all other four-coordinate intermediate-spin ($S = 1$) Fe(II) porphyrins studied to date.[4,16,20] The spin delocalization mechanism for $S = 1$ Fe(II) porphyrins has been shown to be P $\rightarrow$ Fe π charge transfer.[16,21,22] It has been argued[16] that contact contributions to the isotropic shifts of the *phenyl* protons of Fe(TPP) are very small, so that these isotropic shifts are dominated by dipolar contributions[23,24]

$$(\Delta H/H)^{\mathrm{dip}} = (-1/3N)[\chi_{zz} - \tfrac{1}{2}(\chi_{xx} + \chi_{yy})]\langle(3\cos^2\theta - 1)/r^3\rangle - (1/2N)[\chi_{xx} - \chi_{yy}]\langle(\sin^2\theta\cos 2\phi)/r^3\rangle$$

Note that for Fe(TPP) $\chi_{xx} = \chi_{yy}$ so that the second (rhombic) term does not contribute to $(\Delta H/H)^{\mathrm{dip}}$. For simplicity, we treat the loss of 4-fold symmetry from the reduction of one or two pyrrole rings as a perturbation. Thus, z is perpendicular to the plane of Fe(TPC) and Fe(TPiBC) and y is coincident with the molecular C_2 axis in each compound (see Figures 1 and 3). Since $\cos 2\phi \approx 0$ for the phenyl protons of Fe(TPC), a comparison of Curie plot slopes for the phenyl protons of Fe(TPP) and Fe(TPC) allows the ratio of the terms $[\chi_{zz} - {}^1/_2(\chi_{xx} + \chi_{yy})]\langle(3\cos^2\theta - 1)/r^3\rangle$ for these two compounds to be estimated: the term for Fe(TPC) is *less than half* that for Fe(TPP). The solid-state structure of Fe(TPC),[25] while disordered, is nearly identical with that of Fe(TPP).[17] If the conformations in solution are also similar for the two compounds, then $\Delta\chi_{\parallel}$[24] for Fe(TPC) may be considerably less than $\Delta\chi_{\parallel}$ for Fe(TPP).

An analysis of isotropic shifts for protons situated parallel or perpendicular to the molecular C_2 axis for Fe(TPC) (pyrrole and pyrroline protons, Figure 2) and Fe(TPiBC) (phenyl protons,[19] not shown) shows the same upfield and downfield pattern observed for Fe(OEC)[4] and *strongly suggests in-plane magnetic anisotropy for these two compounds* (i.e. $\chi_{xx} \neq \chi_{yy}$). Even though the pyrrole and pyrroline protons for Fe(TPC) should have large dipolar *and contact* contributions to their isotropic shifts, the phenyl protons for Fe(TPiBC) should only experience sizable dipolar shifts. Thus, our data provide unambiguous proof that the isobacteriochlorin ring system *can* induce rhombicity in the magnetic properties of a metal.

Curie plots for Fe(TPC) and Fe(TPiBC) show large apparent temperature-independent paramagnetism (TIP) for these compounds, as was seen for Fe(OEC) (large deviations in $1/T = 0$ intercepts, as much as ~60 ppm, from diamagnetic values). While none of the protons in Fe(OEP) is chemically similar to those in Fe(TPP), the compounds Fe(OEC) and Fe(TPC) have β-pyrroline protons that are similar. The Curie plot slopes and intercepts for these protons in the two compounds *are nearly identical*: -12.2×10^3 ppm·K and 65.5 ppm for Fe(OEC)[4] and -12.2×10^3 ppm·K and 60.5 ppm for Fe(TPC). Since these two chlorins must have some structural and electronic differences, this coincidence suggests that there is something fundamental about the magnetic properties that can be induced in metals by chlorins.

In summary, the hydroporphyrin complexes Fe(TPC) and Fe(TPiBC) are magnetically different from Fe(TPP) despite their common $S = 1$ ground state: they are rhombic instead of axial and they exhibit sizable apparent TIP. In addition, $\Delta\chi_{\parallel}$ *may* be much smaller for Fe(TPC) than for Fe(TPP). Experiments designed to probe further the molecular and electronic structures of these compounds are in progress.

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Registry No. Fe(TPC), 52155-40-5; Fe(TPiBC), 102133-42-6.

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Substituted Cyclopentadienyl(dithiolene)tungsten(IV) Products from Alkyne Addition to Tungsten(II) Dithiocarbamate Reagents

Sir:

Reactions that form or cleave C–C[1] or C–S[2] bonds are important in organometallic chemistry. Protonation of $M(RC{\equiv}CR)_2(S_2CNMe_2)_2$ (M = Mo or W) has been shown to induce alkyne coupling and form η^4-C_4R_4H ligands.[3] We now report that photochemical addition of $PhC{\equiv}CH$ to $W(PhC_2H)_2(S_2CNMe_2)_2$ involves dissection of a dithiocarbamate ligand into three components which are ultimately coupled to alkyne units in the isolated product.

A compound of stoichiometry $W(PhC_2H)_3(S_2CNMe_2)_2$ (**1**) is formed in low yield upon photolysis of $W(PhC_2H)_2(S_2CNMe_2)_2$[3] in the presence of excess phenylacetylene (eq 1).[4] Two sets of

$$W(PhC_2H)_2(S_2CNMe_2)_2 + PhC_2H \xrightarrow[\text{THF}]{h\nu} \underset{\mathbf{1}}{\text{“}W(PhC_2H)_3(S_2CNMe_2)_2\text{”}} \quad (1)$$

signals in both ^1H and ^{13}C NMR spectra indicated a 1.4:1.0 mixture of isomers. The magnitudes of the $^1J_{CH}$ coupling constants of the CH moieties derived from the original three $PhC{\equiv}CH$ units were less than 200 Hz (171–183 Hz), from which we inferred that no simple alkyne ligands were retained in the product.[5]

Efforts to unravel the connectivity of the coupled alkyne product from NMR data were unsuccessful, and an X-ray structural determination was undertaken.[6] The structure of “$W(PhC_2H)_3(S_2CNMe_2)_2$” revealed a π-bound 1-(dimethyl-

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(1) Carbon–carbon bond formation is central to organometallic chemistry; see: (a) Swan, J. M.; Black, D. S. C. *Organometallics in Organic Synthesis*; Chapman Hall: London, 1974. (b) Heck, R. F. *Organotransition Metal Chemistry*; Academic: New York, 1974.

(2) Heterogeneous hydrodesulfurization is the dominant industrial reaction involving C–S bond cleavage; see: Massoth, F. E. *Adv. Catal.* **1978**, *27*, 265.

(3) Morrow, J. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 5004.

(4) A tetrahydrofuran solution of $W(PhC_2H)_2(S_2CNMe_2)_2$ (0.5 mmol in 200 mL) and a 10-fold excess of PhC_2H was photolyzed with a Hanovia 750W medium-pressure Hg arc lamp for 1 h. Solvent evaporation followed by alumina chromatography with an increasing ratio of CH_2Cl_2 to $PhCH_3$ as the eluant first yielded a band of reagent bis(alkyne), which was followed by a dark gold product band. Solvent removal and recrystallization from Et_2O gave pure **1** in yields of 8–12%.

(5) In our experience $^1J_{CH}$ values for $RC{\equiv}CH$ ligands lie between 200 and 240 Hz: (a) Ward, B. C.; Templeton, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 1532. (b) Templeton, J. L.; Ward, B. C.; Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1981**, *20*, 1248. (c) Herrick, R. S.; Templeton, J. L. *Organometallics* **1982**, *1*, 842.

(6) The crystal selected was triclinic (space group $P\bar{1}$) with unit cell dimensions of a = 18.803 (4) Å, b = 10.291 (3) Å, c = 16.186 (3) Å, α = 80.42 (2)°, β = 84.79 (3)°, and γ = 89.81 (3)° with Z = 2. Of the 6141 reflections monitored, 4210 independent reflections with $I > 3\sigma(I)$ were used in the structure solution and refinement, which converged to 2.6 and 2.1% for R_w and R, respectively. Hydrogen positions were calculated, and all other atoms were refined anisotropically.

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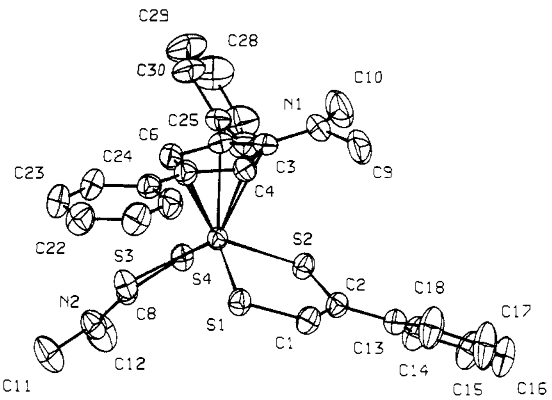
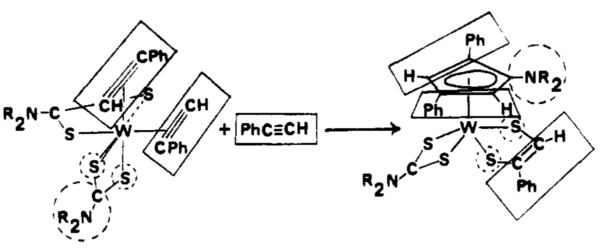


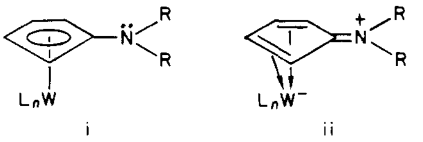
Figure 1. Molecular structure of W(π-$C_5Ph_2H_2NMe_2$)(S_2C_2PhH)(S_2CNMe_2) indicating the atomic labeling scheme.

amino)-2,4-diphenylcyclopentadienyl ligand and a bidentate 1-phenyl-1,2-dithiolene ligand bound to tungsten(IV) with a normal dithiocarbamate completing the coordination sphere. The origins of the components that have been welded into the new ligands are evidently those traced in eq 2. The net reaction reflects cleavage of two C–S bonds and formation of two new C–S bonds and three new C–C bonds.



(2)

The atomic labeling scheme for W[η^5-C(Ph)C(H)C(Ph)C(H)C(NMe$_2$)][η^2-SC(Ph)C(H)S][η^2-S_2CNMe_2] is presented in Figure 1. The dimethylamino-substituted carbon atom of the C_5 ring (C3) is 2.53 Å from the metal due to resonance contribution ii (cf. 2.28 Å average for C(4)–C(7)). The usual resonance

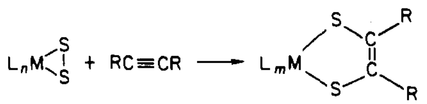


forms are available to the dithiolene ligand,[7] which is bound more tightly to the tungsten than is the dithiocarbamate chelate (2.35 vs. 2.47 Å average for W–S distances, respectively).

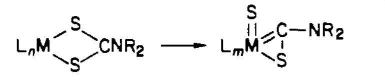
Satisfactory assignments for ^1H and ^{13}C NMR spectra are evident with the structure in hand;[8] reversal of the PhC_2H orientation in the 1,2-dithiolene could produce the diastereomer observed in NMR samples. The unique low-field proton signal at 8.60 ppm in toluene-d_8 is assigned to the S_2C_2PhH ligand as is the 142.7-ppm ^{13}C signal with $^1J_{CH}$ = 171 Hz. The C–H resonances at higher field (^1H 4.43, 3.82 ($^4J_{HH}$ = 2.5 Hz); ^{13}C 77.2 (J_{CH} = 183 Hz), 72.1 (J_{CH} = 182 Hz)) are attributable to the C_5 ring.

How does this complex reaction proceed? Literature precedent suggests that the C_5 ring could form from alkyne addition to a tungsten carbyne (eq 3)[9-11] and that the 1,2-dithiolate ligand could result from alkyne addition to a tungsten disulfide unit (eq 4).[12] Since a dithiocarbamate ligand is the only source of (dimethylamino)carbyne and sulfide fragments, two dithiocarbamate C–S bond cleavages must occur along the reaction coordinate. Ample precedent exists for internal oxidative addition of one such C–S bond to tungsten (eq 5).[13]

$$L_nM{\equiv}CR + 2RC{\equiv}CR \longrightarrow L_mM(\pi\text{-}C_5R_5) \quad (3)$$



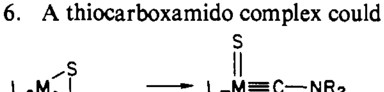
(4)



(5)

Tungsten carbynes are known to react with alkynes to form both monomeric[9] and dimeric[10] products containing newly formed cyclopentadienyl rings. A tantalum alkylidyne complex has also recently yielded π-C_5R_4R' products from addition of two alkyne units.[11]

Heating W(CO)(PhC_2Ph)(S_2CNMe_2)$_2$ in toluene produces W(S)(PhC_2Ph)(S_2CNMe_2)(SCNMe$_2$).[14] Given literature precedent for reaction types (3),[9-11] (4),[12] and (5),[13] the only additional bond cleavage required to construct a plausible mechanism is shown in eq 6. A thiocarboxamido complex could be generated



(6)

here, and cleavage of the η^2-SCNMe$_2$ C–S bond (as in eq 6) would yield a W≡CNMe$_2$ moiety. In the presence of alkyne this (dimethylamino)tungsten carbyne could lead to the observed cyclopentadienyl product via a metallocyclobutadiene[9] or, less likely, a metallotetrahedrane[15] intermediate.

Dioxocyclopentadienyltungsten derivatives are formed from (η^2-OMe$_2$CCMe$_2$O)(t-BuO)W(C_3Et_3) by addition of alkyne and elimination of tetramethylethylene (eq 7).[9] A related sulfido

$$(OMe_2CCMe_2O)(RO)W(C_3Et_3) + EtC_2Et \rightarrow WO_2(OR)(C_5Et_5) + Me_2C{=}CMe_2 \quad (7)$$

species formed in our system might undergo a reaction resembling the reverse of eq 7, namely alkyne insertion. We believe the existence of reactants and products for eq 7 suggests that comparable sulfur species could be mechanistically accessible intermediates. While two terminal sulfide ligands in a S=W=S moiety could precede the 1,2-dithiolate, formation of a persulfide

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(8) ^1H NMR (CDCl$_3$): δ 8.45, 8.44 (each a s, total of 1 H, SC(Ph)C*H*S), 7.89–7.10 (m, 15 H, 3 Ph), 4.46, 4.40, 4.28, 4.16 (each a d, $^4J_{HH}$ = 2.5 Hz, total of 2 H, $C_5Ph_2H_2NMe_2$), 3.20, 3.16, 3.13 (each a s, total of 6 H, $S_2CN(CH_3)_2$), 2.76, 2.70 (each a s, total of 6 H, $C_5Ph_2H_2N(CH_3)_2$). ^{13}C NMR (CDCl$_3$): δ 215.9, 215.7 (s, S_2CNME_2), 160.5, 159.7 (s, S*C*(Ph)CHS), 142.7, 141.8 (d, $^1J_{CH}$ = 171 Hz, SCPh*C*HS), 140.1–126.6 (C_6H_5), 89.5, 89.3, 87.5, 87.2 (s, *C*(Ph)CH*C*(Ph)CHCNMe$_2$), 77.2, 72.1, 70.5 (d, C(Ph)*C*HC(Ph)*C*HCNMe$_2$), 41.7, 41.5, 39.1, 38.9 (q, $^1J_{CH}$ = 131 Hz, N(CH$_3$)$_2$).

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S–S ligand is more attractive in view of eq 4 and the unreasonably high oxidation state required for a tungsten simultaneously accommodating two sulfide(2−) ligands and either a carbyne(3−) or a C_3R_3(3−) fragment.

Numerous mechanisms can be pieced together from eq 3–6 and various insertion and coupling sequences.[16] Independent of mechanism, however, it is clear that a dithiocarbamate ligand here serves as a source of one (dimethylamino)carbyne and two sulfide fragments. Efforts to isolate compounds along the reaction coordinate connecting these reagents and products are under way.

Acknowledgment. We thank the National Science Foundation (J.L.T., Grant CHE-8310121) for financial support.

Supplementary Material Available: Tables of positional and thermal parameters and selected bond distances and angles for **1** (4 pages). Ordering information is given on any current masthead page.

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(16) Addition of excess PhC_2D, PhC_2Ph, or HC_2Me to a solution of $W(CO)(PhC_2H)(S_2CNMe_2)_2$ in THF followed by photolysis yielded cyclopentadienyl tungsten products analogous to the PhC_2H product, but extensive alkyne scrambling was evident in the resulting isomer mixtures. Photolysis of reagents containing only internal alkynes did not lead to isolation of comparable products.

Articles

Contribution from the Department of Chemistry,
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Transmetalation of Tetranuclear Copper Complexes. 4. Structural Implications of the Kinetics of Direct Transmetalation of Tetranuclear Copper(II) Complexes by $Ni(NS)_2$ Reagents

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The rate laws for direct transmetalations of excesses of tetranuclear copper(II) complexes $(\mu_4\text{-O})[NCu]_4X_6$ (A) (N = monodentate *N,N*-diethylnicotinamide (DENC), pyridine (py); X = Cl, Br) by $Ni(NS)_2$ reagents B and C in nitrobenzene to give $(\mu_4\text{-O})[N_4Cu_3Ni]X_6$ products (D) depends on the molecular geometries of B and C. For B, with cis-coordinated sulfur atoms in a distorted square-planar geometry, rate = $k_B[A]^2[B]$, while C, which is a trans square-planar species, obeys rate = $k_C[A][C]$. It is concluded that rapid exchange of nickel for copper takes place in $\overline{\text{Cu–X–Ni–S}}$ rings.

Introduction

Direct transmetalation is the exchange of metal centers in a polynuclear complex with retention of its core structure.[1,2] Examples of partial and complete metal exchange are shown in eq 1 and 2. Here, N is a monodentate pyridine, X is Cl or Br, and

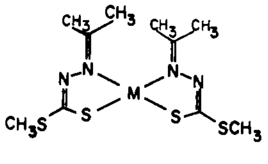
$$(\mu\text{-O})_2[NCuX]_4 + 4Ni(NS)_2 \xrightarrow{H_2O} (\mu\text{-O})_2[NCuNi(H_2O)X_2]_2 + 2Cu(NS)_2 + 2Ni(NS)_2N \quad (1)$$

$$(\mu_4\text{-O})[NCu]_4X_6 + 4Ni(NS)_2 \xrightarrow{H_2O} (\mu_4\text{-O})[NNi(H_2O)]_4X_6 + 4Cu(NS)_2 \quad (2)$$

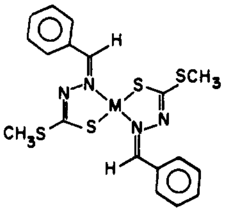
NS is a monoanionic *S*-methyl hydrazinecarbodithioate Schiff base ligand. The thermodynamic driving force for these reactions, which are rapid at room temperature in aprotic solvents like methylene chloride and nitrobenzene, is the formation of very stable $Cu(NS)_2$ coproducts. Efficient gel permeation chromatographic separation of product mixtures results in the coordination of one water molecule by each new nickel center in the original polynuclear core structure.[1,2]

Direct transmetalation has considerable potential in the synthesis of partially and completely substituted polynuclear structures that cannot be obtained by other means. Reactions 1 and 2 are stoichiometric because of favorable thermodynamics. An understanding of the structural–mechanistic factors that also lead to practical rates of metal exchange will be useful in extending direct transmetalation to other polynuclear systems. This information can be obtained from kinetic studies of transmetalation systems involving reactants of known molecular structure.

We demonstrate here that the direct transmetalations of tetranuclear complexes $(\mu_4\text{-O})[NCu]_4X_6$ (A) (N = monodentate *N,N*-diethylnicotinamide (DENC), pyridine (py); X = Cl, Br), by $Ni(NS)_2$ reagents B and C (Figure 1[3–6]) are stoichiometric processes but with rate laws for the first step, eq 3, which depend on the structures of B[5] and C.[6]



B



C

$$A + B \text{ or } C \xrightarrow[\text{solvent}]{\text{aprotic}} \underset{D}{(\mu_4\text{-O})[N_4Cu_3Ni]X_6} + B \text{ or } C \text{ (M = Cu)} \quad (3)$$

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† On leave of absence from the Department of Chemistry, Faculty of Science, University of Alexandria, Alexandria, Egypt.

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