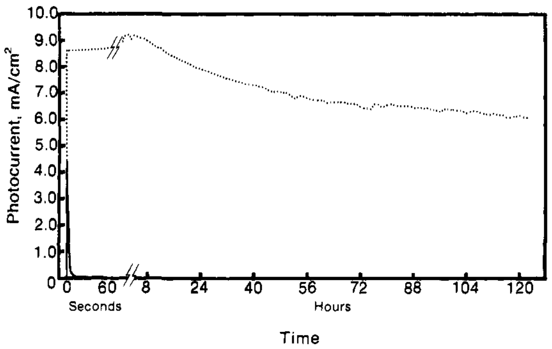

Figure 2. Photocurrent–time behavior of naked (—) and polypyrrole-covered (• • •) polycrystalline n-type Si electrodes illuminated with tungsten–halogen light at 143 mW/cm² under short-circuit conditions. Solution containing 0.15 M $\mathrm{FeSO_4}$, 0.15 M $\mathrm{FeNH_4(SO_4)\cdot 12H_2O}$ and 0.1 M $\mathrm{Na_2SO_4}$ in water at pH 1 was stirred continuously. No precaution was taken to exclude air.

with an average conversion efficiency of 10% at AM 1 reported[7] for polycrystalline silicon grown similarly to that used in this work and employed in a solid-state p–n junction cell. The thickness of the film was calculated to be 1200 Å. Presumably, a thinner film would result in a higher current density.

The current–time behavior (Figure 2) of the polypyrrole-coated n-type Si photoanode in aqueous solution containing a $\mathrm{Fe^{3+}/Fe^{2+}}$ redox couple contrasts dramatically with that of unprotected naked n-type Si. The photocurrent of the naked electrode drops precipitiously to zero from its initial value in less than 30 s. However, the photocurrent of the polypyrrole-coated n-type Si first increased by ca. 6% over the first 5 h followed by decay. During 122 h of irradiation (143 mW/cm² of unfiltered light from a tungsten–halogen lamp) the photocurrent decayed by only ca. 30%. No precaution was taken to exclude air from the photoelectrochemical cell, and there were no signs that the polypyrrole film was peeling off the electrode or dissolving into solution after the passage of ca. 3100 C/cm² at a current density between 6 and 9.2 mA/cm². The magnitude of the charge density is particularly noteworthy, since less than 10 mC/cm² is required to form the film. The detailed mechanism for the stability[8] produced by polypyrrole films is currently being investigated. The good adhesion and induced stability characteristics of the electrode system are also representative of other polypyrrole-covered electrodes that we have studied.

In conclusion, polypyrrole polymer films have been shown to produce a dramatic improvement in the stability of n-type Si against photooxidation in aqueous electrolyte. The polymer film is very easy to apply to the semiconductor electrode and exhibits excellent adhesion. Other n- and p-type semiconductors are being examined with polypyrrole films. The mechanism by which the conducting polymer films stabilize semiconductors is also under investigation.

Acknowledgment. We gratefully acknowledge J. A. Turner for the determination of the flatband potential of the polycrystalline n-type Si and T. F. Ciszek and J. L. Hurd for kindly providing us with the material. This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences and the Secretariat of Conservation and Solar Energy, U.S. Department of Energy, under Contract EG-77-C-01-4042.

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(8) A referee proposed that the stability of the polypyrrole-coated electrode arises from iron–pyrrole complexes which produce a high concentration of oxidizable $\mathrm{Fe^{2+}}$ ions at the film–electrode interface. The $\mathrm{Fe^{2+}}$ ions compete with oxide formation, and the film behaves only as an inert matrix that does not conduct photogenerated holes. The suggestion of a complex with polypyrrole can be dismissed because polypyrrole-coated n-GaAs exhibits stability with $\mathrm{Fe(CN)_6{}^{3-/4-}}$ and with $\mathrm{Fe^{III}EDTA/Fe^{II}EDTA}$ redox couples as described in ref 5. We believe, however, that both charge conduction by the film and the availability of oxidizable $\mathrm{Fe^{2+}}$ species are important in the stabilization of n-type Si.

Low-Valent Molybdenum Porphyrin Derivatives: Synthesis and Structure of a π-Bonded Diphenylacetylene Adduct of Molybdenum(II) (*meso*-Tetra-*p*-tolylporphyrin)

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Metalloporphyrin derivatives in which olefins or acetylenes are π bonded to the central metal have been postulated as transient intermediates during the formation of σ carbon–metal bonds with metalloporphyrins.[1] To our knowledge no such compound has ever been characterized. We report now the preparation and structural characterization of a novel molybdenum(II) porphyrin derivative $\mathrm{[MoTTP(PhC{\equiv}CPh)]\cdot C_6H_5CH_3}$ (**1**) in which a diphenylacetylene molecule is π bonded to the metal atom enclosed in the porphyrin ring. Moreover, the acetylenic carbon–carbon and the carbon-to-metal bond distances present in **1** indicate by comparison with the same structural parameters present in $(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{Mo(PhC{\equiv}CPh)}$ (**2**)[2] that the acetylenic group acts as a four-electron donor in **1**. It can only act as a two-electron donor in **2**.[3]

Reduction by lithium aluminum hydride of a toluene solution (50 mL) containing $\mathrm{Mo^{IV}(TTP)Cl_2}$[4] (100 mg), an excess of diphenylacetylene (100 mg), and a few drops of THF led to a green solution after 1 h of vigorous stirring. After the solvents were evaporated under vacuum, the residue was eluted on alumina with toluene. A violet compound **1** $\mathrm{[MoTTP(PhC{\equiv}CPh)]\cdot C_6H_5CH_3}$ was crystallized from this solution by addition of pentane (25 mL). [Visible spectral data in benzene: λ (log ε) 426 (5.20), 544 (3.98), 624 nm (3.36)]. Complex **2** $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{(PhC{\equiv}CPh)}]$ was prepared by the method of A. Nakamura and S. Otsuka.[2]

Crystals suitable for X-ray studies were obtained for complex **1** by slow diffusion of pentane into a toluene solution of the complex and for compound **2** by slow diffusion of pentane into a chlorobenzene soluton.[5,6]

The structure of **1** is shown in Figure 1. The geometry about the metal is best described as pseudo square pyramidal with the four porphynato nitrogens $\mathrm{N_p}$ constituting the basal plane and the middle of the acetylenic carbon–carbon triple bond occupying the apical position. The molybdenum(II) atom is displaced out of the 4-nitrogen $\mathrm{N_p}$ plane by 0.63 Å and by 0.73 Å from the mean plane of the 24-atom core. Thus a net doming is present; yet two opposite pyrrole rings $\mathrm{N_1}$ and $\mathrm{N_3}$ tilt upward out of the mean plane toward the molybdenum(II) atom, while the $\mathrm{N_2}$ and $\mathrm{N_4}$ pyrrole rings tilt downward.[7] The conformation of the core presents thus

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(1) I. Ogoshi, J. I. Setsune, Y. Nambo, and Z. I. Yoschida, *J. Organomet. Chem.* **1978**, *159*, 329.

(2) A. Nakamura and S. Otsuka, *J. Am. Chem. Soc.*, **1972**, *94*, 1886.

(3) $\mathrm{(C_5H_5)_2Mo(PhC{\equiv}CPh)}$ is an 18-electron species when the acetylenic group donates two electrons to the metal. MO treatment is similar to that for olefin complexes as discussed by R. Hoffmann and J. W. Lauher, *J. Am. Chem. Soc.*, **1976**, *98*, 1729; see also H. H. Brintzinger, L. L. Lohr, J. Tang Wong, and K. L. Tang Wong, *J. Am. Chem. Soc.*, **1975**, *97*, 5146.

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(5) $\mathrm{Mo(TTP)(PhC_2Ph)(CH_3C_6H_5)}$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 21.815$ (4), $\beta = 16.414$ (3), $c = 15.055$ (3) Å; $\beta = 94.08$ (6)°; $Z = 4$, $V = 5377$ Å³. The calculated density based on four molecules ($\mathrm{C_{69}H_{54}N_4Mo}$, M = 1035.2) per unit cell is 1.28 g/cm³. The data were collected in the range $2.5 < \theta < 57°$ by a flying step scan technique using Cu Kα radiation on a Philips PW1100 diffractometer. Independent reflections (5825) corrected for absorption were coded as observed $[I > 3\sigma(E)]$. All nonhydrogen atoms were given anisotropic temperature factors to yield, after introduction of the hydrogen atom positions, R = 0.075, $Rw = 0.105$.

(6) $\mathrm{Cp_2MoC_2(C_6H_5)_2}$ belongs to the orthorhombic space group *Pbcn* with $a = 22.042$, $b = 13.017$, $c = 12.689$ Å; $V = 3640.7$ Å³, $Z = 8$. Data were collected by using Cu Kα radiation in the range $2° < \theta < 60°$ with a Philips PW1100 diffractometer. Reflections (1902) with $I > 3\sigma(I)$ were used in refinement ($R = 0.050$, $Rw = 0.079$).

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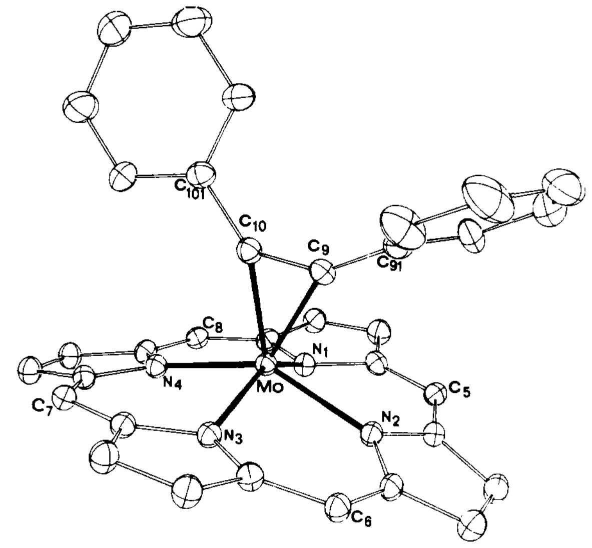

Figure 1. ORTEP drawing of Mo(TTP)(PhC_2Ph). All atoms are represented by 50% probability thermal ellipsoids. For clarity the phenyl groups of the porphyrin were omitted. Main distances (Å) are $Mo–N_1$, 2.104 (3); $Mo–N_2$, 2.150 (3); $Mo–N_3$, 2.105 (3); $Mo–N_4$, 2.147 (3); $Mo–C_9$, 1.983 (4); $Mo–C_{10}$, 1.965 (4); $C_9–C_{10}$, 1.324 (5); $C_{10}–C_{101}$, 1.485 (5); $C_9–C_{91}$, 1.455 (5). Main angles (deg) are $N_1–Mo–N_4$, 85.1 (1); $N_2–Mo–N_4$, 145.1 (1); $N_2–Mo–N_3$, 85.2 (1); $N_3–Mo–N_4$, 84.6 (1); $C_9–C_{10}–C_{101}$, 136.4 (4); $C_{10}–C_9–C_{91}$, 145.4 (4).

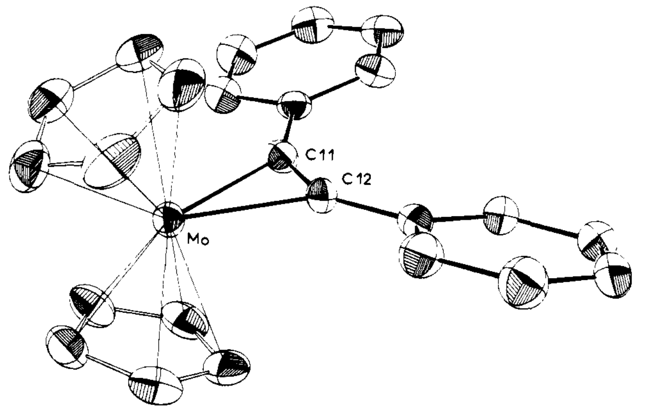

Figure 2. ORTEP drawing of $(C_5H_5)_2Mo(C_6H_5)_2C_2$. Main distances (Å) are Mo–C11, 2.143 (6); Mo–C12, 2.144 (6); C11–C12, 1.269 (7). Average C–C distances (Å) are phenyl rings, 1.39 ± 0.01; Cp rings 1.42 ± 0.03; $Mo–C_5H_5$ distances range from 2.14 to 2.35.

the shape of a flattened saddle. The acetylenic carbon–carbon bond eclipses almost perfectly the opposite $Mo–N_2$ and $Mo–N_4$ bonds.[8] Thus the $Mo–N_p$ bonds are not equivalent: while the two staggered $Mo–N_p$ bond distances are equal to 2.104 (3) and 2.105 (3) Å, the two eclipsed $Mo–N_p$ bond lengths are 2.150 (3) and 2.147 (3) Å.

Evidence has been provided recently that it is possible for an acetylenic ligand to donate more than two electrons to the metal center in a mononuclear complex.[9-12] It has also been shown that the acetylenic carbon–carbon bond length provides a poor estimate of the number of electrons donated from acetylene to metal, a better indication being metal–carbon distances.[9] The values found in complex **1** for these bond distances: $Mo–C_9 = 1.983$ (4), $Mo–C_{10} = 1.965$ (4), and $C_9–C_{10} = 1.324$ (5) Å suggest that the acetylenic group acts as a four-electron donor, the metal to carbon bond distances being the shortest ever found in an acetylenic complex of molybdenum.[9] The same conclusion is reached by comparison with the structure of **2**: $(\eta\text{-}C_5H_5)_2Mo(PhC{\equiv}CPh)$. **2** is an 18-electron species if the acetylenic moiety donates two electrons. While the molybdenum–acetylenic bond distances are equal to 2.143 (5) and 2.144 (5) Å, the acetylenic carbon–carbon bond length is 1.27 (1) Å.

Simple molecular symmetry arguments also support the same conclusion. Complex **1** is diamagnetic and Mo(II) has formally a spin-paired $4d^4$ electronic configuration. With C_{2v} symmetry for the coordination sphere of molybdenum, the 24-atom core of the porphyrin ring being the xy plane, the metal atom located on the z axis, and the acetylenic C≡C group parallel to x axis, most probably the $4d_{xy}$ and $4d_{xz}$ metal orbitals are doubly occupied. The empty $4d_{yz}$ orbital is thus able to accept π electron density from the acetylenic group by interaction with one bonding orbital π_{u2} in addition to that coming from π_{u1}, by interaction with d_{z^2}. Furthermore the back-donation from the metal to the acetylenic moiety can be realized by interaction of the filled $4d_{xz}$ metal orbital and one π_g antibonding orbital of the acetylenic group. The geometry of **1** is thus compatible with the donation from both of the filled acetylene π_u bonding orbitals by interaction between $4d_{z^2}–\pi_{u1}$ and $4d_{yz}–\pi_{u2}$, with an acetylenic ligand acting as a four-electron donor.

Acknowledgment. This work was supported in part by the C.N.R.S. (Equipe de Recherche Associée 08).

Supplementary Material Available: Complete listings of atomic coordinates and thermal parameters for **1** (Table I) and **2** (Table II) and computed and observed structure factor amplitudes for **1** (Table III) and **2** (Table IV) (40 pages). Ordering information is given on any masthead page.

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Enantiospecific Total Synthesis of Dendrobatid Toxin 251D. A Short Chiral Entry to the Cardiac-Active Pumiliotoxin A Alkaloids via Stereospecific Iminium Ion-Vinylsilane Cyclizations

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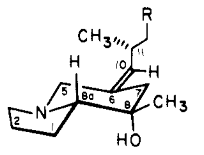
Received December 1, 1980

Recently, Daly and co-workers reported[1] the crystallographic structure determination of the dendrobatid toxin 251D (**1**), which was isolated from the Ecuadoran poison-dart frog, *Dendrobates tricolor*. Analysis of mass and magnetic resonance spectra allowed



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2, R = CH_2CH_3

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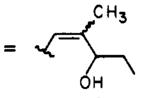

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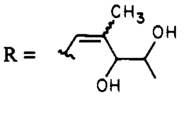

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