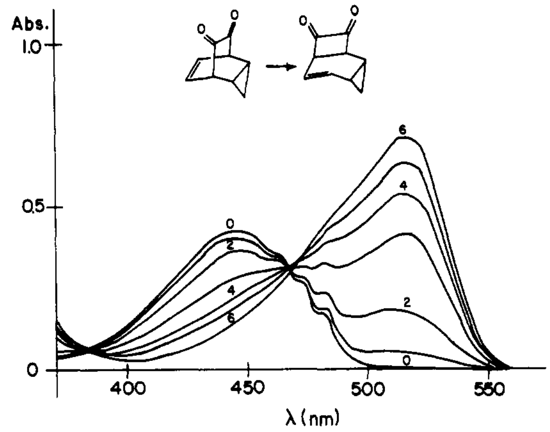

Figure 1. Progress of 404-nm irradiation of 3.4×10^{-3} M **3** in air-saturated cyclohexane at room temperature.

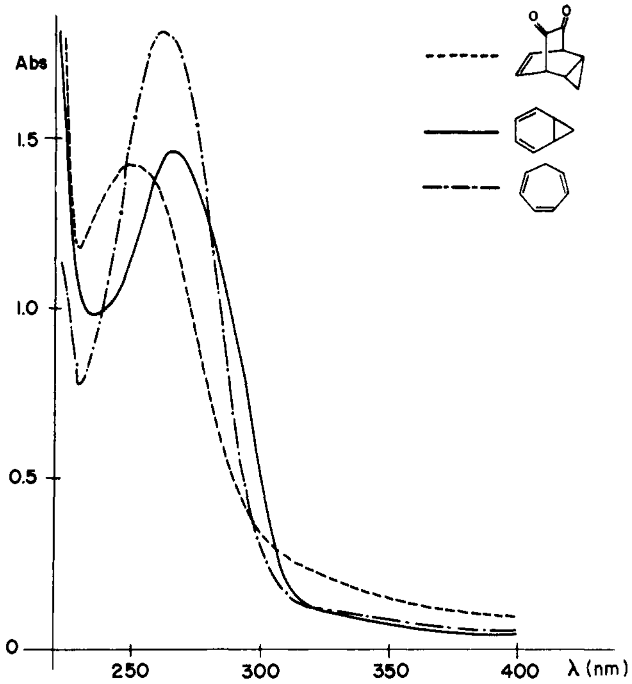

Figure 2. Ultraviolet spectra in 1:1:1 methylcyclohexane–isohexane–isopentane at 77 K: (---) 3.94×10^{-4} M **3**; (—) after 50 min of irradiation at 240–400 nm; (-·-·) after warming to 110 K and recooling.

sorption was observed. We therefore attribute the norcaradiene structure to the thermally unstable product of low-temperature photolysis of **3**. The ultraviolet spectrum is consistent with this assignment,[14] and the infrared spectrum rules out any thermally labile ketone such as the cyclopropanone **7** as a precursor for **2**.[15] The contrast in the photochemical behavior of **3** and **4** at low temperature is a matter of continuing interest.

Differences in the ultraviolet spectra of **1** and **2** (cf. Figure 2) were sufficiently great to allow measurement of the kinetics of the isomerization **1** → **2** by monitoring the increase in optical density at 261 nm. Good first-order behavior was observed at 93, 98, and 103 K; the results fit the Arrhenius expression

$$k_{1\to2} = (6.0 \pm 0.3) \times 10^{11} e^{(-6500\pm1000)/RT}$$

The value of the preexponential term gives $\Delta S^{\ddagger}_{100} = -2.5$ eu and $\Delta G^{\ddagger}_{100} = 6100$ cal/mol. The calculated rate constant for **1** → **2** at 25 °C is 1×10^{7} s^{-1}. The corresponding values at 25 °C are $\Delta S^{\ddagger} = -4.5$ eu and $\Delta G^{\ddagger} = 7.2$ kcal/mol which are quite similar to those determined[5c] by variable-temperature NMR ($E_a = 7$ kcal/mol, $\Delta S^{\ddagger} = -4$ eu) for the isomerization of 7,7-bis(methoxycarbonyl) norcaradiene to the cycloheptatriene isomer, even though the relative stabilities of the two isomers are very different in these two cases.

It has been suggested[16] that the equilibrium concentration of **1** in **2** at 20 °C is 0.1%. Using the equilibrium constant based on this proposal, the free energy difference between **1** and **2** at 25 °C is of the order of −4 kcal/mol and $\Delta G^{\ddagger}_{2\to1} \simeq 11$ kcal/mol. Assuming that the entropy of activation for **2** → **1** is close to zero, the approximate Arrhenius expression becomes

$$k_{2\to1} \simeq 6 \times 10^{12} e^{-12000/RT}$$

Application of the low-temperature photochemical method described above to synthesis of substituted norcaradienes is being investigated. We note that the analogous monoketone, tricyclo[$3.2.1.0^{2,4}$]oct-6-en-8-one[17] (**8**), afforded **2** quantitatively under the same conditions used for successful conversion of **3** to **1**.

Acknowledgment. A generous gift of compound **3** by Professor H.-D. Scharf is gratefully acknowledged as are stimulating discussions with Professors R. Huisgen, E. A. Halevi, and Y. Apeloig. Partial financial support was provided by the Technion Fund for the Promotion of Research.

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[14] For example, 7,7-dicyanonorcaradiene[4] has λ_{max} (cyclohexane) 271 nm (2900).

[15] The NMR spectrum would constitute an ideal proof of structure for **1**. Unfortunately, the required temperature is so low ($t_{1/2}^{-170} = 63$ s) that this was not feasible.

[16] Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 755.

[17] Clarke, S. C.; Johnson, B. L. *Tetrahedron* **1971**, *27*, 3555 and references therein.

Tertiary Phosphine Derivatives of the f-Block Metals. Preparation of $X_4M(Me_2PCH_2CH_2PMe_2)_2$, where X Is Halide, Methyl, or Phenoxo and M Is Thorium or Uranium. Crystal Structure of Tetra(phenoxo)bis[bis(1,2-dimethylphosphino)ethane]uranium(IV)

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Though a number of tertiary phosphine complexes of uranium halides have been claimed,[1] most of the claims have been shown to be false.[2] In this communication we describe the synthesis of some authentic bis(1,2-dimethylphosphino)ethane (dmpe) complexes of uranium(IV) and thorium(IV) halides of the type $X_4M(dmpe)_2$ and their conversion to the tetramethyl and tetraphenoxo derivatives. The crystal structure of the phenoxo derivative, $(PhO)_4U(dmpe)_2$, is described.

Uranium tetrachloride dissolves in a mixture of dichloromethane and a threefold molar excess of bis(1,2-dimethylphosphino)ethane (dmpe) at room temperature to give a blue green solution from

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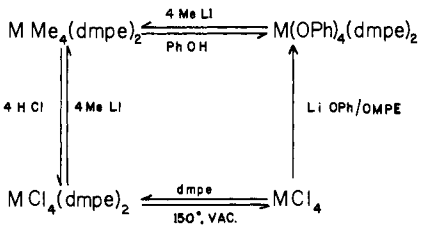
[1] (a) Allison, J. A. C.; Mann, F. G. *J. Chem. Soc.* **1949**, 2915–2921. (b) Mannerskantz, H. C. E.; Parshall, G. W.; Wilkinson, G. *Ibid.* **1963**, 3163–3164. (c) Majumdar, A. K.; Mukherjee, A. K.; Bhattacharya, R. G. *J. Inorg. Nucl. Chem.* **1964**, *26*, 386–387. (d) Selbin, J.; Ahmad, N.; Pribble, M. J. *Ibid.* **1970**, *32*, 3249–3258. (e) The trimethylphosphine derivative, $(Me_5C_5)_2UCl(PMe_3)$, readily loses coordinated PMe_3 when exposed to vacuum. Manriquez, J. M.; Fagan, P. J.; Marks, T. J.; Vollmer, S. H.; Day, C. J.; Day, V. W. *J. Am. Chem. Soc.* **1979**, *101*, 5075–5078.

[2] (a) Gans, P.; Smith, B. C. *J. Chem. Soc.* **1964**, 4172–4176. (b) Day, J. P.; Venanzi, L. M. *J. Chem. Soc. A* **1966**, 1363–1367. (c) Fitzsimmons, B. W.; Gans, P.; Hayton, B.; Smith, B. C. *J. Inorg. Nucl. Chem.* **1966**, *28*, 915–916. (d) Hart, F. A.; Newberry, J. E. *Ibid.* **1966**, *28*, 1344–1336. (e) McAuliffe, C. A.; Levason, W. "Phosphine, Arsine, and Stilbine Complexes of the Transition Metals"; Elsevier: New York, 1979; p 72 and 215.

0002-7863/81/1503-7792$01.25/0

Scheme I



which green prisms of paramagnetic (f^2) $UCl_4(dmpe)_2$ may be crystallized on cooling (−20 °C).[3,4] The complex is a nonconductor in CH_2Cl_2 and gives only free dmpe upon hydrolysis with water as judged by $^{31}P\{^1H\}$ NMR spectroscopy. The complex may be quantitatively recrystallized from either diethyl ether or tetrahydrofuran. Thus, in a qualitative sense, the basicity of the ligands toward the Lewis acid (UCl_4) lies in the order dmpe > THF, Et_2O. Further, the complex may be sublimed at 160 °C (10^{-3} mm) with only partial decomposition to UCl_4, and a molecular ion is observed in the mass spectrum. Thus the phosphine complex is rather robust, suggesting that the uranium–phosphine interaction is not thermodynamically weak.

The uranium tetrabromide and thorium tetraiodide complexes, $MX_4(dmpe)_2$ where M is U and X is Br[5] or M is Th and X is I,[6] may be prepared similarly. The iodide complex is a nonconductor (CH_2Cl_2) and only gives free dmpe upon hydrolysis with water as shown by $^{31}P\{^1H\}$ NMR spectroscopy. In contrast, thorium tetrachloride does not dissolve in a solution of dmpe in dichloromethane. However, $ThCl_4$ dissolves in neat phosphine at 80 °C to give a colorless solution from which diamagnetic $ThCl_4(dmpe)_2$ may be obtained. The complex is crystallized from dichloromethane as colorless prisms (−20 °C)[8] and is a nonconductor (CH_2Cl_2).

The chlorophosphines of uranium or thorium react with 4 molar equiv of methyllithium in diethyl ether at 0 °C to yield the tetramethyl derivatives $Me_4U(dmpe)_2$[9] as brown-yellow prisms from pentane (−70 °C) or $Me_4Th(dmpe)_2$[10] as colorless prisms from pentane (−70 °C), respectively. Though $Me_4M(dmpe)_2$, where M is Th or U, must be prepared at 0 °C, they are sufficiently thermally stable at 25 °C to afford satisfactory elemental analyses. They appear to be indefinitely stable below −20 °C in absence of air and moisture. The relative thermal stability of the phosphine complexes is noteworthy, since the tetravalent, anionic, methyl derivatives, e.g., $[Li_2(OEt_2)_8]Me_6U$, decompose at approximately −20 °C.[11] Both dmpe complexes react with hydrogen chloride in toluene to give $Cl_4M(dmpe)_2$, where M is Th or U, and methane.

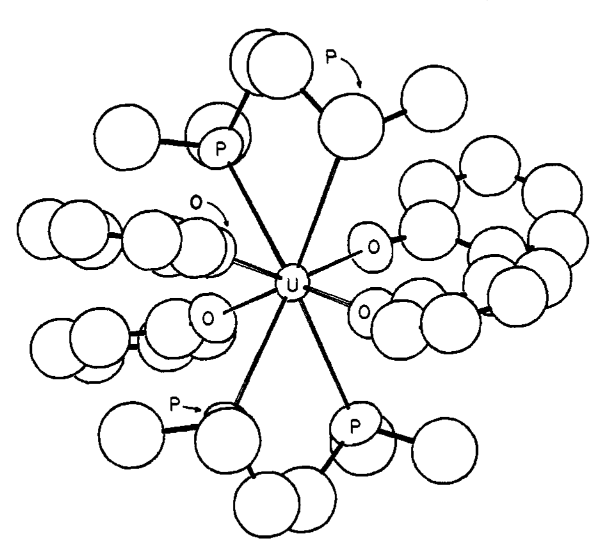


Figure 1. View of the $U(OPh)_4(dmpe)_2$ molecule showing the phenoxy groups in a distorted equatorial environmental.

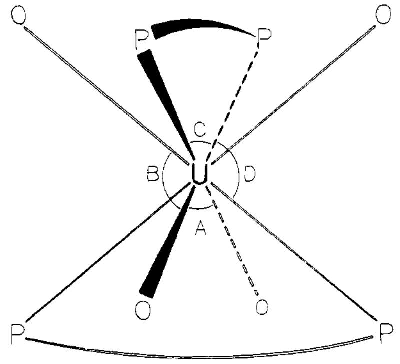


Figure 2. Schematic representation of the structure of $U(OPh)_4(dmpe)_2$ showing relevant averaged bond angles and bond lengths. Angle A = 94.6 ± 0.4°, angle B = 147.2 ± 0.1°, angle C = 64.7 ± 0.6°, angle D = 135.5 ± 2.2°; U···O = 2.17 ± 0.01 Å, U···P = 3.104 ± 0.006 Å.

The alkyl–phosphine complexes react with phenol in toluene to give green $(PhO)_4U(dmpe)_2$ and colorless $(PhO)_4Th(dmpe)_2$.

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(3) Anal. Calcd for $C_{12}H_{32}Cl_4P_4U$: C, 21.2; H, 4.71; Cl, 20.9; P, 18.2. Found: C, 21.6; H, 4.77; Cl, 22.0; P, 18.5; M^+, 680. ^1H NMR (PhMe-d_8, 26 °C) δ 2.09 (s, $\nu_{1/2} = 4.1$ Hz, 12 H) and −19.6 (s, $\nu_{1/2} = 6$ Hz, 4 H); $^{13}C\{^1H\}$ NMR (PhMe-d_8, −60 °C) δ −2.04 (s, $\nu_{1/2} = 14.7$ Hz) and −6.84 (s, $\nu_{1/2} = 17.6$ Hz). No resonance was observed in the $^{31}P\{^1H\}$ NMR experiments, not even a resonance due to free dmpe.

(4) The trimethylphosphine derivative, $UCl_4(PMe_3)_3$, was prepared similarly. Anal. Calcd for $C_9H_{27}Cl_4P_4U$: C, 17.8; H, 4.44; Cl, 23.3; P, 15.3. Found: C, 17.0; H, 4.63; Cl, 22.7; P, 14.9. The sample must be crystallized from neat PMe_3; otherwise analyses were not reproducible due to ready loss of phosphine.

(5) Green prisms were obtained from CH_2Cl_2. Anal. Calcd for $C_{12}H_{32}Br_4P_4U$: C, 16.8; H, 3.73; Br, 37.3; P, 14.5. Found: C, 16.9, H, 3.81; Br, 37.0; P, 14.6. ^1H NMR (PhMe-d_8, 26 °C) δ 3.55 (s, $\nu_{1/2} = 5.5$ Hz, 12 H) and −13.82 (s, $\nu_{1/2} = 14.7$ Hz, 4 H).

(6) Colorless prisms were obtained from CH_2Cl_2. Anal. Calcd for $C_{12}H_{32}I_4P_4Th$: C, 13.9; H, 3.08; I, 48.8; P, 11.9. Found: C, 14.0; H, 3.22; I, 47.4; P, 11.4. ^1H NMR (CD_2Cl_2, 26 °C): the methylene protons appear as a filled-in doublet centered at δ 2.11 with a separation between the outer lines of 14 Hz and the methyl protons appear as a five-line pattern centered at δ 1.76 with a separation between the outermost lines of 7.6 Hz, in area ratio 4:12, respectively. The spin system of $X_4M(dmpe)_2$ in the ^1H NMR spectrum is, in its simplest form, $[X_6AY_2Y'_2A'X'_6]_2$ where X and Y are ^1H and A is ^{31}P nuclei. In the $^{13}C\{^1H\}$ NMR spectrum it is ABCDX where X is the ^{13}C nucleus. The complex nature of the spin systems accounts for the "deceptively simple" spectra.[7] $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ −17.8. The coordination chemical shift, defined as the chemical shift of the complex less that of the free ligand, is 31.6 ppm.

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(8) Anal. Calcd for $C_{12}H_{32}Cl_4P_4Th$: C, 23.5; H, 5.23; Cl, 23.7; P, 18.4. Found: C, 23.5; H, 5.16; Cl, 22.9; P, 18.1. ^1H NMR (CH_2Cl_2-d_2, 27 °C): the methylene protons appear as a filled-in doublet centered at δ 1.95 (4 H), the separation between the two outermost lines being 13.6 Hz, and the methyl protons appear as an apparent triplet centered at δ 1.42 (12 H); the separation between the outermost lines is 5.3 Hz.[7] $^{13}C\{^1H\}$ NMR (PhMe-d_8, −60 °C): the methylene carbon atoms appear as a seven-line pattern centered at δ 25.9 with the separation of the outermost lines being 26.6 Hz, and the methyl carbon atoms appear as an apparent singlet at δ 11.6 ($\nu_{1/2} = 2$ Hz).[7] $^{31}P\{^1H\}$ NMR (PhMe-d_8, 26 °C): a singlet at δ −4.87. The coordination chemical shift is 39.6 ppm.

(9) Anal. Calcd for $C_{16}H_{44}P_4U$: C, 32.1; H, 7.36; P, 20.7. Found: C, 31.7; H, 7.29; P, 20.2. ^1H NMR (PhMe-d_8, −70 °C): three apparent singlets ($\nu_{1/2} = 40.5$, 12.1, and 32.4 Hz) are observed at δ −42.4, −1.76, and 10.1, respectively, in area ratio 8:24:12 due to Me_2PCH_2 (*CH*$_2$), *Me*$_2$PCH$_2$, and Me_4U, respectively. The ^{13}C NMR (PhMe-d_8, −40 °C) yields an apparent quartet centered at δ −38.8 ($J_{CH} = 137$ Hz) and an apparent triplet centered at δ −63.2 ($J_{CH} = 137$ Hz) and an apparent triplet centered at δ −63.2 ($J_{CH} = 137$ Hz) due to the methyl and methylene groups of coordinated dmpe, respectively. No resonance was observed for the Me–U carbon atom.

(10) Anal. Calcd for $C_{16}H_{44}P_4Th$: C, 32.4; H, 7.43; P, 20.9. Found: C, 32.7; H, 7.30; P, 20.4. ^1H NMR (PhMe-d_8, −50 °C): the Me–Th resonance appears as a binomial pentet centered at δ −0.09 ($J_{PH} = 2.87$ Hz, 12 H) and the Me–P and CH_2–P resonances appear as an apparent singlet at δ 1.33 ($\nu_{1/2} = 2$ Hz, 24 H) and an apparent doublet centered at δ 1.45 (8 H); the separation between the outer lines in the latter resonance is 23 Hz. ^{13}C NMR (PhMe-d_8, −80 °C): a quartet centered at δ 10.5 ($J_{CH} = 128$ Hz), a triplet centered at δ 28.0 ($J_{CH} = 134$ Hz), and a quartet centered at δ 46.3 ($J_{CH} = 107$ Hz) due to Me_2P, CH_2P, and Me_4Th, respectively. The $\nu_{1/2}$ of each resonance is ca. 4 Hz. $^{31}P\{^1H\}$ NMR (PhMe-d_8, −80 °C): a singlet at δ −27.6.

(11) Sigurdson, E. R.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 812–818.

The phenoxides react with 4 molar equiv of methyllithium to give the tetraalkyls, $Me_4M(dmpe)_2$, where M is Th or U. Both phenoxides crystallize from toluene as toluene solvates $(PhO)_4M(dmpe)_2 \cdot C_7H_8$ (M = U,[12] M = Th[13]).

Since the uranium complexes may be converted into each other, in isolated yields of ≥85% (Scheme I), the crystal structure of any one of them proves the existence of all of them as authentic tertiary phosphine complexes of uranium. In addition, the infrared spectrum and powder X-ray diffraction pattern of $U(OPh)_4(dmpe)_2 \cdot C_7H_8$ are identical with those of $Th(OPh)_4(dmpe)_2 \cdot C_7H_8$. Thus, the thorium phenoxide is isostructural with its uranium analogue. Since the thorium derivatives may be converted into each other, they are also authentic phosphine complexes.

An ORTEP[14] diagram of $U(OPh)_4(dmpe)_2$ is shown in Figure 1, and a line drawing is shown in Figure 2 with some bond angles and lengths. The coordination polyhedron is related to that of a D_{2d} dodecahedron with the four phosphorus atoms and the four oxygen atoms occupying the A and B sites, respectively.[15] The shape parameters will be discussed in a full paper. The average uranium–oxygen bond length of 2.17 ± 0.01 Å is in the range observed for other uranium alkoxide–oxygen bonds.[16] The average uranium–phosphorus bond length of 3.104 ± 0.006 Å is unique, so no direct comparison is possible, though an estimate can be made. The tetrahedral covalent radius of a phosphorus atom is 0.44 Å larger than that of an oxygen atom.[17] Hence a uranium–phosphorus bond length of 2.6 Å may be estimated, rather shorter than that observed. On the other hand, a value of 2.9–3.0 Å may be estimated from the eight-coordinate $MX_4(diars)_2$ complexes, where M is a group 4b or 5b metal, when the radii of arsenic and the transition metals are taken into account.[18] The latter estimated value is much closer to the value observed.

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy, under Contract W-7405-ENG-48. We thank the NSF for an equipment grant to the Chemistry Department used for the purchase of the X-ray diffractometer. We thank Dr. F. L. Hollander, staff crystallographer of the U.C. Berkeley X-ray facility (CHEXRAY) for collecting the X-ray data.

Note Added in Proof. The preparation and crystal structure of $U(Me_5C_5)_2H(dmpe)$ was announced in a lecture by T. J. Marks at the 28th I.U.P.A.C. congress in Vancouver, B.C. (August 17–20, 1981).

Supplementary Material Available: Positional and thermal parameters and estimated standard deviations and estimated atomic parameters for the hydrogen atoms and anisotropic thermal parameters (3 pages). Ordering information is given on any current masthead page.

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[12] Anal. Calcd for $C_{43}H_{60}O_4P_4U$: C, 51.5; H, 5.99; P, 12.4. Found: C, 51.3; H, 5.98; P, 12.2. ^1H NMR (PhMe-d_8, −24 °C): three resonances are attributable to the phenyl protons at δ 33.45, doublet (J = 7.3 Hz), δ 15.59, binomial triplet (J = 7.3 Hz), and δ 13.59, binomial triplet (J = 7.3 Hz), in area ratio 8:8:4 due to ortho, meta, and para protons, respectively. The resonances due to dmpe occur as broad, apparent singlets at δ −3.78 (Me_2P) and δ −32.86 (CH_2P) ($\nu_{1/2}$ = 40 Hz in each case) in area ratio 24:8, respectively. Resonances due to toluene of crystallization appear at δ 7.04 (s) and δ 2.12 (s), due to the phenyl and methyl protons, in area ratio 5:3, respectively.

[13] Anal. Calcd for $C_{43}H_{60}O_4P_4Th$: C, 51.8; H, 6.02; P, 12.5. Found: C, 52.1; H, 5.98; P, 12.9. ^1H NMR (PhMe-d_8, 40 °C): the phenyl resonance appears on a broad ($\nu_{1/2}$ = 41 Hz) complex multiplet centered at δ 7.04 and includes the phenyl resonance of toluene of crystallization. The methyl protons of toluene give rise to a singlet (δ 2.14); dmpe methylene protons produce an apparent three-line pattern with the central line at δ 1.16 and the separation between the two outer lines being 12.2 Hz and a broad singlet, δ 0.82 ($\nu_{1/2}$ = 6 Hz, Me_2P). The resonances have relative area ratios 25:3:8:24. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −50 °C): the aromatic carbons give rise to four singlets at δ 167.44 (α to oxygen), 128.91 (β to oxygen), 119.50 (γ to oxygen), and 115.99 (δ to oxygen). Assignment is confirmed by the ^{13}C spectrum where the three high field signals are observed as doublets ($J_{C\text{-}H}$ = 148.4, 159.2, and 161.1 Hz, respectively) and the quaternary carbon (δ 167.44) remains as a singlet. Two broad singlets at δ 27.06 (P-CH_2, $\nu_{1/2}$ = 32 Hz) and δ 13.23 (Me_2P, $\nu_{1/2}$ = 35 Hz) are due to dmpe. $^{31}P\{^1H\}$ NMR (PhMe-d_8, −60 °C): δ −12.0. The coordination chemical shift is 30.2 ppm.

[14] The crystals are triclinic, $P\bar{1}$, with cell dimensions a = 12.560 (4) Å, b = 12.831 (4) Å, c = 15.012 (4) Å, α = 77.84 (3)°, β = 83.28 (3)°, and γ = 88.94 (3)°. For two molecules in the unit cell the calculated density is 1.29 g/cm³. Intensity data were collected with a Nonius CAD-4 automated X-ray diffractometer by using Mo Kα X-rays. The structure was solved by the "heavy-atom" technique and refined by full-matrix least squares to an R factor of 0.052 using 5090 reflections for which $F^2 > 3\sigma(F^2)$.

[15] Hoard, J. L.; Silverton, J. V. *Inorg. Chem.* **1963**, *2*, 235–243.

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Kinetics of the Anaerobic Reduction of Ferricytochrome cd_1 by $Fe(EDTA)^{2-}$. Evidence for Bimolecular and Intramolecular Electron Transfers to the d_1 Hemes

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Received July 6, 1981

One of the major goals of bioinorganic chemistry is the elucidation of the pathways employed by metalloenzymes that are involved in multielectron oxidation–reduction catalytic reactions. Our recent work in this area has centered on *Pseudomonas aeruginosa* cytochrome cd_1 (ferrocytochrome c_{551}:oxygen oxidoreductase, EC 1.9.3.2), a water soluble enzyme in which spectroscopically distinct heme groups (one c and one d_1) are contained in each of two identical 63 000-dalton subunits.[1-5] The enzyme is particularly well suited for detailed electron-transfer mechanistic investigations, because the oxidation levels of the two different hemes [$E(c^{3+/2+})$ = 0.294; $E(d_1{}^{3+/2+})$ = 0.287 V vs. NHE)[6] can be monitored readily by electronic absorption spectroscopy.

We have completed an investigation of the kinetics of anaerobic $Fe(EDTA)^{2-}$ reduction of ferricytochrome cd_1.[7] The reduction of the heme c groups is monophasic, whereas biphasic kinetics are observed for electron transfer to the d_1 hemes. Pseudo-first-order rate constants for reduction of the c hemes and those for the fast d_1 phase vary linearly with the concentration of $Fe(EDTA)^{2-}$; in contrast, the slow d_1 phase exhibits rate saturation (Figure 1). The amplitudes of the two phases of the heme d_1 reaction are approximately equal, and the absorbance vs. time curves reveal clearly defined induction periods.

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[7] The enzyme was purified from bacterial paste by a modification[5] of a standard procedure.[1] Crystalline material[4] was used in all experiments. Stopped-flow kinetic measurements under anaerobic conditions and data analyses were performed as described previously (Scott, R. A.; Gray, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 3219–3224).