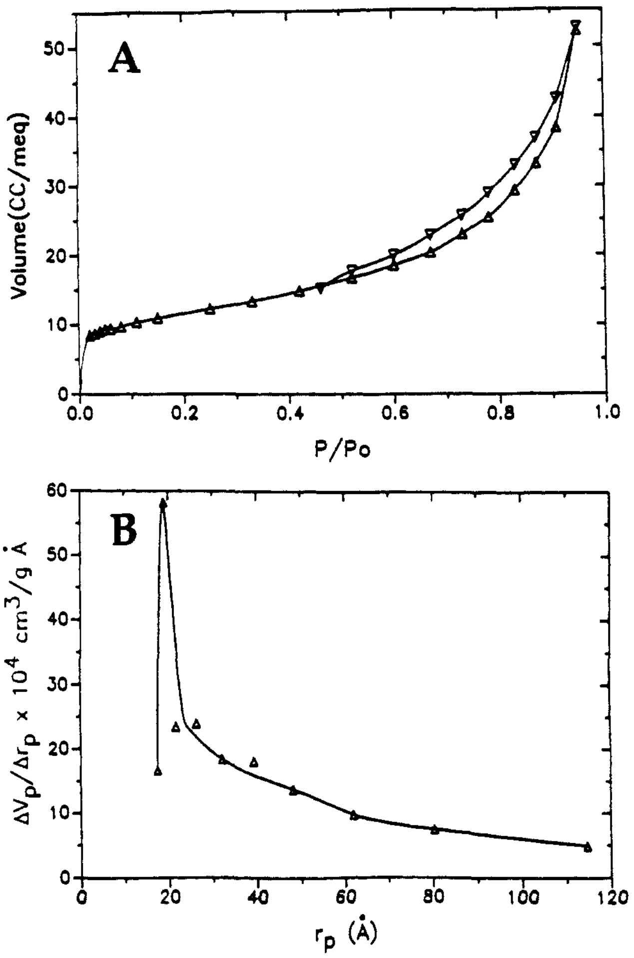


Figure 2. (A) N_2 adsorption (Δ) and desorption (∇) isotherms at 196 °C for the $Zn_2Cr-V_{10}O_{28}$ intercalate. (B) Mesopore distribution derived from the hysteresis loop beginning at $P/P_0 = 0.42$.

integrity in the intercalated state.

On the basis of the estimated size of $V_{10}O_{28}^{6-}$[9] and the unit cell sizes of the LDH hosts,[10] the surface areas should be between 25 and 60 m^2/mequiv. We observe N_2 BET surface areas in the range 35–41 m^2/mequiv indicating that the intracrystalline gallery surfaces indeed have been made accessible by pillaring.[11]

The N_2 adsorption/desorption isotherms for the $Zn_2Cr-V_{10}O_{28}$ systems are shown in Figure 2A. The substantial adsorption in the low P/P_0 region indicates the presence of micropores (<20 Å),[13] whereas the hysteresis starting at $P/P_0 = 0.42$ is indicative of the presence of some mesopores with a maximum near 20 Å (cf. Figure 2B). Analogous features were absent in the N_2 adsorption isotherm of the unpillared Zn_2Cr-Cl system.

Layered double hydroxides typically decompose at relatively low temperatures (<350 °C).[12] Nevertheless, there is considerable promise for the use of pillared LDH's for intracrystalline catalytic reactions. Certain POM's, including decavanadate, exhibit photocatalytic properties at ambient temperatures.[14] To illustrate the potential utility of LDH–POM intercalates, we carried out the photooxidation of isopropyl alcohol to acetone. A suspension of the $Zn_2Al-V_{10}O_{28}$ intercalate (0.0506 g, 0.0164 mmol) in isopropyl alcohol (11.0 mL) was irradiated in 48 h by a 450-W Hg vapor lamp equipped with a water filter and a 295-nm long pass filter. For the reaction under an argon atmosphere, only a stoichiometric amount of acetone was produced, and the intercalated decavanadate was converted to the blue reduced form. However, under oxygen, the decavanadate was partially reoxidized, and the reaction became catalytic, producing 6 mol of acetone per mol of decavanadate. Under equivalent oxygenated reaction conditions in homogeneous solution, the acetone yield was only 2.0 mmol/mequiv. Thus, the LDH intercalated catalyst is substantially more active than the homogeneous catalyst, despite scattering by the host particles.

The results reported here demonstrate for the first time that high-charge density LDH's can be pillared by POM anions, providing that the pillaring anion has a relatively high charge density. Preliminary studies indicate that LDH's can be pillared by other POM anions. For instance, we have observed that Keggin ions such as $H_2W_{12}O_{40}^{6-}$ and $BVW_{11}O_{40}^{7-}$ can be successfully intercalated in LDH's, affording derivatives with gallery heights of 9.6 Å. Future studies will focus on the possibility of shape selective catalysis for these new microporous solids.

Acknowledgment. The support of this research by the Michigan State University Center for Fundamental Materials Research and by the National Science Foundation through the Division of Materials Research Grant no. 85-14154 is gratefully acknowledged.

Registry No. ^{51}V, 7440-62-2; N_2, 7727-37-9.

---

[9] Evans, H. T., Jr., *Inorg. Chem.* **1966**, *5*, 967.

[10] (a) Allman, R. *Acta Crystallogr.* **1968**, *1324*, 972. (b) Ingram, L.; Taylor, H. F. W. *Mineral. Mag.* **1967**, *36*, 465.

[11] LDH's with small gallery cations can have appreciable external surface areas if the coprecipitated crystals are small and thin.[12] However, the surface areas observed here for the $V_{10}O_{28}^{6-}$ derivatives are at least four times as large as those for the parent starting materials containing intercalated chloride ions. Surface areas are reported here in m^2/mequiv rather than on a more conventional mass basis in order to compensate for differences in equivalent weights.

[12] (a) Reichle, W. T.; Kang, S. Y.; Everhardt, D. S. *J. Catal.* **1986**, *101*, 352. (b) Reichle, W. T. *Chem. Tech.* **1986**, 58.

[13] Gregg, S. J.; Sing, K. S. W. *Adsorption, Surface Area, and Porosity*, 2nd ed.; Academic Press: 1982.

[14] (a) Hill, C. L.; Bouchard, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 5148. (b) Fox, M. A.; Cardona, R.; Gaillard, E. *J. Am. Chem. Soc.* **1987**, *109*, 6347.

η^1-Coordination versus η^2-Coordination in Transition-Metal Phosphinomethanide Complexes: Synthesis and X-ray Structure of $Cp_2Zr(Cl)[C(PMe_2)(SiMe_3)_2]$

Hans H. Karsch,* Brigitte Deubelly, Josef Hofmann,
Ursula Pieper, and Gerhard Müller

Anorganisch-chemisches Institut
Technische Universität München, Lichtenbergstr. 4
D-8046 Garching, Federal Republic of Germany

Received December 2, 1987

Phosphinomethanides $[R_2PCH_2]^-$ (R = Ph, Me) have been shown to exhibit powerful coordinative ability to transition-metal centers. Frequently, the ligand is formed at the metal center via intramolecular C–H activation of coordinated methylphosphines,[1] but, in other cases, the latter have to be metalated by addition of a strong base.[2] A more general method involves the reaction of lithium phosphinomethanides with metal halides (eq 1).[3,4]

$$M-Cl + LiCH_2PR_2 \rightarrow M-CH_2PR_2 \qquad (1)$$

At coordinatively unsaturated metal centers η^2-coordination of the ligands via their P and carbanionic C atoms occurs spontaneously in most cases, thereby leading to the formation of three-membered rings $\overline{M-C-P}$. This requirement is also met by

---

[1] (a) Karsch, H. H.; Klein, H.-F; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 637. (b) Rathke, J. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1975**, *97*, 3272.

[2] (a) Karsch, H. H.; Klein, H.-F.; Kreiter, C. G.; Schmidbaur, H. *Chem. Ber.* **1974**, *107*, 3692. (b) Abicht, H.-P. *Z. Chem.* **1985**, *25*, 318.

[3] Karsch, H. H.; Schmidbaur, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1977**, *32B*, 762.

[4] Karsch, H. H. *Chem. Ber.* **1984**, *117*, 783.

0002-7863/88/1510-3654$01.50/0

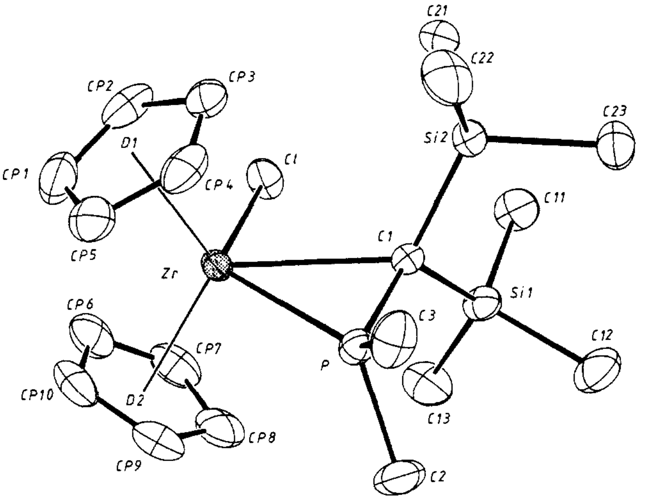
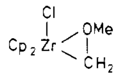


Figure 1. Molecular structure of **4** (ORTEP plot, displacement ellipsoids at the 50% probability level, without hydrogen atoms, D = centroids of the Cp rings). Important distances (Å) and angles (°) are as follows: Zr–Cl, 2.554 (1); Zr–P, 2.606 (1); Zr–C1, 2.607 (3); Zr–D1, 2.23; Zr–D2, 2.26; C1–P, 1.761 (4); C1–Si1, 1.889 (4); C1–Si2, 1.892 (4); Cl–Zr–C1, 81.4 (1); Cl–Zr–P, 120.0 (1); C1–Zr–P, 39.5 (1); D1–Zr–D2, 122.6; Si1–C1–Si2, 106.8 (2); Si1–C1–P, 119.3 (2); Si2–C1–P, 120.3 (2); Si1–C1–Zr, 118.7 (2); Si2–C1–Zr, 118.3 (2); Zr–C1–P, 70.2 (1).

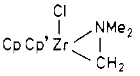
the 16-electron complex Cp_2ZrCl_2, and, consequently, η^2-coordination is also expected for complexes **1** (eq 2).

$$Cp_2ZrCl_2 + LiCH_2PR_2 \rightarrow \underset{\textbf{1a–c}}{Cp_2Zr(Cl)(CH_2PR_2)} \qquad (2)$$

As has been shown by Schore et al., however, in **1a** (R = Ph) the ligand is coordinated monohapto (η^1) via carbon to the zirconium center.[5] This result is even more puzzling, as in similar α-heteroatom substituted zirconium alkyls **2**[6] and **3**,[7] likewise three-membered rings are observed.[8]



2



3

Thorough computational studies suggested the P substituents in **1** exert a decisive influence. The hypothetical complex **1c** (R = H) was predicted to exhibit η^2-coordination (global minimum).[9] In an experimental approach, **1b** (R = Me) was synthesized but again was found to contain η^1-(C) bound phosphinomethanide ligands.[10] This failure and the lack of η^2-coordination in similar complexes[10a,c] led to the conclusion that "it would thus appear that observation of the predicted Zr–P bonding in structures such as these will be an elusive goal".[10c]

In an extensive series of studies, we could show that the coordination behavior of phosphinomethanides toward lithium is not only controlled by the nature of the P but also by that of the C substituents.[11] The P versus C nucleophilicity is enhanced considerably by -$SiMe_3$ or -PMe_2 substituents at the carbanionic carbon atom. With, e.g., $[Me_2P\text{-}C(SiMe_3)_2]^-$ as ligand η^2-coordination therefore was expected to be most favored also at a zirconium center.

Reaction of $Li[Me_2P\text{-}C(SiMe_3)_2]$[12] with Cp_2ZrCl_2 in Et_2O affords **4** (yellow crystals from toluene) in 65% yield (eq 3).[13]

$$Cp_2ZrCl_2 + Li[Me_2P\text{-}C(SiMe_3)_2] \rightarrow \underset{\textbf{4}}{Cp_2Zr(Cl)[Me_2P\text{-}C(SiMe_3)_2]} \qquad (3)$$

The ^{31}P chemical shift (toluene-d_8, 85% H_3PO_4 ext) of the Me_2P group at δ +2.73 indicates P coordination (cf. **1b**: δ P = −36.2;[10a] $Me_2P\text{-}CH(SiMe_3)_2$: δ P = −42.2[12]). The signal is only slightly broadened on cooling to −80 °C, while shifting to +2.17 and, hence, a fluctional behavior in solution is not obvious (but may not be excluded).[13]

X-ray structure determination of **4**[14] (Figure 1) proves the coordination of both the phosphino group and the carbanionic C atom to the Cp_2ZrCl center. The P and C atoms are nearly coplanar with the Cl ligand. The best plane through all three atoms bisects the angle formed by the Cp rings. Several points deserve comment: (i) The heteroatom P occupies a lateral, the carbon atom a central position, which is opposite to the situation as observed in, e.g., **2** or in η^2-acyl complexes $Cp_2Zr(R)COR$. For η^2-**1c** both possibilities (lateral and central P) are predicted to have similar energies.[9] (ii) The Zr–C distance (2.607 (3) Å) is extremely long (cf. **1a**: 2.281 Å; **1b**: 2.272 Å; **2**: 2.271 Å). (iii) The Zr–Cl distance (2.554 (1) Å) is much longer than, e.g., in **1a** (2.453 Å) or **1b** (2.457 Å) but virtually identical with that in **2**, thus reflecting the higher coordination number at the zirconium center. (iv) The Zr–P bond (2.606 (1) Å) is somewhat shorter than the computationally predicted bond for **1c**.[15] The bond P–C1 is significantly shorter (1.761 (4) Å) than P–C2 and P–C3 as well as the respective P–C bonds in **1a** (1.834 Å) or **1b** (1.833 Å). This reflects a residual ylidic character in **4**, as was also observed in other phosphinomethanide complexes with simultaneous phosphorus–metal and carbon–metal interaction.[10a,17]

In summary, complex **4** represents the first example of Zr–P bonding in phosphinomethylzirconium (IV) complexes (η^2-(P,C)-coordination). The three-membered ring formation is induced by the double $SiMe_3$ substitution at the carbanionic C atom of the ligand.

Hence, an increase in the steric bulk of the ligand (in going e.g., from $H_2C\text{-}PMe_2^-$ to $(Me_3Si)_2C\text{-}PMe_2^-$) results in an increase in the coordination number (number of electrons) at the zirconium center (e.g., **1b**: 16e, **4**: 18e). On the other hand, this steric bulk prevents the carbanionic C atom to approach further to the zirconium center. Thus, a perfect η^2-coordination with normal bond lengths is still lacking and probably may be achieved by further optimizing the substitution pattern of the phosphinomethanide ligand. Respective work is in progress.

---

[5] (a) Schore, N. E.; Hope, H. *J. Am. Chem. Soc.* **1980**, *102*, 4251. (b) Schore, N. E.; Young, S. J.; Olmstead, M. M.; Hofmann, P. *Organometallics* **1983**, *2*, 1769.

[6] Erker, G.; Schlund, R.; Krüger, C. *J. Chem. Soc., Chem. Commun.* **1986**, 1403.

[7] Barefield, E. K., private communication (Cp′ = $C_5H_4CPhMe_2$).

[8] Similar Cp$_2$Zr(IV) complexes with sulfur as the heteroatom also seem to have η^2-coordinated ligands: Ward, A. S.; Mintz, E. A.; Ayers, M. R. *Organometallics* **1986**, *4*, 1585.

[9] Hofmann, P.; Stauffert, P.; Schore, N. E. *Chem. Ber.* **1982**, *115*, 2153.

[10] (a) Karsch, H. H.; Müller, G.; Krüger, C. *J. Organomet. Chem.* **1984**, *273*, 195. (b) Engelhardt, L. M.; Jacobsen, C. E.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1984**, 220. (c) Young, S. J.; Olmstead, M. M.; Knudsen, M. J.; Schore, N. E. *Organometallics* **1985**, *4*, 1432.

[11] Karsch, H. H.; Appelt, A.; Deubelly, B.; Müller, G. *J. Chem. Soc., Chem. Commun.* **1987**, 1033 and cited references. Karsch, H. H.; Deubelly, B.; Riede, J.; Müller, G. *J. Organomet. Chem.* **1988**, *342*, C29.

[12] Karsch, H. H.; Deubelly, B., unpublished results.

[13] ^1H NMR (C_6D_6) δ 0.50s (18 H, $SiCH_3$), 1.27 d (6 H, 9.0 Hz, PCH_3), 5.80 d (10 H, 2.0 Hz, C_5H_5); ^{13}C NMR (C_6D_6) δ 9.20 s ($SiCH_3$), 18.28 d (5.3 Hz, PCH_3), 114.06 s (C_5H_5).

[14] Crystal structure determination of **4**. 0.5 toluene: Syntex P2$_1$ diffractometer, Mo Kα radiation, λ = 0.71069 Å, graphite monochromator, T = −40 °C, $C_{19}H_{34}ClPSi_2Zr\cdot 0.5C_7H_8$, monoclinic, space group $P2_1/c$, a = 18.585 (2) Å, b = 8.809 (1) Å, c = 16.102 (2) Å, β = 103.93 (1)°, V = 2558.6 Å^3, D_{calcd} = 1.356 g/cm^3, Z = 4, μ (Mo Kα) = 6.9 cm^{-1}, $F(000)$ = 1092; 4987 measured reflexions, 4517 of which were unique and 3890 "observed" with $F_o \geq 4.0\sigma(F_o)$ $(+h,+k,\pm l$, $(\sin \vartheta/\lambda)_{max} = 0.595$, ω = scan, $\Delta\omega$ = 0.8°). Solution was by Patterson methods. Refinement with anisotropic displacement parameters (H atoms constant) converged at $R(R_w)$ = 0.051 (0.053), $w = 1/\sigma^2(F_o)$ for 229 refined parameters and all unique reflexions. The disordered toluene molecule was treated as a half occupied rigid hexagon with isotropic displacement parameters. The methyl group could not be located, but the presence of benzene can be excluded on the basis of synthesis and analysis. The final difference map had maxima of 1.9 e/Å^3 near the disordered toluene but was featureless otherwise. See note at the end of the paper for Supplementary Material.

[15] Zr–P in η^2-**1c** (computational): 2.67 Å;[9] in $Cp_2(PMe_2)Zr(C_6H_4)$: 2.687 Å.[16]

[16] Buchwald, S. L.; Watson, B. T. *J. Am. Chem. Soc.* **1986**, *108*, 7411.

[17] See, for instance: (a) Karsch, H. H.; Appelt, A.; Müller, G. *Organometallics* **1985**, *4*, 1624. (b) Karsch, H. H.; Appelt, A.; Müller, G. *Organometallics* **1986**, *5*, 1664.

Acknowledgment. H.H.K. thanks the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

Supplementary Material Available: Complete tables of atomic coordinates and displacement parameters (5 pages); lists of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

Methyl Viologen Mediated Oxidation–Reduction Across Dihexadecylphosphate Vesicles Involves Transmembrane Diffusion

Brian C. Patterson, David H. Thompson, and
James K. Hurst*

Department of Chemical and Biological Sciences
Oregon Graduate Center
19600 Northwest Von Neumann Drive
Beaverton, Oregon 97006-1999

Received December 14, 1987
Revised Manuscript Received March 23, 1988

Numerous reports have appeared describing oxidation–reduction across bilayer membranes.[1,2] Mechanisms proposed for specific systems include the following:[1] (i) electron tunneling across the hydrocarbon barrier between interfacially bound redox partners,[3–6] (ii) molecular diffusion of bound redox components across the barrier,[7–9] and (iii) formation of barrier-penetrating aggregates, or electron-conducting "channels", across the bilayer.[10,11] Nonetheless, the actual reaction mechanisms remain obscure due to the general unavailability of transverse diffusion rates, possible loss of compartmentation of reactants, particularly in photochemical systems,[12,13] and the ambiguities inherent in deducing reaction mechanisms from rate data, which form the primary evidence in most systems studied.[1,2] The reactions of dihexadecylphosphate (DHP) vesicle-bound methyl viologen (MV^{2+}) described in this report are unique in allowing deduction of molecular details of a transmembrane redox event from the product composition and microphase distribution. Specifically, we have found that MV^{2+} bound at the outer vesicle interface mediates reduction of inner-localized MV^{2+} by dithionite ion in bulk solution in a manner that requires comigration of MV^{+} with the electron transferred across the membrane barrier.

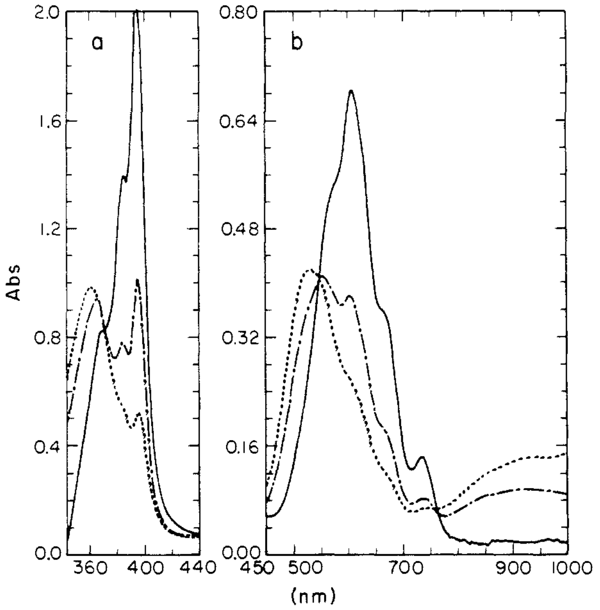


Figure 1. Optical spectra of dithionite-reduced MV^{2+}-DHP vesicles. Conditions: 4 mM DHP in 20 mM Tris, pH 8.0, 23 °C; solid line, 9 μM MV^{2+} outside only; dotted line, 40 μM MV^{2+} on both surfaces; dot-dashed line, 20 μM MV^{2+} inside, 30 μM MV^{2+} outside. All spectra were scaled to a total concentration of 50 μM MV^{+} for comparison purposes.

Vesicles containing widely varying ratios of externally and internally bound MV^{2+} were prepared[14] by sonication of DHP in the presence of MV^{2+} followed by removal of external MV^{2+} by chromatography on cation exchange or dextran gels.[13] After spectrophotometrically determining the amount of occluded MV^{2+}, viologen was readded to the external medium to give the desired inside/outside ratio. Passive diffusion of MV^{2+} across the bilayer is very slow;[13] these ratios are maintained until vesicle integrity is lost by aggregation/fusion processes occurring over a period of several days. Dithionite ion does not penetrate the membrane and is incapable of directly reducing MV^{2+} bound at the opposite vesicle interface. Thus, no MV^{+} was formed when $S_2O_4^{2-}$ was added to vesicle suspensions containing only internal MV^{2+}. Viologen reduction did occur in vesicles containing MV^{2+} bound at only the outer or at both interfaces.[6] When the amount of external MV^{2+} exceeded the internal MV^{2+}, all of the viologen was $S_2O_4^{2-}$-reducible; when the amount of internal MV^{2+} exceeded the external MV^{2+}, only a fraction of the total MV^{2+} equal to twice the external MV^{2+} was reducible. Upon oxygenation, MV^{2+} distributions were redetermined by using the chromatographic/spectrophotometric methods described above. Because O_2 is freely membrane-permeable, the MV^{2+} distribution should closely approximate the original MV^{+} distribution following the reductive reaction. It was found that approximately one MV^{2+} had translocated from outside to inside the vesicle per internal MV^{2+} reduced.[15] Identical results were obtained when Cr^{II}(EDTA) was used in place of $S_2O_4^{2-}$ as the reductant.

The forces driving inward migration of MV^{+} apparently arise from membrane polarization; i.e., in the absence of ion movement, transmembrane electron transfer is electrogenic. Electroneutrality can be restored by diffusion of ions in response to the developing potential; in this instance, lipophilic MV^{+} comigrates with the electron. Addition of 50 μM tetraphenylphosphonium ion as an alternate lipophilic cation decreased the percentage of outer MV^{+} migration by about 30–40%. When $Fe(CN)_6^{3-}$, which is not membrane-permeable, was used in place of O_2 as the oxidant, the

---

(1) Reviews: Hurst, J. K.; Thompson, D. H. P. *J. Membrane Sci.* **1986**, *28*, 3–29. Thompson, D. H. P.; Hurst, J. K. In *Proceedings of the 3rd International Symposium on Molecular Electronic Devices*; Carter, F. L., Siatkowski, R., Eds.; Elsevier: Amsterdam, 1987; in press.

(2) Dannhauser, T. J.; Nango, M.; Oku, N.; Anzai, K.; Loach, P. A. *J. Am. Chem. Soc.* **1986**, *108*, 5861–5871.

(3) Mettee, H. D.; Ford, W. E.; Sakai, T.; Calvin, M. *Photochem. Photobiol.* **1984**, *39*, 679–683, and earlier references cited therein.

(4) Ford, W. E.; Tollin, G. *Photochem. Photobiol.* **1983**, *38*, 441–449.

(5) Lee, L. Y. C.; Hurst, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 7411–7418.

(6) Thompson, D. H. P.; Barrette, W. C., Jr.; Hurst, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 2003–2009.

(7) Tabushi, I.; Kugimiya, S. *J. Am. Chem. Soc.* **1985**, *107*, 1859–1863.

(8) Runquist, J. A.; Loach, P. A. *Biochim. Biophys. Acta.* **1981**, *637*, 231–244.

(9) Khramov, M. I.; Lymar, S. U.; Parmon, V. N.; Zamaraev, K. I. *Dokl. Phys. Chem.* (*Engl. Trans.*) **1987**, *289*, 598–601.

(10) Tabushi, I.; Nishiya, T.; Shimomura, M.; Kunitake, T.; Inokuchi, H.; Tatsuhiko, K. *J. Am. Chem. Soc.* **1984**, *106*, 219–226.

(11) Yusupov, R. G.; Asanov, A. N.; Khairutdinov, R. F. *Izv. Akad. Nauk SSSR Ser. Khim.* **1985**, 277–282.

(12) This phenomenon, first demonstrated in DHP vesicles binding both MV^{2+} and photosensitizers,[13] also occurs in pigmented phosphatidylcholine vesicles (Kuhn, E., unpublished results).

(13) Lee, L. Y. C.; Hurst, J. K.; Politi, M.; Kurihara, K.; Fendler, J. H. *J. Am. Chem. Soc.* **1983**, *105*, 370–373.

(14) Hurst, J. K.; Thompson, D. H. P.; Connolly, J. S. *J. Am. Chem. Soc.* **1987**, *109*, 507–515.

(15) When $S_2O_4^{2-}$ was in large excess and the initial external/internal MV^{2+} ratio exceeded unity, the amount of translocated MV^{+} was greater than the initial internal MV^{2+} concentration. Under these conditions, translocation of the additional MV^{+} was $S_2O_4^{2-}$ concentration-dependent, suggesting that it arose by additional transmembrane redox cycling during aerobic oxidation of the system.