(IR, NMR) in agreement with the expected structures.
(3) G. Stork and L. Maldonado, *J. Am. Chem. Soc.*, **92,** 5286 (1971).
(4) R. U. Lemieux and E. Von Rudloff, *Can. J. Chem.*, **33**, 1701, 1710 (1955).
(5) This substance has previously been made by a combination of chemical and microbiological methods: C. J. Sih, R. G. Salomon, P. Price, R. Sood, and G. Peruzzotti, *J. Am. Chem. Soc.*, **97,** 857 (1975). Reported: mp 60–61 °C, $[\alpha]^{24}{}_{D}$ +17.2.
(6) A. F. Kluge, K. G. Untch, and J. H. Fried, *J. Am. Chem. Soc.*, **94,** 9256 (1972). See ref 7, footnote 13a.
(7) J. G. Miller, W. Kurz, K. G. Untch, and G. Stork, *J. Am. Chem. Soc.*, **96,** 6774 (1974).
(8) ^{13}C NMR 214.9, 174.0, 136.6, 133.0, 71.06, 66.83, 55.17, 51.36, 49.43, 46.49, 36.81, 33.92, 31.80, 29.36, 28.88, 27.78, 26.60, 25.16, 24.81, 22.61, 14.01; IR (neat) 3600–3100, 2950, 1740, 1720, 1475, 1450 cm^{-1}; CD (c = 1.218 × 10^{-3}, methanol, 25 °C, 296 nm) 10 600. CI–MS 351 (M + 1)$^+$, 333 (M + 1 − H_2O)$^+$; R_f 0.11 (hexane:ethyl acetate, 55:45); HPLC (retention time 62–80 min, on Porasil-A, 2 × ⅜ in. × 2 ft) in hexane–ethyl acetate 1:2, 3 ml/min.
(9) We are indebted to R. Davis and K. Untch (Syntex Research) for repeating this conjugate addition. Under conditions which had given them a ratio of 86:14 in favor of the desired isomer, they were unable to detect *any* of the unwanted isomer by direct comparison (TLC, NMR, HPLC on the silylated product). As little as 0.5% of the unwanted isomer would have been detected.
(10) For a previous chiral synthesis of a prostaglandin (PGA_2), see G. Stork and S. Raucher, *J. Am. Chem. Soc.*, **98,** 1583 (1976).

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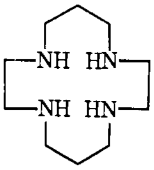
Homolytic Photochemical Processes in an Organo-Cobalt Complex Containing Saturated Ligands and the Nature of the Cobalt-Carbon Bond[1]

Sir:

Photoredox processes in most cobalt(III) complexes are stimulated by the absorption of radiation of energies comparable to the energies of ligand to metal charge transfer absorption bands.[2] For most cobalt complexes this means that the homolytic cleavage of metal ligand bonds is a process characteristic of ultraviolet or high energy visible excitations. In contrast, homolytic processes are known to occur throughout the visible absorption region for most organo-cobalt complexes.[3-7] Unfortunately, the assignment of electronic transitions for most organo-cobalt complexes is ambiguous since these complexes exhibit intense electronic transitions probably mediated by unsaturated equatorial ligands. Thus it has not been possible to critically explore the relationship of homolytic processes to the nature of the absorption bands irradiated. We have therefore undertaken a photochemical investigation of $Co([14]aneN_4)(OH_2)CH_3{}^{2+}$.[8] This complex



$[14]aneN_4$

has an absorption spectrum[9] (Figure 1) very similar to that of $Co(NH_3)_6{}^{3+}$, with charge transfer and other strongly allowed absorptions confined to the ultraviolet and with two weakly forbidden transitions in the visible–near-ultraviolet region.

We have been able to detect only one photochemical process (eq 1)

$$Co([14]aneN_4)(OH_2)CH_3{}^{2+} + h\nu \rightarrow Co^{II}([14]aneN_4) + CH_3 + H_2O \quad (1)$$

following irradiation of any absorption band of $Co([14]aneN_4)(OH_2)CH_3{}^{2+}$. The quantum yield for this homolytic process is essentially independent of excition wavelength (Φ = 0.30 ± 0.04). The contrasts to the photochemical behavior of acidopentaamminecobalt(III) complexes are striking: (1) homolysis is induced by irradiations of absorption bands much lower in energy than the charge transfer absorptions; (2) homolytic cleavage of the $Co{-}CH_3$ bond requires less energy than homolytic cleavage of most $Co^{III}{-}X^-$ bonds;[2] (3) most acidopentaammine complexes exhibit strongly wavelength dependent photochemistry;[2] (4) there is no distinct absorption feature which can be attributed to a $CH_3{}^- \rightarrow Co(III)$ transition (note: $Co([14]aneN_4)(OH_2)_2{}^{3+}$ has a charge transfer band at about 200 nm).

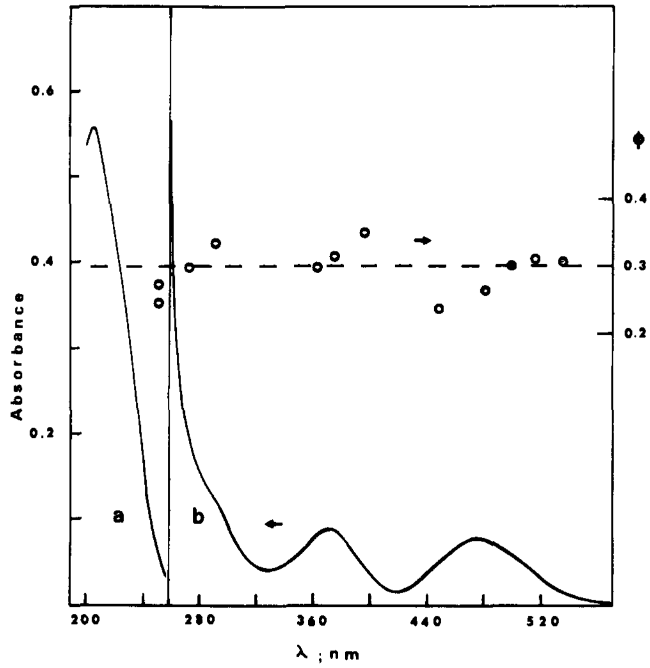


Figure 1. Absorption spectrum and wavelength dependence of homolysis quantum yield, ϕ, for $Co([14]aneN_4)(OH_2)CH_3{}^{2+}$: curve a 2.35 × 10^{-5} M $Co([14]aneN_4)(OH_2)CH_3{}^{2+}$ in 10^{-3} M $HClO_4$; curve b, 9.78 × 10^{-4} M $Co([14]aneN_4)(OH_2)CH_3{}^{2+}$ in 10^{-3} M $HClO_4$. Dashed line represents average value of quantum yields.

The spectroscopy and the photochemistry of $Co([14]aneN_4(OH_2)CH_3{}^{2+}$ combine to provide new and unique information about the nature of the cobalt–methyl bond. To illustrate this we first designate the $Co{-}CH_3$ bonding orbital by ψ_B and the $Co{-}CH_3$ antibonding orbital by ψ_{AB}. In the approximate C_{4v} symmetry of the complex the $\psi_B \rightarrow \psi_{AB}$ transition is strongly allowed. From the absorption spectrum it is evident that the difference in orbital energies (i.e., not including the Franck–Condon contributions to the optical transitions) is $E_0(\psi_{AB}) - E_0(\psi_B) = 3.4\ \mu m^{-1}$. The bond energy is given by the energy threshold for process 1 and we find that $E_{th} \leqslant 1.8\ \mu m^{-1}$. Consequently $E_0(\psi_{AB}) - E_0(\psi_B) \gg E_{th}$, no doubt owing to a relatively large contribution of the exchange integral[10] to the transition energy for the cobalt complexes. For more conventional complexes of cobalt(III) (e.g., acidopentammines), the close correspondence of $E_0(\psi_{AB}) - E_0(\psi_B)$ to E_{th} suggests that contributions of the exchange integral are small compared to those of the Coulomb integral. This contrast between halo and methyl complexes is consistent with the much larger electron affinity of $\cdot X$[11] than $\cdot CH_3$,[12] and with the consequent transfer of more electron density from cobalt(II) to $\cdot X$ (as in $Co^{III}{-}X^-$) than from cobalt(II) to $\cdot CH_3$ in the methyl–cobalt complexes. Further to this point, the 0.2 Å longer $Co{-}OH_2$ bond in $Co([14]aneN_4)(OH_2)CH_3{}^{2+}$[13,14] than in related acido–aquo–cobalt(III) complexes can be regarded as the manifestation of a relatively large amount of electron density in the d_{z^2} orbital, and the small homolysis energy may be a consequence of the relatively small transfer of charge to the metal during the homolysis process.[15] Finally, we note that while the lowest energy "d-d" transition in acidopentaammine complexes may be assigned as (d_{xz}, d_{yz}, or d_{xy}) → d_{z^2}, the small energy for Co-CH_3 homolysis suggests that the 478-nm transition in $Co([14]aneN_4)(OH_2)CH_3^{2+}$ should be assigned as $\psi_B \rightarrow d_{x^2-y^2}$. A more traditional assignment of the weakly allowed transitions in $Co([14]aneN_4)(OH_2)CH_3^{2+}$ as "ligand field" transitions (analogous to those of $Co(NH_3)_6^{3+}$) is not compatible with the photochemical observations.[15]

More detailed analyses of the bonding energetics and the electronic structures of the organo-cobalt complexes will be presented elsewhere.[15,16] Consideration of our observations on $Co([14]aneN_4)(OH_2)CH_3^{2+}$ should lead to more correct spectroscopic assignments, since the transition energies should vary in a predictable manner with changes of the equatorial ligands.[17] Furthermore, homolysis threshold energies can be used as measures of Co-alkyl bond energies, and the limited information available suggests that cobalt-alkyl bonds are generally relatively weak.

Photochemical techniques and synthesis of compounds have been described elsewhere.[2,9,13,16] Photolyses were performed anaerobically in solutions containing 10^{-3} M $HClO_4$ and 2.5 M 2-propanol (as a $\cdot CH_3$ scavenger). The quantitative determination of $Co^{II}([14]aneN_4)$ was accomplished by aerating aliquots of photolyte and determining the amount of μ-peroxodicobalt species developed, based on the absorbance at 420 nm.[18] Dark reactions of primary products were not directly detected and observed isosbestic points in spectroscopic scans of photolyte were consistent with reaction 1.[16]

References and Notes

(1) Partial support of this research by the National Institutes of Health and the National Science Foundation are gratefully acknowledged. (b) Partial support of C.Y.M. by a Faculty Fellowship and leave from Nanyang University, Singapore, is also gratefully acknowledged.

(2) (a) J. F. Endicott in "Concepts of Inorganic Photochemistry", A. W. Adamson and P. D. Fleischauer, Ed., Chapter 3, p 83; (b) J. F. Endicott, G. J. Ferraudi, and J. R. Barber, *J. Phys. Chem.*, **79**, 630 (1975); (c) J. F. Endicott and G. J. Ferraudi, *Inorg. Chem.*, **14**, 3133 (1975).

(3) H. P. C. Hogenkamp, *Biochemistry*, **5**, 417 (1966).

(4) (a) G. N. Schrauzer, *Acc. Chem. Res.*, **1**, 97 (1968); (b) G. N. Schrauzer, J. W. Sibert, and R. J. Windgassen, *J. Am. Chem. Soc.*, **92**, 2997 (1970); (c) G. N. Schrauzer, L. P. Lee, and J. W. Sibert, *Ibid.*, **92**, 2997 (1970).

(5) (a) J. M. Pratt, *J. Chem. Soc.*, 5154 (1964); (b) J. M. Pratt and B. R. D. Whitear, *ibid.*, 252 (1971); (c) J. M. Pratt, "Inorganic Chemistry of Vitamin B_{12}".

(6) (a) C. Giannotti, A. Gaudemer, and C. Fontaine, *Tetrahedron Lett.* **37**, 3209 (1970); (b) C. Giannotti and J. R. Bolton, *J. Organomet. Chem.*, **80**, 379 (1974); (c) C. Giannotti and G. Merle, VII International Conference on Photochemistry, Edmonton, Canada, Aug 7–13, paper X2.

(7) R. T. Taylor, L. Smucker, M. L. Hanna, and J. Gill, *Arch. Biochim. Biophys.*, **156**, 521 (1973).

(8) Abbreviations: $[14]aneN_4$ = 1,3,8,11-tetraazacyclotetradecane; $[14]teteneN_4$ = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene.

(9) T. S. Roche and J. F. Endicott, *Inorg. Chem.*, **13**, 1575 (1974).

(10) The authors wish to thank Professor Harry B. Gray for some stimulating discussions of these problems.

(11) J. E. Huheey, "Inorganic Chemistry", Harper and Row, New York, N.Y., 1972, p 52.

(12) J. E. Williams, Jr., and A. Streitweiser, Jr., *J. Am. Chem. Soc.*, **97**, 2634 (1975).

(13) The Co–OH_2 bond length in $Co([14]aneN_4)(OH_2)CH_3^{2+}$ is 2.15 Å (J. F. Endicott, D. Halko, W. Butler, and M. D. Glick, manuscript in preparation), which may be compared to Co–OH_2 bond lengths of 1.94–2.00 Å in most cobalt(III) complexes and 2.29–2.48 Å in related six-coordinate low spin cobalt(II) complexes.[14]

(14) J. F. Endicott, J. Lilie, J. M. Kuszaj, B. S. Ramaswamy, W. G. Schmonsees, M. G. Simic, M. D. Glick, and D. P. Rillema, *J. Am. Chem. Soc.*, in press.

(15) The homolysis energy of CoL_5X^{2+} may be approximately partitioned into components due to ionic (I), covalent (C), and changes in ligand field stabilization energy (ΔLFSE) per the cycle:

$$\begin{tikzcd}
\underbrace{Co^{3+}(g) + 5L(g) + X^-(g)}_{} \arrow[r, "IP(Co) + EA(X)"] \arrow[d, "{[LFSE(Co^{III}) + U_0]}"] & \underbrace{Co^{2+}(g) + 5L(g) + \cdot X(g)}_{} \arrow[d, "{[LFSE(Co^{II}) + U_0']}"'] \\
M^{III}L_5(X^-)(g) \arrow[r, "\Delta H_B"] & \{M^{II}L_5, \cdot X\}(g)
\end{tikzcd}$$

Thus the homolysis energy is given by $\Delta H_B = [\Delta U_0 + IP + EA] + \Delta LFSE$, where $[\Delta U_0 + IP + EA] \simeq I + C$. In this approach, the contrast between the homolysis energies of $Co(NH_3)_5Br^{2+}$ ($\Delta H_B \simeq 236$ kJ/mol) and $Co([14]aneN_4)(OH_2)CH_3^{2+}$ ($\Delta H_B < 217$ kJ/mol) would be attributed to a smaller value (by about 25% of ΔLFSE for Co–CH_3 homolysis than for Co–Br homolysis since a larger "covalent" contribution would be expected for the Co–CH_3 bond than for the Co–Br bond (J. F. Endicott, *Inorg. Chem.*, in press).

(16) C. Y. Mok and J. F. Endicott, submitted.

(17) C. K. Jorgensen, "Modern Aspects of Ligand Field Theory", North-Holland, Amsterdam, 1971.

(18) B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, **5**, 1514 (1966).

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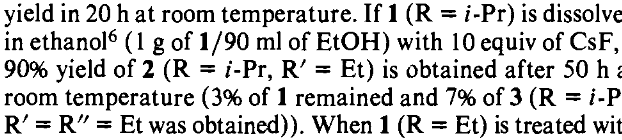
A General Transesterification Method for the Synthesis of Mixed Trialkyl Phosphates

Sir:

The synthesis of mixed trialkyl phosphates continues to be an important goal. Such compounds are of current interest in such diverse areas as pesticides, phospholipids, and nucleic acids. There have been several recent reports on new methods of synthesis of mixed alkyl phosphates.[1-3] We wish to report on a very simple exchange reaction involving readily available starting materials which allows the synthesis of mixed trialkyl phosphates.

The general reaction is shown below where a bis(trichloroethyl) alkyl phosphate[4] (**1**) is dissolved in an alcohol and in the presence of fluoride ion (CsF) the product **2** is obtained.[5]



$(Cl_3CCH_2O)_2P(O)OR \xrightarrow[CsF]{R'OH} Cl_3CCH_2OP(O)(OR')OR \xrightarrow[CsF]{R''OH} R''OP(O)(OR')OR$

1 2 3

The yields of **2** range from 85 to 100%. For example, when **1** (R = Et) is dissolved in isopropyl alcohol (1 g of **1**/20 ml of *i*-PrOH) with 15 molar equiv (per mole of **1**) of cesium fluoride the product **2** (R = Et, R′ = *i*-Pr) is obtained in quantitative yield in 20 h at room temperature. If **1** (R = *i*-Pr) is dissolved in ethanol[6] (1 g of **1**/90 ml of EtOH) with 10 equiv of CsF, a 90% yield of **2** (R = *i*-Pr, R′ = Et) is obtained after 50 h at room temperature (3% of **1** remained and 7% of **3** (R = *i*-Pr, R′ = R″ = Et was obtained)). When **1** (R = Et) is treated with methanol[6] (1 g of **1**/35 ml of MeOH) using 15 equiv of CsF, an 82% yield of **2** (R = Et, R′ = Me) is obtained in 23 h along with 9% of **1** and 9% of **3** (R = Et, R′ = R″ = Me). All of the products are easily isolated by silica gel chromatography or for very large scale reactions by fractional distillation.[7]

The conversion of **2** into **3** is slower than the above exchange and reactions are usually heated at 80 °C. Thus on dissolving **2** (R = Me, R′ = Et) in isopropyl alcohol (1 g of **2**/20 ml of *i*-PrOH) with 10 equiv of CsF, a quantitative yield of **3** (R = Me, R′ = Et, R″ = *i*-Pr) is obtained after 25 h at 80 °C. This reaction when applied to **2** (R = Et, R′ = *n*-Pr) in *n*-octanol (300 mg of **2**/10 ml) with 5 equiv of CsF yielded 87% of **3** (R = Et, R′ = *n*-Pr, R″ = *n*-oct) after 6 days at 80 °C (13% of **2** was recovered).

These reactions occur equally well when tetra-*n*-butylammonium fluoride is used in place of cesium fluoride. However, the reactions do not occur in the absence of fluoride ion. In addition, ordinary alkyl groups are not displaced under these conditions. For example, trimethyl phosphate is unaffected by heating at 80 °C for extended periods of time in alcohol solu-