystallogr.*, **8**, 59 (1955).

(18) E. E. Havinga, K. H. Boswijk, and E. H. Wiebenga, *Acta Crystallogr.*, **7** 487 (1954).

(19) H. A. Bent, *Chem. Rev.*, **68**, 587 (1968).

(20) J. Dirand, L. Ricard, and R. Weiss, *Transition Met. Chem.*, **1**, 2 (1975–1976).

(21) D. F. Lewis and R. C. Fay, *J. Am. Chem. Soc.*, **96**, 3843 (1974).

(22) T. J. Pinnavaia and R. C. Fay, *Inorg. Chem.*, **7**, 502 (1968).

(23) J. J. Park, D. M. Collins, and J. L. Hoard, *J. Am. Chem. Soc.*, **92**, 3636 (1970).

(24) M. Elder, *Inorg. Chem.*, **8**, 2103 (1969).

(25) Other PBP examples containing ligands other than R_2dtc^- include $Zr(acac)_3X$, (X = Cl, Br, I; acac = acetylacetonato),[22] $Sn(trop)_3X$, (X = Cl, OH; trop = tropolonato),[23] and $Zr(hfac)_3Cp$, (hfac = hexafluoroacetylacetonato; Cp = η^5-cyclopentadienyl).[24]

(26) L. H. Pignolet, *Inorg. Chem.*, **13**, 2051 (1974).

(27) Y. S. Sohn, A. W. Schlueter, D. N. Hendrickson, and H. B. Gray, *Inorg. Chem.*, **13**, 301 (1974).

(28) L. Pauling, "The Nature of the Chemical Bond", 3d ed, Cornell University Press, Ithaca, N.Y., 1960, p 260.

(29) E. A. Pasek and D. K. Straub, *Inorg. Chem.*, **11**, 259 (1972).

(30) B. M. Mattson, J. R. Heiman, and L. H. Pignolet, *Inorg. Chem.*, **15**, 564 (1976).

(31) $Fe(Me_2dtc)_2I$ was identified by elemental analysis; its electronic absorption spectrum and solid magnetic moment (Experimental Section) were almost identical with published values for $Fe(Et_2dtc)_2I$.[8]

Contribution from the Department of Chemistry,
University of Pittsburgh, Pittsburgh, Pennsylvania 15260

Hemochromes with Phosphorus Ligands[1]

William M. Connor and Darel K. Straub*

Received September 20, 1976 AIC60698Z

Hemes (porphinatoiron(II) complexes) readily add two axial ligands to form 6-coordinated hemochromes. Interest in the nonprotein hemochromes arises because they provide simple models of known structure for several iron(II) hemoproteins. Hemochromes with various amines, and with carbon monoxide, have been investigated extensively by electronic[2] and Mössbauer[3-5] spectroscopy. Mössbauer spectroscopy has proven particularly valuable in work with hemochromes, as well as with other classes of iron porphines, since each class has a characteristic isomer shift and quadrupole splitting range.

In order to determine more precisely the effect of π-bonding axial ligands on the isomer shift and quadrupole splitting of hemochromes, several new hemochromes with phosphine and phosphite ligands of varying π-bonding capabilities (chosen to provide π-acceptor strengths between the non-π-bonding cyclic amines such as piperidine and the strongly π-bonding carbon monoxide) have been prepared and characterized by Mössbauer spectroscopy.

Experimental Section

Tri-*n*-butylphosphine was obtained from MC/B Chemicals. All other phosphorus ligands used in this study were gifts from Arapahoe Chemical Co., Boulder, Colo. Bis(piperidine)tetrakis(*p*-methoxyphenyl)porphinatoiron(II) [PMXPPFe·2pip], bis(pyrrolidine)tetrakis(*p*-methoxyphenyl)porphinatoiron(II) [PMXPPFe·2pyrr], and bis(tetrahydropyridine)tetrakis(*p*-chlorophenyl)porphinatoiron(II) [PClPPFe·2thp], were prepared by reaction of the hemin chloride with the neat hot amine.[3]

Bis(triethyl phosphite)tetrakis(*p*-methoxyphenyl)porphinatoiron(II) [PMXPPFe·2(EtO)$_3$P]. Approximately 0.7 g of the piperidine hemochrome, [PMXPPFe·2pip], was dissolved in 60 ml of triethyl phosphite and held at 100 °C for 10–15 min. The solution was cooled to room temperature and filtered. The filtrate was reduced to a volume of 15–20 ml by vacuum distillation at a maximum temperature of 100 °C. The solution in the distillation flask was cooled to room temperature and the crystalline product which formed was collected on a glass frit. The compound was recrystallized from triethyl phosphite, washed well with pentane, and then dried under vacuum at room temperature for 24 h. Anal. Calcd for $C_{60}H_{66}N_4O_{10}P_2Fe$: C, 64.29; H, 5.93; N, 5.00; P, 5.53. Found: C, 64.02; H, 5.90; N, 5.55; P, 5.48.

Bis(tri-*n*-butylphosphine)tetrakis(*p*-methoxyphenyl)porphinatoiron(II) [PMXPPFe·2(*n*-Bu)$_3$P]. The same procedure was used to prepare this complex as described for the triethyl phosphite hemochrome. A maximum temperature of 130 °C was attained during the vacuum distillation. Anal. Calcd for $C_{72}H_{90}N_4O_4P_2Fe$: N, 4.70; P, 5.19. Found: N, 4.75; P, 5.25.

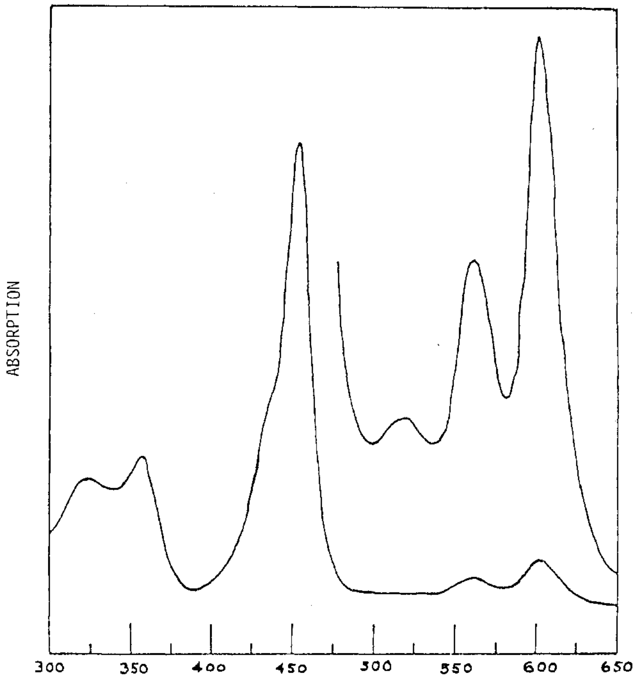

Figure 1. Visible spectrum of PMXPPFe·2(n-Bu)$_3$P in (n-Bu)$_3$P.

The following were prepared by the same procedure.

Bis(di-n-butoxyphenylphosphine)tetrakis(p-methoxyphenyl)porphinatoiron(II) [PMXPPFe·2(n-BuO)$_2$PhP]. Anal. Calcd for $C_{76}H_{82}N_4O_8P_2Fe$: N, 4.32; P, 4.78. Found: N, 4.31; P, 4.79.

Bis(methoxydiphenylphosphine)tetrakis(p-methoxyphenyl)porphinatoiron(II) [PMXPPFe·2MeOPh$_2$P]. Anal. Calcd for $C_{74}H_{62}N_4O_6P_2Fe$: N, 4.01; P, 6.23. Found: N, 3.99; P, 6.18.

Bis(n-butoxydiphenylphosphine)tetrakis(p-methoxyphenyl)porphinatoiron(II) [PMXPPFe·2n-BuOPh$_2$P]. Anal. Calcd for PMXPPFe·2n-BuOPh$_2$P, $C_{80}H_{74}N_4O_6P_2Fe$: N, 4.30; P, 4.74. Calcd for [PMXPPFe·2n-BuOPh$_2$P]·n-BuOPh$_2$P, $C_{96}H_{93}N_4O_7P_3Fe$: N, 3.59; P, 5.94. Found: N, 3.06; P, 5.52.

The latter two complexes were extremely soluble in the phosphine solvent and were precipitated from solution by pentane.

Bis(trimethylolpropanephosphine ester)tetrakis(p-methoxyphenyl)porphinatoiron(II) [PMXPPFe·2TMPPE]. This compound was prepared by heating the bis(pyrrolidine) hemochrome, PMXPPFe·2pyrr, with excess trimethylolpropanephosphine ester to 100 °C in a test tube under vacuum for 40 min. The reaction mixture, after cooling to room temperature, was extracted with pentane to remove excess trimethylolpropanephosphine ester. Anal. Calcd for $C_{60}H_{58}N_4O_{10}P_2Fe$: N, 5.04; P, 5.57. Found: N, 5.55; P, 5.26.

Bis(trimethylolpropanephosphine ester)tetrakis(p-chlorophenyl)porphinatoiron(II) [PClPPFe·2TMPPE]. This compound was prepared from [PClPPFe·2Thp] using the method described for PMXPPFe·2TMPPE. It was not analyzed.

Elemental analyses were performed by Chemalytics, Tempe, Ariz. Infrared spectra were recorded on a Beckman IR-8 spectrophotometer, and visible spectra, on a Cary 14 spectrophotometer. Nuclear magnetic resonance spectra were obtained on a Varian A-60 instrument. Mössbauer spectra were measured on a scanned-velocity spectrometer operating in the time mode and calibrated with both sodium nitroprusside and ^{57}Fe foil. Spectra were fitted with a least-squares approximation assuming two Lorentzian line shapes of equal width. Estimated error limits on the isomer shift, δ, and quadrupole splitting, Δ, are ±0.03 mm/s. A Calcomp plotter was used to plot data.

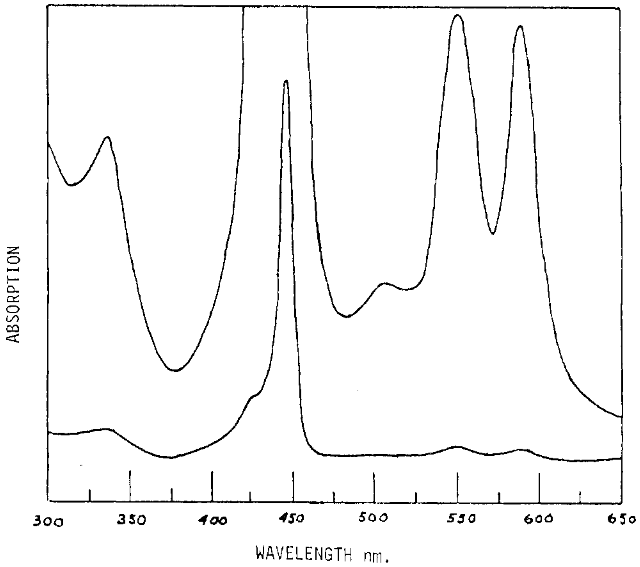

Figure 2. Visible spectrum of PMXPPFe·2(EtO)$_3$P in (EtO)$_3$P.

Table I. Electronic Spectral Data for Bis(phosphine and phosphite) Hemochromes (Range 1000–300 nm)

Compd	Solvent	λ_{max}[a] and rel intens[b]
PMXPPFe·2(n-Bu)$_3$P	(n-Bu)$_3$P	322 (0.28), 356 (0.33), 432 (0.38),[c] 455 (1.0), 519 (0.02), 563 (0.05), 603 (0.09), 821 (0.006), 927 (0.004)[c]
PMXPPFe·2(EtO)$_3$P	(EtO)$_3$P	335 (0.11), 423 (0.17),[c] 455 (1.0), 510 (0.03),[c] 551 (0.05), 589 (0.04), 814 (0.006)[c]

[a] Wavelength at maximum absorption in nm. [b] The intensity of absorption relative to the intensity of the Soret band is shown in parentheses. [c] Band is not resolved and appears as a shoulder or inflection.

Table II. Mössbauer Data for Bis(phosphine and phosphite) Hemochromes

Compd	Temp, K	δ[a]	Δ[b]	Γ[c]	N[d]
PClPPFe·2TMPPE	298	+0.52	0.46	0.32	1.45
PMXPPFe·2TMPPE	298	+0.49	0.47	0.29	2.97
PMXPPFe·2(n-BuO)$_2$PhP	298	+0.51	0.59	0.26	3.07
PMXPPFe·2(EtO)$_3$P	298	+0.54	0.69	0.27	2.83
PMXPPFe·2(n-Bu)$_3$P	298	+0.55	0.82	0.25	1.64
	4.2	+0.67	+0.75	0.23	0.80
PMXPPFe·2n-BuOPh$_2$P	298	+0.55	0.83	0.26	1.71
PMXPPFe·2MeOPh$_2$P	298	+0.58	1.06	0.28	2.29

[a] Isomer shift relative to sodium nitroprusside; ±0.03 mm/s. [b] Quadrupole splitting; ±0.03 mm/s. Sign determined only for the (n-Bu)$_3$P hemochrome. [c] Line width at half-maximum, mm/s. [d] Number of γ-ray counts under nonresonant conditions $\times 10^6$.

Results

Magnetism. The solution magnetic moment of PMXPPFe·2(n-Bu)$_3$P was measured in (n-Bu)$_3$P at 308 K by the Evans[6] method using the sodium salt of 3-trimethylsilylpropanesulfonic acid as a reference. The uncorrected molar susceptibility was found to be 1150 × 10^{-6} cgsu. When a −995 × 10^{-6} cgsu correction for the diamagnetic susceptibility was applied, the magnetic moment was calculated as 0.6 μ_B. It is difficult to assign error limits to this measurement, but they are probably within ~0.2 μ_B.

Electronic Spectra. These hemochromes in solution were sensitive to air oxidation, readily forming the μ-oxo complex. The compounds were more stable, however, in solutions of their corresponding phosphine or phosphite. Figures 1 and 2 show the spectra in the visible region of two of these compounds, and the data are summarized in Table I. The spectra are characterized by several sharp and relatively narrow bands, with the (n-Bu)$_3$P complex having two more absorptions than the (EtO)$_3$P complex. The Soret bands in both cases came at unusually low energies, 455–455 nm.

Mössbauer Spectra. Mössbauer parameters for the seven phosphorus hemochromes are given in Table II; a representative spectrum is shown in Figure 3. All spectra were nearly symmetrical quadrupole-split doublets with sharp, narrow lines. The (n-Bu)$_3$P hemochrome at 4.2 K showed the

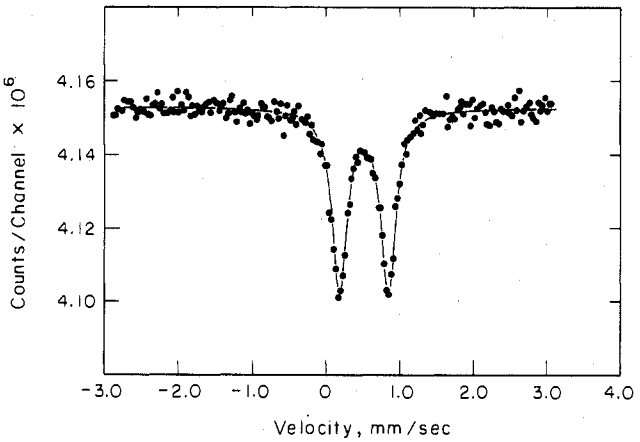

Figure 3. Mössbauer spectrum of PMXPPFe·2$(\text{EtO})_3$P at 298 K.

expected increase in isomer shift (from the 298 K value) and a slight decrease in quadrupole splitting.

Discussion

Hemochromes of six phosphorus ligands, from the pure trialkylphosphine (i.e., $(n\text{-Bu})_3$P) to the pure phosphite (TMPPE, $(\text{EtO})_3$P) type were prepared. These ligands were selected to cover a range of π-bonding possibilities. The bis(tri-*n*-butylphosphine) complex, which gave large, well-formed crystals, was studied in most detail.

The slight paramagnetism of the $(n\text{-Bu})_3$P hemochrome was surprising since all reported hemochromes are diamagnetic.[3] It is conceivable that it could be due to some iron(III) impurity, such as the binuclear μ-oxo derivative $(\text{PMXPPFe})_2\text{O}$ which probably has a magnetic moment of ~1.7 μ_B at room temperature,[7] but visible, infrared, and Mössbauer measurements failed to show any such contamination. No EPR signals were found at 298 K. However, a very recent paper reports some paramagnetism in a bis(piperidine) hemochrome.[8]

Some attention was paid to establishing the exact identity of PMXPPFe·2$(n\text{-Bu})_3$P by infrared spectroscopy. Tri-*n*-butylphosphine oxidizes readily, and as no special precautions were taken to exclude oxygen during the preparation of the hemochrome, it is conceivable that the final product might contain some $(n\text{-Bu})_3$PO. Analytical results cannot distinguish between PMXPPFe·2$(n\text{-Bu})_3$P (N, 4.70; P, 5.19) and PMXPPFe·2$(n\text{-Bu})_3$PO (N, 4.57; P, 5.06). The infrared spectra of $(n\text{-Bu})_3$PO and several of its metal complexes have been reported.[9] The PO stretch occurred as a strong band at 1157 cm^{-1} in the free oxide and decreased by 25–50 cm^{-1} upon forming a metal complex. A careful inspection of the 1100–1160-cm^{-1} region in the infrared spectrum of PMXPPFe·2$(n\text{-Bu})_3$P and comparison with spectra of $(n\text{-Bu})_3$P and PMXPPFeCl showed no PO peaks in the hemochrome spectrum.

Electronic spectra of PMXPPFe·2$(n\text{-Bu})_3$P in $(n\text{-Bu})_3$P and PMXPPFe·2$(\text{EtO})_3$P in $(\text{EtO})_3$P were very similar to one another but were rather different from the spectra of the bis(amine) hemochromes.[2] The Soret band in both was at an unusually low energy (for the bis(amines) the Soret band is at 420 nm) and in this respect resembled the 446-nm band of cytochrome P-450_cam carbonyl[10] and the 443-nm band of chloroperoxidase carbonyl.[11]

The isomer shifts at 298 K averaged +0.52 ± 0.03 mm/s (Table II), omitting the MeOPh_2P derivative, which gave somewhat discordant δ and Δ values. These shifts lay between the shifts for the bis(amine)[3] (+0.67 ± 0.03 mm/s) and the carbonylamine[5] (+0.46 ± 0.03 mm/s) hemochromes. The iron d-electron density in these phosphorus hemochromes is less than in the bis(amine) but greater than in the carbonylamine hemochromes.

Quadrupole splittings in these complexes are expected to increase with (1) a decrease in σ basicity, (2) a decrease in π acidity, and (3) an increase in steric requirements of the axial phosphorus ligands. Relative orderings of the six ligands given in Table II with respect to these three characteristics are as follows: (1) σ basicity,[12,13] $(n\text{-Bu})_3\text{P} \gg \text{MeOPh}_2\text{P} \sim n\text{-BuOPh}_2\text{P} > (n\text{-BuO})_2\text{PHP} > (\text{EtO})_3\text{P} \sim$ TMPPE; (2) π acidity,[14] $\text{TMPPE} \gg (\text{EtO})_3\text{P} > (n\text{-BuO})_2\text{PhP} > \text{MeOPh}_2\text{P} \sim n\text{-BuOPh}_2\text{P} \gg (n\text{-Bu})_3\text{P}$; (3) size,[15] $\text{TMPPE} < (\text{EtO})_3\text{P} < (n\text{-BuO})_2\text{PhP} < (n\text{-Bu})_3\text{P} < \text{MeOPh}_2\text{P} \sim n\text{-BuOPh}_2\text{P}$. The only ambiguity in these orders concerns the π acidity of $(n\text{-BuO})_2$PhP vs. that of $(\text{EtO})_3$P; Gray et al.[12] have suggested that $(\text{RO})_2$PhP is a better π acceptor than $(\text{RO})_3$P, R = alkyl.

The measured splittings (Table II) cover a rather wide range of more than 0.5 mm/s and increase in the order $\text{TMPPE} < (n\text{-BuO})_2\text{PhP} < (\text{EtO})_3\text{P} < (n\text{-Bu})_3\text{P} \sim n\text{-BuOPh}_2\text{P} < \text{MeOPh}_2\text{P}$. Clearly, none of the three factors listed above, taken alone, can account for such an order. One possible rationalization for this order involves both π acidity and steric factors. In *trans*-(4-pyridyl)(tri-*n*-butylphosphine)bis(dimethylglyoximato)cobalt(I),[16] the only complex structurally similar to these phosphorus hemochromes for which a crystal structure is available, there are some steric repulsions between the butyl groups and the atoms in the equatorial dimethylglyoximate plane, but these are not great enough to affect the normal length of 2.34 Å found for the Co–P bond. If these data can be extrapolated to PMXPPFe·2$(n\text{-Bu})_3$P, it would seem that $(n\text{-Bu})_3$P represents about the limiting ligand size for a normal Fe–P bond length. Thus, the larger RO(Ph)_2P ligands form weaker bonds to iron in the hemochromes than their π acidity would suggest. The large difference in Δ values between n-BuOPh_2P and MeOPh_2P is difficult to rationalize.

The $(n\text{-Bu})_3$P hemochrome showed a slight dependence of Δ on temperature, decreasing by 0.07 mm/s upon going from 298 to 4.2 K. Bis(pyridine)deuterioheme shows a similar decrease, from Δ = 1.18 mm/s at 298 K to 1.08 mm/s at 4 K.[4] Eicher and Trautwein[17] attributed the large Δ value to some mixing into a $^1\text{A}_1$ ground state of low-lying excited ^3E and perhaps $^5\text{B}_2$ states. On the other hand, bis(pyridine) meso heme has Δ = 0.64 mm/s at 4.6 and 77 K;[4] the ^3E state must be much higher lying in this case. If this argument is correct, the $(n\text{-Bu})_3$P hemochrome occupies an intermediate position, with a ^3E state ~750 cm^{-1} about the ground $^1\text{A}_1$ state.

A Mössbauer spectrum of PMXPPFe·2$(n\text{-Bu})_3$P, measured at 4.2 K in the presence of a longitudinally applied magnetic field of 50 kOe, showed V_{zz} to be positive.

Acknowledgment. This research was supported in part by Grant No. AM16996 BBCB, National Institutes of Health. We wish to thank Professor William Oosterhuis and Dr. Kevork Spartalian for the Mössbauer data at 4.2 K, measured at Carnegie-Mellon University, and Arapahoe Chemical Co., Boulder, Colo., for generous gifts of phosphorus compounds.

Registry No. PClPPFe·2TMPPE, 60920-56-1; PMXPPFe·2TMPPE, 60920-57-2; PMXPPFe·2$(n\text{-BuO})_2$PhP, 60920-58-3; PMXPPFe·2$(\text{EtO})_3$P, 60920-59-4; PMXPPFe·2$(n\text{-Bu})_3$P, 60920-60-7; PMXPPFe·2n-BuOPh_2P, 60920-61-8; PMXPPFe·2MeOPh_2P, 60920-62-9; PMXPPFe·2pip, 50914-77-7.

References and Notes

(1) Taken in part from the Ph.D. dissertation of W. M. Connor, University of Pittsburgh, 1973.

(2) M. Weissbluth, *Struct. Bonding (Berlin)*, **2**, 1–125 (1967); H. A. O. Hill, A. Roder, and R. J. P. Williams, *ibid.*, **8**, 123–151 (1970); H. Kobayashi and Y. Yanagawa, *Bull. Chem. Soc. Jpn.*, **45**, 450–456 (1972).

(3) L. M. Epstein, D. K. Straub, and C. Maricondi, *Inorg. Chem.*, **6**, 1720–1724 (1967); D. K. Straub and W. M. Connor, *Ann. N.Y. Acad. Sci.*, **206**, 383–395 (1973).

(4) A. J. Bearden, T. H. Moss, W. S. Caughey, and C. A. Beaudreau, *Proc. Natl. Acad. Sci. U.S.A.*, **53**, 1246–1253 (1965).

(5) W. M. Connor and D. K. Straub, *Inorg. Chem.*, **15**, 2289 (1976).

(6) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).
(7) I. A. Cohen, *J. Am. Chem. Soc.*, **91**, 1980–1983 (1969); C. Maricondi, W. Swift, and D. K. Straub, *ibid.*, **91**, 5205–5210 (1969).
(8) J. P. Collman, J. L. Hoard, N. Kim, G. Lang, and C. A. Reed, *J. Am. Chem. Soc.*, **97**, 2676–2681 (1975).
(9) N. M. Karayannis, C. M. Mikulsi, L. L. Pytlewski, and M. M. Labes, *Inorg. Chem.*, **9**, 582–587 (1970).
(10) C.-A. Yu, I. C. Gunsalus, M. Katagiri, K. Suhara, and S. Takemori, *J. Biol. Chem.*, **249**, 94–101 (1974).
(11) P. M. Champion, E. Munck, P. G. Debrunner, P. F. Hollenberg, and L. P. Hager, *Biochemistry*, **12**, 426–435 (1973).
(12) B. B. Chastain, E. A. Rick, R. L. Pruett, and H. B. Gray, *J. Am. Chem. Soc.*, **90**, 3994–4000 (1968).
(13) W. McFarlane and R. F. M. White, *Chem. Commun.*, 744 (1969).
(14) W. Strohmeier and F.-J. Müller, *Chem. Ber.* **100**, 2812–2821 (1967); C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 2953–2956 (1970).
(15) C. A. Tolman, W. C. Seidel, and L. W. Goser, *J. Am. Chem. Soc.*, **96**, 53–60 (1974); W. C. Trogler and L. G. Marzilli, *Inorg. Chem.*, **14**, 2942–2948 (1975).
(16) W. W. Adams and P. G. Linhert, *Acta Crystallogr., Sect. B.*, **29**, 2412–2425 (1973).
(17) H. Eicher and A. Trautwein, *J. Chem. Phys.*, **50**, 2540–2551 (1969).

Correspondence

Homolytic Single-Bond Dissociation Energies and the Nature of the Coordinate-Covalent Bond[1]

AIC60192G

Sir:

Recent studies of photoredox reactions of transition metal complexes have resulted in reasonably good estimates of the minimum or threshold energy (E_{th}) required for the process described by eq 1.[2] Correlations of thermodynamic and

$$L_5M^{III}\text{-}(X^-) \xrightarrow{h\nu_0 = E_{th}} \{L_5M^{II}, \cdot X\} \qquad (1)$$

photochemical parameters indicate that most feasible processes occur with some sort of yield.[2] These values of E_{th} may be taken as measures of "single-bond dissociation energies" for homolytic bond cleavage in the respective transition metal complexes. It is the purpose of this correspondence to examine the bonding information contained in such threshold energies. Such an analysis should contribute to a better understanding of these complexes, especially of those in which the bonding has been claimed to be predominantly "ionic" (e.g., $FeBr^{2+}$)[3] or unusually "covalent" (e.g., organo–cobalt bonds).[4] Despite the contrasting descriptions of $FeBr^{2+}$ and the organo–cobalt complexes, homolytic processes occur in both kinds of systems following absorption of relatively low-energy radiation (e.g., λ ≥550 nm).[3-7]

Components of Bond Dissociation Energies. At this time our most detailed information is for pentaammine complexes of cobalt(III). For these complexes E_{th} seems to be the energy difference between the singlet ground state and a radical pair containing the cobalt(II) fragment $Co(NH_3)_5^{2+}$ in its quartet ground state.[2b,8] Comparisons of bond energy from compound to compound are simpler when not complicated by changes of spin multiplicity, and this requires consideration of a process yielding a thermally equilibrated doublet $Co(NH_3)_5^{2+}$ species. Since the difference in energy between high-spin (quartet) and low-spin (doublet) $Co(NH_3)_5^{2+}$ species has been estimated to be of the order of 48 kJ mol^{-1},[2b,8] this quantity, ΔH_{spin}, may be added to the experimental threshold energies in order to estimate the homolytic bond dissociation energies, $\Delta H_B = E_{th} + \Delta H_{spin} - \Delta H_S$, for the spin-conservative process (2). The

$$^1[(NH_3)_5Co^{III}\text{-}(X^-)] \rightarrow \{^2[(NH_3)_5Co^{II}], \cdot X\} \qquad (2)$$

solvation contribution to ΔH_B, ΔH_S, has been discussed elsewhere.[2a,b]

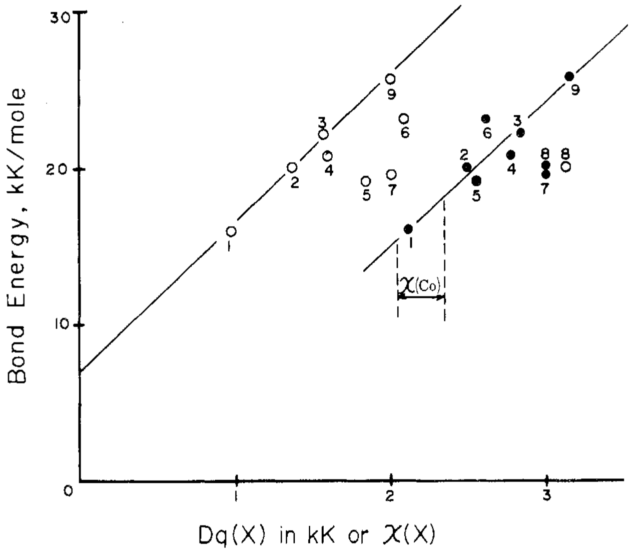

Figure 1. Correlation of homolytic bond dissociation energy (ΔH_B) with ligand field stabilization energy, Dq(X), or electronegativity, χ, of the ligand oxidized. Open circles are for correlation to ligand field strength, closed circles for correlation to electronegativity. Complexes represented: 1, $Co(NH_3)_5I^{2+}$; 2, $Co(NH_3)_5Br^{2+}$; 3, $Co(NH_3)_5Cl^{2+}$; 4, $Co(NH_3)_5N_3^{2+}$; 5, $Co(NH_3)_5SCN^{2+}$; 6, $Co(NH_3)_5NCS^{2+}$; 7, $Co(C_2O_4)_3^{3-}$; 8, $Co(NH_3)_5NO_2^{2+}$; 9, $Co(EDTA)^-$.

Scheme I

$$\begin{tikzcd}
M^{III}(g) + 5L(g) + X^-(g) \arrow[r, "IP + EA"] \arrow[d, "LFSE(III) + U_0"] & M^{II}(g) + 5L(g) + \cdot X(g) \arrow[d, "LFSE(II) + U_0'"] \\
M^{III}L_5(X^-)(g) \arrow[r, "\Delta H_B"] \arrow[d, "H_S"] & \{M^{II}L_5, \cdot X\}(g) \arrow[d, "H_S"] \\
M^{III}L_5(X^-)(aq) \arrow[r, "\Delta H_B + \Delta H_S"] & \{M^{II}L_5, \cdot X\}(aq)
\end{tikzcd}$$

The bond dissociation energies, ΔH_B, of $Co^{III}L_5(X^-)$ complexes are relatively large numbers, only approximately correlated to the crystal field strength, or the electronegativity, of the ligand oxidized (Figure 1): not unexpectedly the bond energy does not appear to approach zero as $Dq(X) \rightarrow 0$ or as $\chi_X \rightarrow \chi_{Co}$ (see Figure 1). The numerical values of ΔH_B are only about 10% smaller than the corresponding C–X bond energies. The large positive value of ΔH_B observed for $\chi_X \rightarrow \chi_{Co}$ (Figure 1) might be interpreted in terms of a large covalent component except that one would expect a very weak $(NH_3)_5Co^{II}\text{–}Co^{II}(NH_3)_5$ bond.[9,10] The homolysis component independent of the ligand X may be more reasonably attributed to the difference in ligand field stabilization energies (ΔLFSE) of cobalt(III) and cobalt(II) pentaammines. The nonspherical components of ΔLFSE for process (2) may be readily estimated from parameters available in the literature (see Table II[11] and ref 12–14) and such estimates are included in Table I. Thus, we may write,[15] per Scheme I, $\Delta H_B = (IP + EA + \Delta U_0) + \Delta LSFE$. The quantities in parentheses can be approximately related to the covalent or ionic character of the $M^{III}\text{-}(X^-)$ bond, while the second term can be interpreted as a "distributed" contribution to bonding due to relative