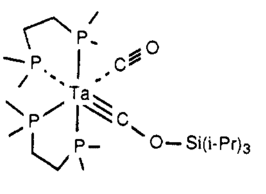
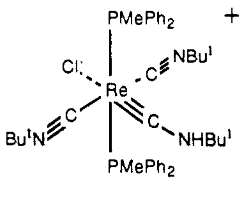
Figure 1 displays the structures of 6[8] and 7,[9] including some metrical data. The Ta–C bond length of 1.85 (1) Å in 6 is identical with the value reported for the alkylidyne complex $[Ta(CPh)(\eta\text{-}C_5H_5)(PMe_3)Cl]$[10] and appreciably shorter than distances found for compounds having tantalum–carbon single (2.25–2.32 Å) and double (2.01–2.03 Å) bonds.[11] The C–$OSiR_3$ distances of 1.34 (1) Å in 5 and 6 are significantly longer than the respective values of 1.17 (1) and 1.20 (1) Å for the C–O bond lengths in the terminal carbonyl ligands, further substantiating the assignment of these molecules as trialkylsiloxycarbynes ($M{\equiv}C\text{-}OSiR_3$). Similar arguments may be used to assign cation 7 as an alkylaminocarbyne, the Re≡C bond length of 1.82 (1) Å being close to the 1.80 (3) Å value previously reported for *trans*-$[Re(CNHMe)(dppe)_2Cl](BF_4)$.[12] The strong trans influence of the M≡C bond in these complexes is nicely illustrated by the 0.13 Å average increase in the trans compared to the cis M–P distances in 5 and 6. Four multiplets in the ^{31}P NMR spectrum of 6[5] dissolved in benzene-d_6 can be fit to an ABMX splitting pattern, indicating that the solid-state structure is retained in solution.



6



7

Coupling of the carbyne and carbonyl ligands in 5 and 6 was accomplished by allowing them to react in THF or glyme with 1 equiv of either Me_3SiCl or $(i\text{-}Pr)_3Si(OTf)$, eq 4. Coupling of

$$[M(CO)\{COSi(i\text{-}Pr)_3\}(dmpe)_2] + R_3SiY \rightarrow [M\{R_3SiOCCOSi(i\text{-}Pr)_3\}(dmpe)_2Y] \quad (4)$$

$$M = Nb, Ta;\ R = Me,\ Y = Cl;\ R = i\text{-}Pr,\ Y = OTf$$

carbonyl with carbyne ligands has been observed for a number of tungsten complexes.[13] Attempts to achieve isocyanide–carbyne coupling by addition of excess HX (X = Cl, Br, or I) to solutions of 7 resulted in no reaction for X = Cl and halide exchange for X = Br or I. Nevertheless, isolation of 7 and 8 under reductive coupling conditions used in analogous Mo(II) and W(II) chemistry (eq 1 and 2)[1,2] and the identification of 5 and 6 as intermediates in eq 3 strongly suggest that alkylaminocarbynes are involved in the reductive coupling of isocyanides.

In conclusion, we find that the reductive coupling of carbon monoxide in $[M(CO)_2(dmpe)_2Cl]$, M = Nb, Ta, to form coordinated bis(trialkylsiloxy)ethyne proceeds through siloxycarbyne intermediates. Although conversion of a thiocarbonyl ligand into a mercaptocarbyne by electrophilic attack at sulfur is known,[14] the present examples are the first where a carbonyl ligand has been so converted into an oxycarbyne bound to a single metal center. This discovery might provide some insight into the chemistry of other CO conversions, such as the Fischer–Tropsch reaction.

Acknowledgment. This work was supported by a grant from the National Science Foundation (NSF-CHE-8711212). We thank Dr. A. Mayr and R. B. Klassen for helpful discussions and Dr. T. H. Tulip for a generous supply of $[Re(CNR)_3(PMePh_2)_2Cl_2]Cl$.

Registry No. 1, 66507-17-3; **2**, 61916-36-7; **5**, 113380-13-5; **6**, 113380-14-6; **7**, 113380-16-8; *cis*-$[Ta(CO)_2(dmpe)_2]Na$, 61916-37-8; *cis*-$[Nb(CO)_2(dmpe)_2]Na$, 113380-12-4; $[Re(CN\text{-}t\text{-}Bu)_3(PMePh_2)_2Cl_2]Cl$, 113380-17-9; $[Nb\{Me_3SiOCCOSi(i\text{-}Pr)_3\}(dmpe)_2Cl]$, 113380-18-0; $[Ta\{Me_3SiOCCOSi(i\text{-}Pr)_3\}(dmpe)_2Cl]$, 113380-19-1; $[Nb\{(i\text{-}Pr)_3SiOCCOSi(i\text{-}Pr)_3\}(dmpe)_2OTF]$, 113380-20-4; $[Ta\{(i\text{-}Pr)_3SiOCCOSi(i\text{-}Pr)_3\}(dmpe)_2OTF]$, 113380-21-5; $(i\text{-}Pr)_3SiCl$, 13154-24-0; Me_3SiCl, 75-77-4; $(i\text{-}Pr)_3Si(OTF)$, 80522-42-5.

Supplementary Material Available: Atomic positional and thermal parameters for **5**, **6**, and **7** (6 pages). Ordering information is given on any current masthead page.

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(7) Anal. Calcd for $C_{41}H_{54}N_3P_2ClReSbF_6$: C, 44.44; H, 4.91; N, 3.79. Found: C, 43.27, 45.36; H, 4.98, 4.93; N, 3.88, 3.69. Spectroscopic data: FTIR (KBr) 2147 (s), 1588 (s) cm^{-1}; ^1H NMR (90 MHz, CD_2Cl_2) δ 0.65 (s, 9 H, $CNH(CH_3)_3$, 1.14 (s, 18 H, $CN(CH_3)_3$), 2.25 (virtual t, 6 H, PCH_3), 4.52 (br, 1 H, CN*H*-*t*-Bu), 7.40–7.46 (m, 20 H, $P(C_6H_5)$); $^{13}C\{^1H\}$ NMR (75.43 MHz, CD_2Cl_2) δ 16.58 (virtual t, PCH_3), 29.57 (s, $CNHC(CH_3)_3$), 29.94 (s, $CNC(CH_3)_3$), 58.32 (s, $CNCMe_3$ and $CNHCMe_3$), 128.74 (virtual t, P-*m*-Ph), 130.34 (s, P-*p*-Ph), 132.58 (virtual t, P-*o*-Ph), 136.03 (virtual t, P-ipso-Ph), 143.15 (t, $^2J_{PC}$ = 9.1 Hz, $CNCMe_3$), 227.54 (t, $^2J_{PC}$ = 11.3 Hz, CNH-*t*-Bu); $^{31}P\{^1H\}$ NMR (36.6 Hz, CD_2Cl_2) δ −11.0.

(8) Crystal data for **6**: $C_{23}H_{53}O_2P_4SiTa$, M_r = 694.6, monoclinic, space group $P2_1/c$, a = 9.836 (2) Å, b = 30.154 (4) Å, c = 12.248 (2) Å, β = 112.53 (2)°, V = 3355.4 Å^3, Z = 4, ρ_{calcd} = 1.375 g cm^{-3}; R_F = 0.048. The Nb analogue is isomorphous [a = 9.821 (4) Å, b = 30.273 (7) Å, c = 12.236 (3) Å, β = 112.47 (2)°, V = 3361.5 Å^3; R_F = 0.046]. Some disorder occurs for the isopropyl and dmpe ethylene groups in both structures and refinement is continuing. Full details will be reported elsewhere.

(9) Crystal data for **7**: $C_{41}H_{54}N_3P_2ClSbF_6Re$, M_r = 1108.2, monoclinic, space group $P2_1/c$, a = 15.378 (3) Å, b = 18.731 (3) Å, c = 16.225 (3) Å, β = 95.94 (1)°, V = 4648.4 Å^3, Z = 4 ρ_{calcd} = 1.584 g cm^{-3}, ρ_{obsd} = 1.58 (1) g cm^{-3}; R_F = 0.042. Details will be described in a separate report.

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Intramolecular Excited-State Electron Transfer in a Covalently Linked Porphyrin-Viologen Molecule: Direct Observation of the Charge-Separated Intermediate by Resonance Raman Spectroscopy

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We wish to report the observation of intramolecular excited-state electron transfer in porphyrin–viologen 1 by resonance Raman (RR) spectroscopy. The literature contains numerous examples of photochemical studies of porphyrins covalently linked to various electron acceptor units.[2-4] Other workers have investigated long-range excited-state electron transfer in rigid model systems.[5] In many instances, electron-transfer quenching of the porphyrin excited state has been inferred from fluorescence quenching experiments or lifetime measurements.[2] Both

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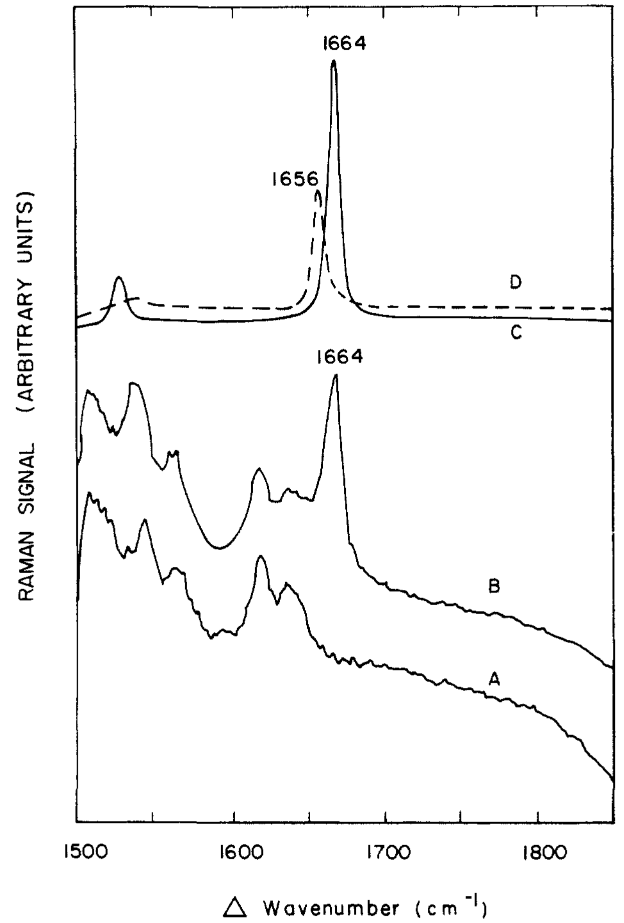
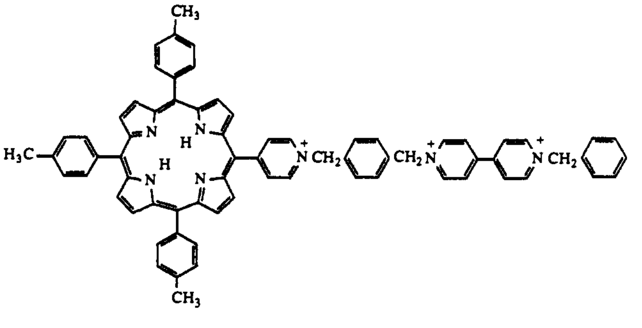


Figure 1. Raman spectra from pulsed-laser excitation (354.7 nm, 10 ns, 3 mJ) of freeze–pump–thaw degassed samples in CH_3CN sealed in Pyrex tubes: (A) porphyrin **2** (3.02×10^{-3} M), (B) porphyrin–viologen **1** (2.91×10^{-3} M), (C) $Bz_2V^{\bullet+}$ (3.45×10^{-3} M), (D) Bz_2V^{2+} (3.45×10^{-3} M). The lower signal-to-noise ratio in A and B is due to the extremely high optical density of the solutions owing to porphyrin absorption.

fluorescence quenching and shortened lifetimes may result from processes other than electron transfer, however. Direct evidence for excited-state electron transfer requires techniques such as absorption spectroscopy[3] or ESR spectroscopy.[4] For example, in a series of porphyrin–viologen molecules related to **1** it was found that fluorescence quenching does occur, but the data were inconclusive with respect to whether the quenching results in electron transfer to the viologen center.[2c] We now describe a study in which we correlate the typical fluorescence and lifetime quenching studies with direct observation of electron transfer by the vibrational spectroscopic technique of RR spectroscopy.[6]

We chose to study a system containing a dibenzylviologen (*N*,*N*′-dibenzyl-4,4′-bipyridinium; Bz_2V^{2+}, **3a**) electron acceptor,



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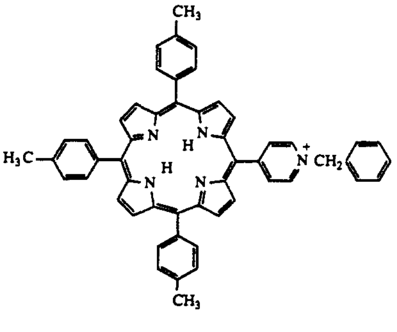

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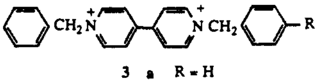

3 **a** R = H
b R = $-CH_2Br$

because the reduced viologen, $Bz_2V^{\bullet+}$ is easily detected by RR spectroscopy.[7] Importantly, the porphyrin–viologen system appears to yield relatively long-lived charge-separated species following photoexcitation.[2c] Our target molecule, **1**, can be prepared by reaction of pyridyltritolylporphyrin[8] with benzyl(4-bromomethylbenzyl)viologen (**3b**) or by stepwise reaction of pyridyltritolylporphyrin with α,α'-dibromo-*p*-xylene, 4,4′-bipyridine, and benzyl bromide. Either method gives **1** with identical ^{1}H NMR spectra, UV-vis absorption spectra, and FAB mass spectra.[9] Additionally, **1** is easily elaborated to include functional groups for oriented attachment to surfaces. We prepared porphyrin **2** as a model for **1** which lacks the viologen electron acceptor subunit.[10] The absorption spectrum of **1** is the simple sum of

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(9) **1** (tris PF_6^- salt): ^{1}H NMR (250 MHz, Me_2SO-d_6) δ −2.92 (s, 2 H), 2.68 (s, 9 H), 5.93 (s, 2 H), 6.03 (s, 2 H), 6.18 (s, 2 H), 7.47 (m, 3 H), 7.60 (m, 2 H), 7.65 (AB, 6 H), 7.83 (AB, 2 H), 7.96 (AB, 2 H), 8.10 (AB, 6 H), 8.7–9.0 (m, 12 H), 9.08 (AB, 2 H), 9.51 (AB, 2 H), 9.58 (dd, 4 H); UV–vis (CH_3CN) λ_{max} (log ϵ) 260 (4.60), 418 (5.32), 518 (4.18), 556 (4.00), 558 (3.79), 648 (3.77) nm; FAB MS (glycerol–sulfolane matrix) m/z = 1151 (**1** − $2PF_6^-$ − $2H^+$).

(10) **2** (PF_6^- salt): ^{1}H NMR (250 MHz, Me_2SO-d_6) δ −2.90 (s, 2 H), 3.39 (s, 9 H), 6.18 (s, 2 H), 7.65 (m, 9 H), 7.87 (d, 2 H), 8.10 (AB, 6 H), 8.8–9.1 (m, 10 H), 9.63 (AB, 2 H); UV–vis (CH_3CN) λ_{max} (log ϵ) 260 (4.15), 418 (5.34), 518 (4.18), 554 (4.04), 592 (3.79), 650 (3.76). **3a** (bis PF_6^- salt): ^{1}H NMR (250 MHz, Me_2SO-d_6) δ 5.98 (s, 4 H), 7.45 (m, 6 H), 8.77 (AB, 4 H), 9.56 (AB, 4 H); UV–vis (CH_3CN) λ_{max} (log ϵ) 260 nm (4.36).

the absorption spectra of **2** and **3a**.[10] This indicates the absence of any ground-state electronic interaction between the electron donor (porphyrin) and electron acceptor (viologen) subunits. The UV-vis spectra of **1** and **2** are each unchanged at concentrations ranging from 2×10^{-7} M (10-mm cell) to 6×10^{-3} M (0.1-mm cell), suggesting the absence of aggregation in this concentration range. Electrochemical reduction of **1** (1.46×10^{-3} M, 0.1 M $[n\text{-}Bu_4N]ClO_4/CH_3CN$, Pt wire electrode) in a solution containing an equimolar concentration of ferrocene (as an internal standard) shows a reversible, one-electron process ($E^{0\prime} = -0.32$ V versus Ag/AgCl), which is essentially the same as observed for **3a**.[11] Electrochemical reduction of **1** results in a decrease in the 260-nm UV absorption (due to the Bz_2V^{2+} moiety) and appearance of a visible absorption (~600 nm) due to the $Bz_2V^{\bullet +}$ moiety. The 390-nm absorption of $Bz_2V^{\bullet +}$ is masked by the Soret absorption of the porphyrin. All spectral and electrochemical data for **1** are thus consistent with the conclusion that **1** represents a simple admixture of porphyrin and viologen.

A Stern-Volmer analysis shows that **3a** can effectively quench the fluorescence of **2**.[12] Quenching presumably occurs by electron transfer with a value for $k_q\tau$ of 46 M^{-1}. **1** exhibits diminished fluorescence ($\Phi_{rel} = 0.74$) compared with **2** ($\Phi_{rel} = 1.0$).[13] The decay of the fluorescence of **1** and **2** was monitored following pulsed-laser excitation at 337 nm.[14] This experiment directly gives lifetimes of 5.3 ± 1.0 ns for **1** and 9.0 ± 1.0 ns for **2**. The lifetimes are independent of concentration in the range 2.9×10^{-6}–2.9×10^{-4} M, thereby ruling out static quenching due to aggregation. Given that the shorter lifetime of **1** relative to **2** is due to electron transfer (vide infra), we calculate a rate constant for electron transfer $k_{et} = 1/\tau_{P\text{-}V} - 1/\tau_P = {\sim}8 \times 10^7\ s^{-1}$. This relatively small value of k_{et} is consistent with the low driving force ($\Delta G^0 \sim -0.4$ eV)[15] and the large distance of the electron transfer.[2d,5,16]

For the RR studies, we employed the pulsed Raman spectrometer described previously.[6b,c] A single 10-ns pulse serves to both photoexcite the sample and perform the Raman scattering experiment. If electron transfer occurs within the pulsewidth, the charge separated intermediate can be observed by RR spectroscopy. Pulsed-laser excitation (354 nm, 10 ns pulse, 3 mJ per pulse at the sample, 10 Hz repetititon rate) of a 2.91×10^{-4} M solution of **1** in CH_3CN yields a RR spectrum which contains all of the bands appearing in the RR spectrum of porphyrin **2**, plus an additional strong band at 1664 cm^{-1}, Figure 1. The new band corresponds precisely to the most intense band in the RR spectrum of an authentic sample of $Bz_2V^{\bullet +}$ (prepared either chemically with Zn dust or electrochemically). However, the band at 1664 cm^{-1} is also very close to the most intense band (1656 cm^{-1}) in the weakly resonance-enhanced Raman spectrum of the nonreduced viologen, Bz_2V^{2+} (**3a**). Two additional experiments remove any ambiguity regarding the assignment of the 1664-cm^{-1} band. First, the RR spectrum of a sample of **1** reduced by one electron, prepared by bulk electrolysis of **1** (1.46×10^{-4} M, 0.1 M $[n\text{-}Bu_4N]ClO_4/CH_3CN$; −0.5 V versus Ag/AgCl, Pt foil electrode), displays a band at precisely 1664 cm^{-1}, characteristic of $Bz_2V^{\bullet +}$. Second, a solution containing a mixture of **2** (3.02×10^{-4} M) and **3a** (2.87×10^{-3} M) gives a RR spectrum containing both Bz_2V^{2+} (1656 cm^{-1}) and $Bz_2V^{\bullet +}$ (1664 cm^{-1}). We thus conclude with certainty that the feature at 1664 cm^{-1} in the RR spectrum of **1** is due to $Bz_2V^{\bullet +}$. Moreover, this experiment shows the fluorescence quenching of **2** by **3a** to occur via excited-state electron transfer. Since the UV-vis spectra and fluorescence lifetime measurements rule out aggregation and since bimolecular processes in homogeneous solution cannot account for either the steady-state (Φ_0/Φ) or dynamic (τ_0/τ) quenching values of **1** compared to **2**, we conclude that the excited-state electron transfer in **1** to give $Bz_2V^{\bullet +}$ is an *intra*molecular process. We have not yet characterized spectral features attributed to the oxidized porphyrin center.

In summary, excitation of porphyrin-viologen **1** leads to intramolecular electron-transfer quenching of the porphyrin singlet excited state. For related porphyrin-viologen molecules it has already been established that the triplet excited state does yield electron transfer to the linked viologen.[2c] These findings are necessary first steps in designing photosensitive interfaces for optical energy conversion. Derivatives of **1** have been prepared to orient the molecules on a surface and to explore interfacial excited-state electron transfer.[17]

Acknowledgment. We thank the United States Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences for support of this research. We also thank Dr. Nicholas Leventis for helpful discussions.

Registry No. **1**·$3Br^-$, 113508-95-5; **1**·$3PF_6^-$, 113508-99-9; **1**·$3PF_6^-$ ($Bz_2V^{\bullet +}$), 113509-04-9; **2**·PF_6^-, 113509-01-6; **3a**·$2PF_6^-$, 68136-91-4; **3b**·$2Br^-$, 113508-97-7; pyridyltritolylporphyrin, 113508-96-6; *α,α′*-dibromo-*p*-xylene, 623-24-5; 4,4′-bipyridine, 553-26-4.

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[11] The second reduction of the viologen moiety of **1** overlaps the ring reduction of the free-base porphyrin moiety near −0.8 V versus Ag/AgCl. Irreversible porphyrin oxidation of **1** occurs at +1.2 V versus Ag/AgCl.

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[13] Optical densities of dilute solutions (ca. 2×10^{-7} M) of **1** and **2** in CH_3CN were matched at the excitation wavelength (420 nm). Samples were degassed with three freeze–pump–thaw cycles and were sealed under vacuum. Emission maxima occur at 655 and 715 nm at room temperature.

[14] The excitation source is a pulsed N_2 laser with a nominal pulse width of 12 ns. The emission signal is observed at 90° with an ISA Model H-20 monochromator and detected with an RCA IP28 PMT wired for fast pulse response. The PMT signal is processed by a PAR 162/165 boxcar averager and displayed on an X-Y recorder and passed to an IBM XT-compatible computer. Iterative least-squares reconvolution assuming single-exponential decay was used to determine the lifetime.

[15] Calculated from $\Delta G^0 = E_{1/2}\,(P^{0/+}) - E_{h\nu} - E_{1/2}(Bz_2V^{2+/+}) = +1.2\ V - 1.9\ V + 0.3\ V = -0.4\ V$. $E_{h\nu}$ is the singlet excitation energy (650 nm).

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A New Class of Stable Head-to-Tail (Z-Type) Langmuir Blodgett Films. A Second Harmonic Generation Study

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The fabrication of polar multilayers currently attracts much interest due to their potential application in microelectronics and optics.[1] Polar assemblies are required in pyro- or piezo-electricity and nonlinear optics to assure constructive summation of dipoles and hyperpolarizability tensors. Multilayers produced by the Langmuir-Blodgett technique are usually of the Y-type, where the layers are deposited in a head-to-head, tail-to-tail fashion.[2]

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