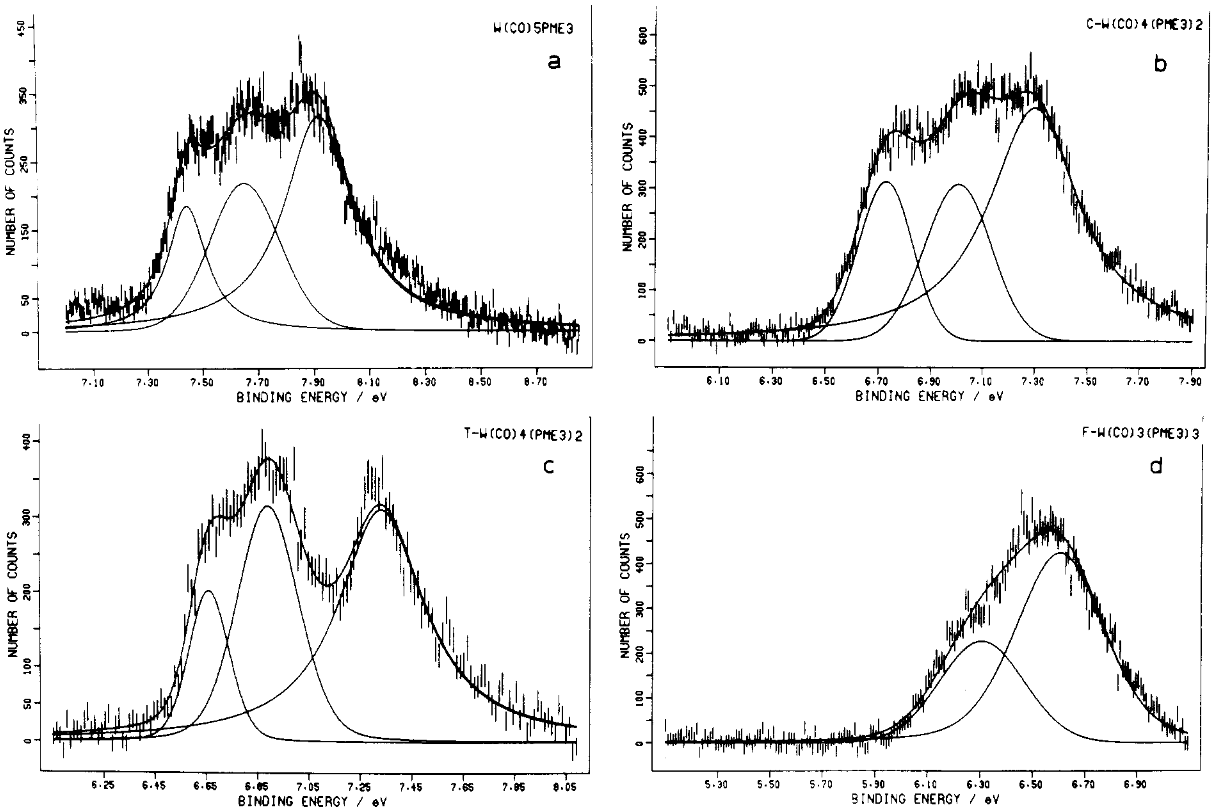

Figure 1. He I photoelectron spectra of the W 5d region in (a) [$W(CO)_5PMe_3$], (b) *cis*-[$W(CO)_4(PMe_3)_2$], (c) *trans*-[$W(CO)_4(PMe_3)_2$], and (d) *fac*-[$W(CO)_3(PMe_3)_3$].

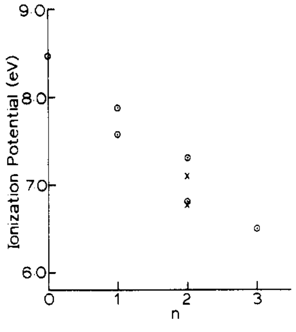

Figure 2. Plot of the W 5d IP vs. n for the series $W(CO)_{6-n}(PMe_3)_n$ for n = 0–3. The IP's (without spin–orbit splitting) are given for the unsplit t_{2g} level (n = 0, 3), the b_{2g} and e_g levels for n = 1 and n = 2 (trans), and the b_2 and e levels (X) for n = 2 (cis).

splittings with use of Hall's equations.[9] The spin–orbit parameters (0.17–0.20 eV) are the same as those obtained for a number of other [$W(CO)_5L$] compounds.[10] More importantly, the ratio of the t_{2g} splittings is 1.0:–1.1:1.7:0 for [$W(CO)_5L$], *cis*-[$W(CO)_4L_2$], *trans*-[$W(CO)_4L_2$], and *fac*-[$W(CO)_3L_3$], respectively—in rather good agreement with the theoretical predictions. The smaller than predicted trans splitting is due to two possible effects. First, the π-acceptor abilities of the CO ligands in the [$W(CO_5L$] and cis species will, on average, be greater than the CO π-acceptor ability in the trans compound. Trans–cis quadrupole splittings in Fe^{II}, Co^{III}, and Ir^{III} compounds are usually less than 2:–1,[35] although the quadrupole splitting is determined by both π-acceptor and σ-donor effects. Second, relaxation effects could readily cause this effect, which would result from very small differences in relaxation energies of <0.1 eV.

Finally, a plot of IP for the W 5d levels vs. n shows a good linear correlation (Figure 2), and the first IP's of cis and trans isomers are very similar as predicted by Bursten.[1] Because the phosphines are better σ donors than CO, the W t_{2g} peaks are chemically shifted to lower IP as n increases. This plot once again shows that differential relaxation effects are very small.

In conclusion, this work confirms the general validity of a ground-state treatment for explaining the shifts and splittings of the W t_{2g} levels in $W(CO)_{6-n}L_n$ compounds. These splittings and shifts should now be more useful for studying structure and bonding in d^6 low-spin systems.

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Registry No. [$W(CO)_6$], 14040-11-0; [$W(CO)_5(PMe_3)$], 26555-11-3; [$W(CO)_5(PEt_3)$], 21321-31-3; *cis*-[$W(CO)_4(PMe_3)_2$], 16104-05-5; *trans*-[$W(CO)_4(PMe_3)_2$], 30513-08-7; *trans*-[$W(CO)_4(PEt_3)_2$], 51154-69-9; *fac*-[$W(CO)_3(PMe_3)_3$], 30513-09-8.

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Bimetallic Porphyrins: Synthesis and Rapid Intramolecular Electron Transfer of *meso*-Tritolyl[*N*-(pentaammineruthenio)pyridyl]porphyrin

Sir:

Interest in electron transfer reactions has increasingly focused on reactions in which the reactants are held at a fixed distance or orientation.[1-10] Such studies are particularly

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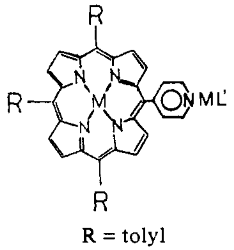
(1) Classic examples are provided by the work on mixed-valence systems, cf.: Taube, H. In "Tunneling in Biological Systems"; Chance, B., Ed.; Academic Press: New York, 1980.

(2) Meyer, T. *Acc. Chem. Res.* **1978**, *11*, 94.

significant for understanding electron transfer in biological systems.[8-10] Particular interest has been paid to bifunctional "stacked" porphyrins,[7,8] both as biological models and as redox catalysts.[7]

We here report the preparation, characterization, and preliminary study of the electron-transfer reactions of a new and synthetically simple class of bifunctional porphyrins of general structure **1**. Here, the meso-pyridyl group provides a ligand for a second, redox-active metal site, which is held at a fixed distance and relatively fixed angle relative to the porphyrin ring.



R = tolyl

1: M = 2H$^+$, (ML') = H (free ligand)
2: M = 2H$^+$, (ML') = $Ru(NH_3)_5{}^{3+}$
3: M = 2H$^+$, (ML') = Ru(trpy)(bpy)
4: M = Zn(II), (ML') = $Ru(NH_3)_5{}^{3+}$

The meso-pyridyl group is roughly perpendicular to the porphyrin ring.[11] This geometry promotes weak coupling between the redox centers, by minimizing overlap of the pyridyl and porphyrin π systems.[12]

The parent ligand, **1**, is prepared by analogy to the procedure of Little et al.,[13] with use of a mixed-aldehyde approach. Four grams of pyridine-4-carboxaldehyde and 13 g of *p*-tolylcarboxaldehyde were mixed in 500 mL of hot propionic acid. Ten grams of pyrrole was added and the mixture refluxed for ca 1 h. The purple crystalline product was collected by filtration and washed with methanol. The crude product was dissolved in chloroform and chromatographed on a 60 × 5 cm column of silica gel (100 mesh, Baker). The second band was the desired product. This fraction was further purified by preparative TLC on alumina plates to give 600 mg of analytically pure product. The product was characterized by UV, visible, and fluorescence spectroscopy, elemental analysis,[14] NMR,[14] and mass spectroscopy.[14]

The pentaammineruthenium derivative (**2**) was prepared by reacting 120 mg of $(Ru(NH_3)_5OH_2)(PF_6)_2$[15] with 40 mg of **1**. The reagents were dissolved in Ar-saturated acetone and stirred at room temperature in acetone for 4 h. The resulting complex was precipitated with concentrated NH_4PF_6, collected on a frit, and washed exhaustively with water. After it was dried on a vacuum line, the product was washed with $CHCl_3$. The recrystallized product was characterized by UV-visible and fluorescence spectroscopy, NMR, elemental analysis, and electrochemistry.[16]

An important aspect of compound **1** is that it provides a simple route to a variety of homologous redox-active compounds by modification of M or (ML'). As an illustration, we have prepared and characterized one homologue, in which (ML') is Ru^{II}(trpy)(bpy),[17] affording a second redox center. With use of standard methods, Ru can be easily replaced by other metals like Co(III). In this way, literally dozens of compounds in a homologous series can be characterized, affording a wide range of excited-state lifetimes, reaction driving forces, and reorganization energies. Techniques for incorporating metals into porphyrins are well-known, affording a wide variety of M derivatives. For example, incorporation of zinc in compound **2** afforded [*meso*-tritolyl(*N*-(pentaammineruthenio)pyridyl)porphyrinato]zinc(II) (**4**).

With such compounds fully characterized, the obvious question is whether intramolecular incorporation of a neighboring Ru(III) center modifies the reactivity of the porphyrin moiety. Preliminary results demonstrate that the porphyrin reactivity is indeed modified in compound **2**. The fluorescence lifetime of compound **1** is 11×10^{-9} s[19,20] while that of compound **2** is reduced to $\sim 7 \times 10^{-9}$ s. A corresponding decrease (40 ± 8%) in the static fluorescence emission intensity of **2** relative to **1** is observed at identical concentrations of **1** and **2**. Such quenching cannot result from energy transfer, since the lowest ruthenium excited state occurs at ca. 35 000 cm^{-1}.[22] A "heavy-atom" quenching is also excluded, since when Ru(III) is reduced to Ru(II) all emission quenching is abolished. The quenching process is therefore assigned to intramolecular electron transfer, with a net driving force of 0.84 V.[21] Rapid intramolecular electron transfer in compound **2** is supported by pulse radiolysis experiments,[23] which demonstrate that intramolecular electron transfer occurs from (porphyrin)$^{-\cdot}$ to Ru(III) with $\tau < 100$ ns.

In summary, a new class of synthetically simple bifunctional photoactive redox reagents has been reported. Preliminary data suggest that intramolecular electron transfer is rapid in these compounds. Given the ready availability of derivatives, these compounds may provide simple tests of current theories

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(14) Anal. Calcd (found) for $\mathbf{1}\cdot 4H_2O$: C, 75.7 (75.7); H, 5.9 (6.1); N, 9.6 (9.2). ^{1}H NMR (ppm vs. Me_4Si, 400 MHz, $COCl_3$): β-H_a, 9.02; β-H_b, 8.88; β-H_c, 8.85; *o*-py H, 8.9; *m*-py H, 8.16; tolyl Me, 2.68; tolyl *o*-CH, 7.61; tolyl *m*-CH, 8.10. MS: M$^+$, 658.1 (657.9 calcd); strong peaks at $M^+ - (C_7H_7)_n$, $n = 1, 2, 3$. UV–visible (λ_{max}, nm (ϵ)): 418 (5.2×10^5), 514 (2.2×10^4), 549 (1.0×10^4), 590 (6.7×10^{13}), 646 (6).

(15) Prepared by the method of J. Curtis: Curtis, J., Ph.D. Dissertation, The University of North Carolina, Chapel Hill, NC, 1981.

(16) Anal. Calcd (found) for $\mathbf{2}\cdot 2\text{-}(CH_3)_2CO$: Ru, 7.2 (7.3); C, 44.8 (45.2); H, 4.48 (4.43); N, 10.0 (10.6). NMR (ppm): 7.60, 8.09, 2.68, 8.7–9.2 (br m) (plus acetone resonance at 3.31). Cyclic voltammetry: *E*(NHE) = 0.4 and 1.47 V in DMF. UV–visible spectra are essentially identical with those of the unmodified system.

(17) $[Ru(trpy)(bpy)H_2O](ClO_4)_2$ was prepared by the method of: Thompson, M.; Meyer, T., personal communication. Anal. Calcd (found) for $\mathbf{3}\cdot 2.5H_2O$: C, 61.16 (61.27); H, 3.98 (4.31); N, 10.05 (10.13); Ru, 7.68 (6.91).

(18) Balzani, V.; Bolletta, F.; Gandolfi, M.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1.

(19) Lifetimes were measured at the University of Rochester Laboratory for Laser Energetics Biological Picosecond Laser Facility. We are grateful to Professor Tom Nordlund for his assistance with these measurements.

(20) For comparison, Harriman has reported a lifetime of 14 ns for tetraphenyl porphyrin: Harriman, A., personal communication.

(21) $E^{**}{}_{\sigma\sigma} = 1.91$ $E(H_2porph^{+\cdot}/H_2porph) \cong 1.47$ V. $E°(Ru^{III/II}) = 0.4$ V. $E°{}^{*} = 1.91 - 1.37 + 0.4 = 0.84$ V.

(22) Fuhrhop, J. In "Porphyrins and Metalloporphyrins"; Smith, K.; Ed.; Elsevier: New York, 1976. Picosecond transient absorption experiments are in progress to attempt to unambiguously measure cation radical formation.

(23) Miller, J.; Franco, C.; McLendon, G., unpublished data. The lower limit is set by the low concentration of porphyrin necessary to avoid aggregation. We observe that while both the isolated porphyrin (**1**) and $Ru^{III}(NH_3)_5py$ are reduced at equivalent, diffusion-controlled rates, *no* porphyrin reduction is observed in compound **2**, suggesting that intramolecular electron transfer occurs more rapidly than electron capture; $k_{intra} > 10^7$ s^{-1}.

of electron transfer, including the existence of "inverted" behavior.[24]

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Electrochemical Characterization of Six-Coordinate Nitrosyl σ-Bonded Iron-Phenylporphyrins

Sir:

The electrochemistry of five-coordinate nitrosyl iron porphyrins has been well documented in the literature.[1-3] The air-stable species contain Fe(II), which (depending on the solvent donor properties and porphyrin ring) is oxidized to Fe(III) in a range of potential between 0.60 and 0.80 V vs. SCE. For the specific case of (TPP)Fe(NO) (TPP = tetraphenylporphyrin), oxidation of Fe(II) to Fe(III) occurs at 0.75 V.[2] In contrast, σ-bonded alkyl or aryl iron porphyrins contain Fe(III) in the air-stable form. These complexes may be reduced to Fe(II) in the range of −0.70 to −1.00 V, depending on the porphyrin ring basicity, the type of bound alkyl or aryl group, and the solvent donor properties.[4-8] For the specific case of $(TPP)Fe(C_6H_5)$ in PhCN, reduction to Fe(II) occurs at −0.70 V.[8]

The above two types of complexes represent opposite extremes in synthetic iron porphyrin electrochemical reactivity. The Fe(III)/Fe(II) potential for (TPP)Fe(NO) is the most positive ever measured for a five-coordinate iron tetraphenylporphyrin and indicates extreme stability of the Fe(II) oxidation state. In contrast, the Fe(III)/Fe(II) reaction of $(TPP)Fe(C_6H_5)$ is one of the most negative ever measured for a five-coordinate iron tetraphenylporphyrin and indicates extreme stability of the Fe(III) oxidation state toward reduction.

In an attempt to better understand the opposite stabilizing effects of the nitrosyl and alkyl groups, we have investigated the electrochemistry of six-coordinate $(P)Fe(C_6H_5)(NO)$ (where P = OEP (octaethylporphyrin) or TPP). These complexes may be obtained by exposure of $(P)Fe(C_6H_5)$ to NO gas either in solution or as a solid powder. The six-coordinate complexes have a slightly bent Fe–N–O bond, as characterized by the 1790-cm^{-1} IR NO stretching frequency.[9] Their UV-visible and ^{1}H NMR spectra have been discussed and the complexes tentatively characterized as low-spin Fe(II) species.[9] The electrochemical oxidation and reduction of $(P)Fe(C_6H_5)(NO)$ were carried out at a Pt electrode in PhCN (benzonitrile) under various NO pressures.

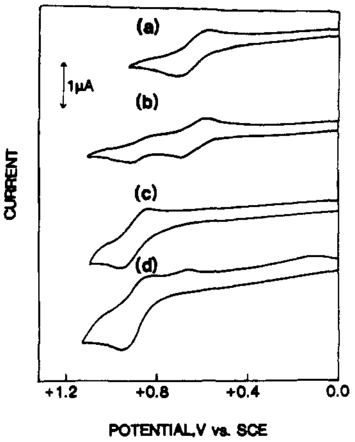

Figure 1. Cyclic voltammograms of 1.09 × 10^{-3} M $(TPP)Fe(C_6H_5)$ and $(TPP)Fe(C_6H_5)(NO)$ in PhCN with 0.1 M $TBA(PF_6)$ (scan rate 0.10 V/s). Total NO pressure: (a) 0 mm; (b) 29 mm; (c) 72 mm; (d) 171 mm.

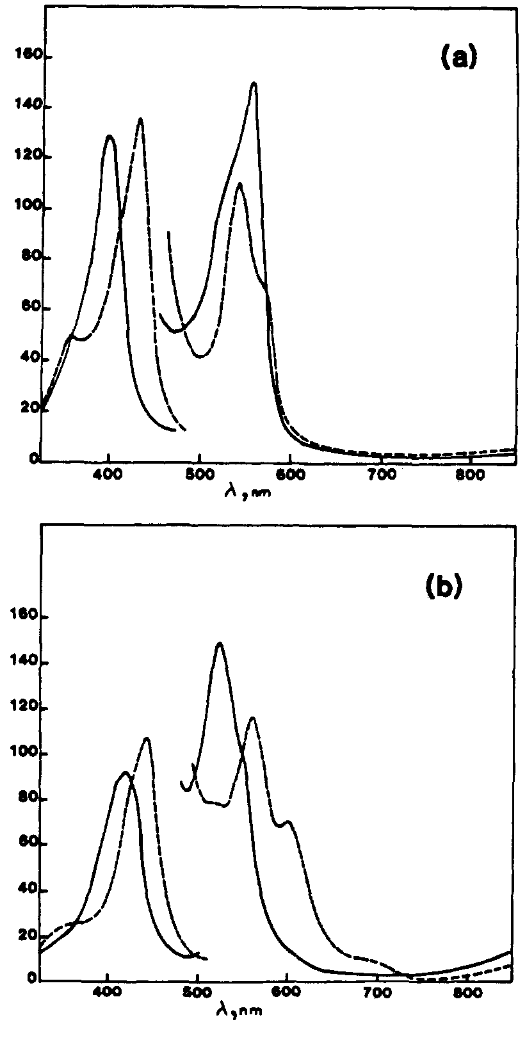

Figure 2. Electronic absorption spectra of (a) 4.96 × 10^{-5} M $(TPP)Fe(C_6H_5)$ in the presence of 7 mm NO and (b) 2.80 × 10^{-5} M $(OEP)Fe(C_6H_5)$ in the presence of 8 mm NO, both in PhCN with 0.1 M $TBA(PF_6)$. $(P)Fe(C_6H_5)$ is represented by the solid lines and $(P)Fe(C_6H_5)(NO)$ by the dotted lines.

As seen in Figure 1a, the electrochemical oxidation of $(TPP)Fe(C_6H_5)$ in PhCN occurs at 0.61 V in the absence of NO gas. Both the shape of the peaks and the current dependence on scan rate suggest a diffusion-controlled one-

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