$$\log k_{YOOH} = \beta_{lg}\, pK_{YOH} + C \qquad (3)$$

$= -0.6$),[10] and both percarboxylic acids and alkyl hydroperoxides are correlated by the same line for any given nucleophile. In Figure 1 there is plotted $\log k_{YOOH}$ for reaction of percarboxylic acids with ClMn^{III}TPP vs. the pK_a of the carboxylic acid leaving groups. The correlation line of Figure 1 is provided by eq 3 with $\beta_{lg} = -1.25$ and $C = 8.0$. For reaction of both percarboxylic acids and alkyl hydroperoxides with ClCr^{III}TPP, $\beta_{lg} = -0.34$ and $C = 4.90$.[5] For ClFe^{III}TPP the rates of heterolysis of the YO–OH bond accompanying oxygen transfer from peracids and hydroperoxides are correlated by eq 3 with $\beta_{lg} = -0.34$ and $C = 4.66$.[5] In comparing the linear free energy expressions that correlate the rates of oxene transfer, one must be aware that different solvents were employed in each case. Thus, for ClCr^{III}TPP the solvent was CH$_2$Cl$_2$ (25 °C), and for ClFe^{III}TPP the solvent was CH$_3$OH (30 °C), while for ClMn^{III}TPP the solvent was PhCN (30 °C). Nevertheless, the lack of reactivity of ClMn^{III}TPP with hydroperoxides (in such divergent solvents as benzene and dichloromethane) would appear to find an explanation in the relatively large but negative β_{lg} value of -1.25 when compared to a value of -0.34 for both ClCr^{III}TPP and ClFe^{III}TPP.

A full appreciation of the meaning of β_{lg} for metalloporphyrin nucleophilic displacements upon YOOH species awaits studies of other metallotetraphenylporphyrins and a determination of the dependence of β_{lg} upon the solvent and axial ligand for a given metalloporphyrin cation. (The importance of ligand is shown by our observation that Mn^{III}TPP reacts readily with alkyl hydroperoxides when the ligand is imidazole due to a change in β_{lg} of fivefold.) At present, we may tentatively suppose that the large negative β_{lg} for ClMn^{III}TPP in PhCN solvent reflects a full negative charge on the departing group in the transition state so that the rds involves the formation of the intimate pair [TPP(Cl)Mn^{V}OH·YO$^-$].

Department of Chemistry   **Lung-Chi Yuan**
University of California at Santa Barbara   **Thomas C. Bruice***
Santa Barbara, California 92106

Improved Synthesis of 4-Vinyl-4'-methyl-2,2'-bipyridine

Sir:

The recent surge in the study of chemically modified electrodes has been due in part to the advent of electroactive polymer films that allow for extensive variation in electrode modification.[1] A particularly versatile reagent in this respect has been 4-vinyl-4'-methyl-2,2'-bipyridine (**1**),[2-4] first reported by Spiro.[5,6] Un-
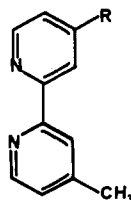
1, R = CH=CH$_2$
2, R = CH$_3$
3, R = CH$_2$CH$_2$OCH$_3$

---

(1) Murray, R. W. In "Electroanalytical Chemistry"; Bard, A. J., Ed.; Marcel Dekker: New York, 1984; Vol. 13.
(2) Abruña, H. D.; Denisevich, P.; Umaña, M.; Meyer, T. J.; Murray, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 1.

fortunately, we and others[7] have found the preparation of **1** difficult to execute. We report herein modifications of Spiro's original synthesis that have allowed us to prepare multigram quantities of **1**. Subsequent to the completion of this work, a closely related procedure was reported in the patent literature.[8]

Experimental Section. Diisopropylamine was distilled over calcium hydride under nitrogen. Tetrahydrofuran (THF) was distilled over Na/benzophenone. The *t*-BuOK, (chloromethyl)-methyl ether, and *n*-BuLi/hexane were obtained from Aldrich Chemical Co. and used as received. The 4,4'-dimethyl-2,2'-bipyridine was obtained from Strem Chemical Co. and used without further purification. Proton NMR spectra were recorded on a 100-MHz Varian CFT-20 spectrometer, and carbon-13 spectra were recorded on a JEOL FX90Q. Chemical shifts are reported in ppm relative to internal tetramethylsilane standards. Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN.

4-Vinyl-4'-methyl-2,2'-bipyridine. To a solution of diisopropylamine (11.4 mL, 81 mmol) in THF (90 mL) at 0 °C under nitrogen was added 1.5 M *n*-BuLi in hexane (54.3 mL, 81.5 mmol) followed by dropwise addition of 4,4'-dimethyl-2,2'-bipyridine (**2**: 15 g, 81.5 mmol) in tetrahydrofuran (350 mL). After the resulting deep brown reaction mixture was stirred for 15 min at 0 °C, (chloromethyl)methyl ether (6.90 mL, 90.9 mmol) in 60 mL of dry THF was added dropwise. The homogeneous, pale yellow reaction was stirred at 0 °C for 30 min and then quenched with water (90 mL) and partitioned between saturated NaHCO$_3$ (50 mL) and diethyl ether (150 mL). Following two additional 150-mL ether extractions, the combined ethereal layers were dried over sodium sulfate and concentrated in vacuo to afford a pale yellow oil. After the oil was filtered through flash grade silica gel (ether elution), concentrated in vacuo, and let stand at 25 °C for 2–3 days, all remaining traces of unreacted **2** deposited as white crystals. Bipyridine **3** (12.6 g, 68% yield) was isolated as a spectroscopically homogeneous, colorless oil: ^{1}H NMR (CDCl$_3$) δ 8.50 (br t, J = approximately 4 Hz, 2 H), 8.19 (br s, 2 H), 7.11 (br t, J = approximately 4 Hz, 2 H), 3.63 (t, J = 6.6 Hz, 2 H), 3.30 (s, 3 H), 2.91 (t, J = 6.6 Hz, 2 H), 2.37 (s, 3 H); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 156.6, 156.5, 149.1, 147.6, 124.7, 124.5, 122.2, 121.9, 72.2, 58.2, 35.9, 20.8; MS (CI) m/z 229 (M + 1, 100%).

To a solution of **3** (12.6 g, 55.2 mmol) in THF (325 mL) at −78 °C under nitrogen was added *t*-BuOK (12.4 g, 110.4 mmol) in THF (210 mL) dropwise. After the mixture was stirred for 1.5 h at −78 °C and at room temperature for an additional 15 min, the reaction was quenched with water (150 mL) and extracted with ether (3 × 300 mL). The combined ethereal layers were dried over sodium sulfate and stripped to a yellow solid. Following filtration through a 2-in. column of 230–400 mesh silica gel (ether elution) to remove polymeric impurities, the resulting yellow solid was recrystallized from ether/hexane, affording analytically pure **1** (5.40 g, 35% overall yield from **2**) as a white, crystalline solid that exhibited the reported[5,6] physical properties as well as the following: ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 149.8, 149.2, 135.4, 124.8, 124.6, 122.3, 120.8, 118.6, 118.1, 20.9. Anal. Calcd for C$_{13}$H$_{12}$N$_2$·^{1}/$_4$H$_2$O: C, 77.81; H, 6.29; N, 13.96. Found: C, 78.11; H, 6.31; N, 13.97.

---

(3) Denisevich, P.; Abruña, H. D.; Leidner, C. R.; Meyer, T. J.; Murray, R. W. *Inorg. Chem.* **1982**, *21*, 2153.
(4) Abruña, H. D.; Calvert, J. M.; Denisevich, P.; Ellis, C. D.; Meyer, T. J.; Murphy, W. R.; Murray, R. W.; Sullivan, B. P.; Walsh, J. L. In "Chemically Modified Electrodes in Catalysis and Electrocatalysis"; Miller, J. S., Ed.; American Chemical Society: Washington, DC, 1982; ACS Symp. Ser. No. 192.
(5) Ghosh, P. K.; Spiro, T. G. *J. Am. Chem. Soc.* **1980**, *102*, 5543.
(6) Ghosh, P. K.; Spiro, T. G. *J. Electrochem. Soc.* **1981**, *128*, 1281.
(7) Murray, R. W.; Meyer, T. J.; Bard, A. J., private communications.
(8) Kashig, J.; Lobmann, D. U.S. Patent 4 424 359, 1984.

Department of Chemistry   **Héctor D. Abruña***
Baker Laboratory   **Anne I. Breikss**
Cornell University   **David B. Collum**
Ithaca, New York 14853

Figure 1. Schematic representation of the isomers of $[Mo_2(en)_4]^{4+}$: (a) chelated (α) isomer; (b) bridged (β) isomer.

Preparation and Circular Dichroism Spectrum of the Tetrakis((R)-1,2-diaminopropane)dimolybdenum Cation: Evidence for a Bridged Structure

Sir:

There is only one report of a dimolybdenum complex containing unsaturated diamine ligands—$[Mo_2(en)_4]^{4+}$—and even that compound has not been structurally characterized.[1] Bowen and Taube suggested,[1] from an inspection of scale models, that $[Mo_2(en)_4]^{4+}$ was more likely to contain chelating than bridging diamine ligands (Figure 1). We have recently shown[2] for complexes of dimolybdenum containing bidentate bis(diphenylphosphino) ligands, such as dppe, that the bridged isomer is thermodynamically more stable than the chelated isomer and that the latter spontaneously isomerizes in dry methylene chloride solution. We wish to report here the synthesis and CD spectrum of $[Mo_2(R\text{-}pn)_4]^{4+}$, the first chiral dimolybdenum complex containing diamine ligands, and conclude from the CD spectrum that the complex must have a staggered configuration and thus bridging ligands.

The complex was synthesized by the method described by Bowen and Taube for the ethylenediamine analogue[1] and gave satisfactory analysis. The absorption and CD spectra of the chloride salt in 0.1 M HCl are shown in Figure 2. The absorption spectrum is very similar to that of $[Mo_2(en)_4]^{4+}$, the major difference being a blue shift and intensification of the $\delta \rightarrow \delta^*$ transition in the R-pn complex. The CD spectrum of $[Mo_2(R\text{-}pn)_4]^{4+}$ bears a close similarity (apart from the absolute wavelengths of the transitions) to that of the structurally characterized complex $Mo_2Cl_4(S,S\text{-}dppb)_2$, which contains bridging diphosphine ligands and a staggered $Mo_2Cl_4P_4$ chromophore. In both complexes large Cotton effects are observed under both the $\delta \rightarrow \delta^*$ transition and under the next highest energy absorption (which is assigned as a magnetic dipole transition). The dissymmetry factors ($\Delta\epsilon/\epsilon$) are similar for the two compounds and are typical for configurationally chiral metal complexes. Indeed, the dissymmetry factor for the magnetic dipole transition of $[Mo_2(R\text{-}pn)_4]^{4+}$ (17×10^{-2}) is among the largest recorded for a solution spectrum of an inorganic compound and is comparable with those found for single-crystal CD spectra of configurationally chiral metal complexes (for example the $^1A_1 \rightarrow {}^1E$ transition of Λ-Co-(en)$_3$Cl$_3$ has $\Delta\epsilon/\epsilon = 22 \times 10^{-2}$.

We have also prepared both the chelated (α) and bridged (β) isomers of $Mo_2Cl_4(R\text{-}dppp)_2$ and obtained their CD spectra. As expected, the bridged isomer has a CD spectrum of magnitude similar (but with inversion of sign) to that of $Mo_2Cl_4(S,S\text{-}dppb)_2$ (the dissymmetry factor of the $\delta \rightarrow \delta^*$ transition is 6×10^{-3}). The chelated isomer, in which the two $MoCl_2P_2$ units are eclipsed, has on the other hand such a weak optical activity that we could detect no CD spectrum (implying $\Delta\epsilon/\epsilon < 5 \times 10^{-5}$). Thus the presence of a chiral center on the ligand backbone is not in itself sufficient to produce a significant Cotton effect under the $\delta \rightarrow \delta^*$ transition and the observation of such an effect must therefore imply a staggered chromophore. Both the magnitude of the CD spectrum
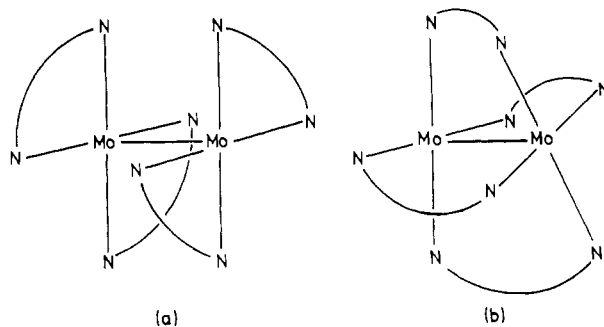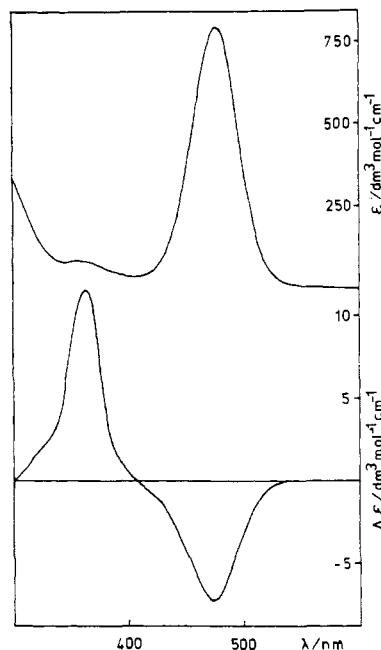

Figure 2. Absorption and CD spectra of a solution (10^{-3} mol L^{-1}) of $[Mo_2(R\text{-}pn)_4]^{4+}$ as the chloride salt in 10^{-2} mol L^{-1} HCl.
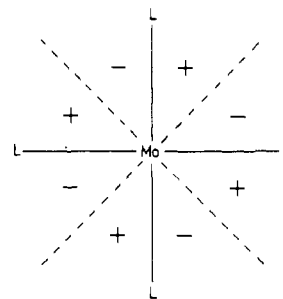

Figure 3. Sector rule for the sign of the CD under the $\delta \rightarrow \delta^*$ transition of $[Mo_2(L\!\!\sim\!\!L)_4]^{n+}$. The sign of the CD is that of the sectors containing the L atoms of the *rear* MoL_4 or $MoL_2L'_2$ unit.

of $[Mo_2(R\text{-}pn)_4]^{4+}$ and its qualitative similarity to those of the β isomers of the diphosphine complexes lead to the conclusion that the complex contains a staggered Mo_2N_8 chromophore. Although it is just possible that chelating diamine ligands could result in a staggered stereochemistry about the Mo–Mo bond, the evidence from complexes with diphosphine and dithiol ligands is that a staggered geometry is produced only by the conformational preference of bridging ligands. We conclude, therefore, that $[Mo_2(R\text{-}pn)_4]^{4+}$ contains bridging diamine ligands. The close similarity of the absorption spectra as well as the similar preparative methods make it extremely likely that $[Mo_2(en)_4]^{4+}$ also has a bridged structure.

The simple metal-localized model for the CD of the $\delta \rightarrow \delta^*$ transition described in ref 3 leads to a sector rule relating the twist

(1) Bowen, A. R.; Taube, H. *Inorg. Chem.* **1974**, *13*, 2245–2249.
(2) Fraser, I. F.; McVitie, A.; Peacock, R. D. *J. Chem. Res., Synop.* **1984**, 420–421.