to a direct interference of the handle upon the bond formation step when the chain is located at a short distance from the iron atom. In spite of similar ΔG_I values, Table I shows that the activation energy remains close to 4 kJ·mol^{-1} for O_2 whereas it is increased by nearly 20 kJ·mol^{-1} for CO with **5**. On the contrary, *A* changes by more than 2 orders of magnitude for O_2, but exhibits little variation for CO along the **3**–**5** series. Accordingly, the origin of the destabilization of transition state I is almost purely entropic for oxygen and predominantly enthalpic for carbon monoxide. This can be understood by considering the structural modifications that must take place during the binding process. A linear orientation of carbon monoxide should be accompanied at first by an increased interaction of this ligand with the chain. At the same time the porphyrin becomes more ruffled, leaving the chain farther away from the iron in order to accommodate CO linearly. Presumably, the shorter the handle length, the more pronounced the increase of distortion required in the binding process. Using the crystallographic data relative to the penta- and hexacoordinated complexes of **5**, we calculated that the distance of the two central C atoms from the iron is increased from about 4.8 to 6.9 Å and that the ruffling distortion increases from 6 to 14° during the binding process. The energy that must be expended appears as a larger activation enthalpy in compounds **4** and **5** as compared to **3**. Binding oxygen, on the contrary, implies a bent conformation. Although crystallographic data for the O_2 complexes are not available, it does not seem necessary to assume an increase of ruffling in this case since the bent orientation would tend to release the steric constraints with the chain. The invariant activation enthalpy supports this view. The destabilization appears as entropy terms. The orientational freedom of oxygen is known to be strongly limited due to H-bonding with the amide protons. However the effect has been shown to be significant only in the bound state.[8] Orientational constraint of a different nature, e.g. the avoiding of transient lateral interactions with the protons of the methylene groups, may play a specific role in the transition state.

Thus, in addition to confirming that hybrid models also react via two sequential energy barriers, the present results indicate that steric discrimination against CO does not occur in either transition state since both are destabilized to the same extent for CO and O_2. This is partly in agreement with the findings of Traylor et al.[21] that steric effects are seen mainly in association rates and that those are changed equally for CO and O_2. However, a previous discussion of the linear free energy relationships observed in various porphyrin series[8] has shown that this behavior is not general and can only be expected for a strong central steric hindrance. Moreover, only a detailed thermodynamic study is able to reveal that the ΔG changes, although very close for O_2 and CO, are brought about by the complex interplay of enthalpic and entropic factors, which intrinsically differ with the nature of the ligand.

Supplementary Material Available: Tables SI–SVI, listing kinetic rate constants for O_2 and CO binding with compounds **3**–**5** as a function of the temperature and 1-MeIm and gaseous ligand concentrations, and Table SVII, giving O_2 and CO solubilities in toluene as a function of the temperature between 343 and 193 K (6 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry and Biochemistry,
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Early/Late Heterobimetallic Complexes: Syntheses and Spectral and Structural Studies of Thiolato-Bridged Ti/Cu and V/Cu Complexes

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The heterobimetallic complexes $[Cp_2Ti(\mu\text{-}SMe)_2CuPCy_3]PF_6$ (**1**), $[Cp_2Ti(\mu\text{-}SR)_2Cu(NCMe)_2]PF_6$ (R = Me (**2**), R = Et (**3**)), and $[(Cp_2Ti(\mu\text{-}SMe)_2)_2Cu]PF_6$ (**4**) have been prepared and characterized. Variable-temperature NMR studies of **1** and **2** show that the preferred orientation in solution of the methyl substituents on sulfur at low temperature is one in which they adopt a cisoid disposition. Inversion at sulfur is proposed as the mechanism that leads to the time-averaged signals at ambient temperature. The energies of the fluxional processes were found to be 77 and 80 kJ/mol for **1** and **2**, respectively. Complex **2** crystallizes in the triclinic space group $P\bar{1}$, with a = 8.038 (2) Å, b = 13.169 (3) Å, c = 11.732 (3) Å, α = 109.31 (2)°, β = 106.12 (2)°, γ = 89.29 (2)°, Z = 2, and V = 1122 (1) Å^3. The structural data are consistent with a cisoid disposition of the methyl groups on sulfur. Cyclic voltammetric studies of **1**–**4** show that reduction of these complexes leads to complex degradation. Electronic analogues of reduced **1** and **2** were prepared by employing V(IV). The complexes $[Cp_2V(\mu\text{-}SEt)_2CuPR_3]PF_6$ (R = Ph (**5**), R = Cy (**6**)), $[Cp_2V(\mu\text{-}SR)_2Cu(NCMe)_2]PF_6$ (R = Me (**7**), R = Et (**8**)) show EPR spectra characteristic of V(IV) complexes. For complexes **5** and **6**, hyperfine coupling to Cu(I) and P is discernible. Computer simulation revealed that the coupling to Cu is 9.5 G and to P is 8.0 G. The implications of both the structural and spectroscopic parameters for these heterobimetallic complexes are discussed. The data are consistent with electronic communication between the metal centers. A dative interaction from the electron-rich d^{10} Cu(I) center to the d^0 Ti(IV) center is suggested.

Introduction

Interest in early/late heterobimetallics[1] has arisen for several reasons. The pairing of the oxophilicity of the early metals and catalytic properties of the later metals seems to be, intuitively, the combination required for carbon oxide reduction chemistry. This view is supported by observations made for heterogeneous catalysts in which late metals are dispersed on early metal supports. In these cases, the reactivity of the dispersed metal is dramatically perturbed from that of the same metal dispersed on an inert support. This phenomenon has been termed strong metal–support interaction.[2] The nature of the interactions between the support and the late metal is not clear, but a number of possibilities have been offered. These include direct metal–metal electronic communication with participation of a reduced support in the chemistry at the surface or, alternatively, cooperative activation of the substrate by the early and late metal centers.

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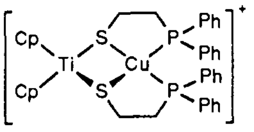
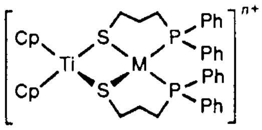
(1) Recent examples of early/late heterobimetallic systems have been cited in ref 3–12 and reviewed in: Stephan, D. W. *Coord. Chem. Rev.* **1989**, *95*, 41.

(2) Baker, R. T. K., Tauster, S. J., Dumesic, J. A., Eds. *Strong Metal-Support Interactions*; American Chemical Society: Washington, DC, 1986.

0020-1669/90/1329-1731$02.50/0

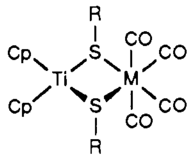
The possibility of similar reactivity perturbations and the potential for CO reduction chemistry has led to a number of recent studies of homogeneous early/late heterobimetallic complexes. These studies have been recently reviewed.[1] A variety of synthetic routes to complexes containing both an early and a late transition metal have been described, including the use of a number of different bridging ligands. In this area, we have described several synthetic routes to early/late heterobimetallic complexes in which thiolate[3-7] or phosphide[8-13] ligands bridge the two metal centers. Our initial work involved the use of chelating phosphinethiolate ligands,[3-5] giving complexes of the form

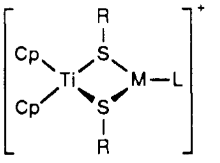



M = Rh, *n* = 1; M = Ni, *n* = 0

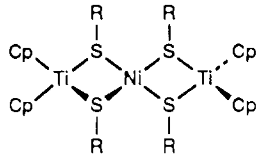
The implied role of reduced Ti centers in SMSI[2] led us to study the redox chemistry of these heterobimetallics. These complexes undergo reversible chemical reduction affording the formally Ti(III)/M(I) (M = Cu, Rh) species. In the case of [$Cp_2Ti(\mu$-$SCH_2CH_2CH_2PPh_2)_2Rh]^+$, the observation of coupling of the unpaired electron on Ti to Rh and P further suggests the possibility of a transannular metal–metal communication.[4]

Previous reports have described related heterobimetallic complexes in which simple titanium thiolate species act as metalloligands, giving compounds of the form $Cp_2Ti(\mu$-$SR)_2M(CO)_4$ (M = Cr, Mo, W)[14-22] and [$Cp_2Ti(\mu$-$SR)_2NiCp]^+$.[23] More recently, we have described complexes of the form [$Cp_2Ti(\mu$-$SEt)_2CuL]^+$ where L is a phosphine,[6] and $(Cp_2Ti(\mu$-$SMe)_2)_2Ni$.[7]


M = Cr, Mo, W; R = H, alkyl, Ph


M = Cu, L = phosphine, R = Me
M = Ni, L = Cp, R = Me

In both cases, the structural data suggest the presence of Ti–M dative interactions; however, attempts to reduce these species led to degradation of the heterobimetallic compound. An isoelectronic analogue of the reduced Ti/Ni species could not be prepared by using $Cp_2V(SMe)_2$; instead, ligand transfer and redox chemistry afforded the Ni–thiolate $(Ni(\mu$-$SMe)_2)_6$.[7]



In this report, we present structural and spectroscopic evidence of such metal–metal interactions. Synthetic routes to new Ti(IV)/Cu(I) thiolato-bridged heterobimetallics are described. A structural study of the complex [$Cp_2Ti(\mu$-$SMe)_2Cu(NCMe)_2$][PF_6] is presented. Electrochemical studies of these new heterobimetallics show that the one-electron-reduction products, that is, the Ti(III)/Cu(I) complexes, are not accessible. However, V(IV)/Cu(I) complexes, which are isoelectronic to the Ti(III)/Cu(I) species, have been prepared and studied by EPR spectroscopy. The results of these studies are presented herein, and their implications regarding the nature of metal–metal interactions in such heterobimetallic species are discussed.

Experimental Section

All preparations were done under an atmosphere of dry, O_2-free N_2. Solvents were reagent grade, distilled from the appropriate drying agents under N_2, and degassed by the freeze–thaw method at least three times prior to use. ^1H NMR spectra were recorded on a Bruker AC-300 spectrometer operating at 300 MHz. Trace amounts of protonated solvents were used as references, and chemical shifts are reported in ppm relative to $SiMe_4$. $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AC-200 spectrometer operating at 81 MHz and are reported relative to external 85% H_3PO_4. Cyclic voltammetry experiments were performed on a BAS CV-27 electrochemistry unit with a platinum working electrode and a Ag/AgCl reference electrode. [NBu_4]BF_4 was used as the supporting electrolyte. EPR spectra were recorded on a Varian E-12 EPR spectrometer and DPPH as a reference. The spectra described herein were recorded at 25 °C in THF solution. Samples were prepared in a glovebox and sealed under an atmosphere of N_2. Simulation of the spectra was achieved by employing a local EPR simulation program operating on an IBM-PC-XT computer. Combustion analyses were performed by Galbraith Laboratories Inc., Knoxville, TN. PPh_3 was purchased from the Aldrich Chemical Co., and PCy_3 was purchased from the Pressure Chemical Co. [$Cu(NCMe)_4$]PF_6, $Cp_2M(SR)_2$ (M = Ti, V; R = Me, Et) were prepared by the literature method.[6,7]

Preparation of [$Cp_2Ti(SMe)_2CuPCy_3$]PF_6 (1). To a 30-mL THF suspension of [$Cu(MeCN)_4$]PF_6 (136 mg, 0.36 mmol) was added PCy_3 (205 mg, 0.72 mmol). To the clear, colorless solution was added a purple THF solution of $Cp_2Ti(SMe)_2$ (100 mg, 0.36 mmol), resulting in a color change to red-orange and precipitation of bright orange solid. The bright orange microcrystalline solid was isolated by filtration, washed with 2 × 10 mL of pentane, and dried in vacuo. Yield: 227 mg, 80%. Anal. Calcd for $C_{30}H_{49}CuF_6P_2S_2Ti$: C, 47.34; H, 6.49. Found: C, 47.22; H, 6.47. ^1H NMR (Me-d_3-CN): δ 6.03 (s, 10 H), 2.50 (s, 6 H), 1.96–1.27 (br m, 33 H). $^{31}P\{^1H\}$ NMR (Me-d_3-CN): δ 29.90 (s), −142.99 (septet).

Preparation of [$Cp_2Ti(\mu$-$SMe)_2Cu(NCMe)_2$]PF_6 (2). To [$Cu(NCMe)_4PF_6$ (136 mg, 0.36 mmoles) in 30 mL of MeCN was added dropwise $Cp_2Ti(SMe)_2$ (100 mg, 0.36 mmol) in 10 mL MeCN, which resulted in a color change from purple to dark red-orange. After the mixture was stirred for 30 min, the solvent was removed under vacuum and the residue washed with 2 × 10 mL of pentane. The product was collected by filtration, washed with 2 × 10 mL of diethyl ether, and dried in vacuo. (Yield: 142 mg, 70%.) Anal. Calcd for $C_{16}H_{22}CuF_6N_2PS_2Ti$: C, 34.14; H, 4.97. Found: C, 33.90; H, 4.90. ^1H NMR (Me-d_3-CN): δ 6.00 (s, 5 H), 2.46 (s, 3 H), 1.95 (s, 3 H).

Preparation of [$Cp_2Ti(\mu$-$SEt)_2Cu(NCMe)_2$]PF_6 (3). This species is prepared in a manner analogous to that used for the methanethiolate species by using [$Cu(NCMe)_4$]PF_6 (136 mg, 0.36 mmol) and $Cp_2Ti(SEt)_2$ (108 mg, 0.36 mmol). Yield: 138 mg, 65%. ^1H NMR (Me-d_3-CN): δ 5.98 (s, 5 H), 2.84 (q, 2 H), 2.05 (s, 3 H), 1.14 (t, 3 H).

Preparation of [$(Cp_2Ti(\mu$-$SMe)_2)_2Cu$]PF_6 (4). To a 30-mL THF suspension of [$Cu(NCMe)_4$]PF_6 (68 mg, 0.18 mmol) was added $Cp_2Ti(\mu$-$SMe)_2$ (100 mg, 0.36 mmol) and the mixture stirred. Upon stirring, the color of the solution changed from purple to red-purple, and after 20 min, precipitation of a dark solid was evident. The solution was filtered and the solid washed with 2 × 10 mL pentane and dried in vacuo. Yield 90 mg, 65%. Anal. Calcd for $C_{24}H_{32}CuF_6PS_4Ti_2$: C, 38.28; H, 4.28. Found: C, 37.22; H, 4.21. ^1H NMR (acetone-d_6): δ 6.23 (s, 5 H), 2.77 (s, 3 H).

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Table I. Crystallographic Data for Molecule **1**

formula: $C_{16}CuF_6H_{22}N_2PS_2Ti$	fw = 562.4
$a = 8.038$ (2) Å	space group: $P\bar{1}$ (No. 2)
$b = 13.169$ (3) Å	$T = 24$ °C
$c = 11.732$ (3) Å	$\lambda = 0.71069$ Å
$\alpha = 109.31$ (2)	$\rho = 1.67$ g cm^{-3}
$\beta = 106.12$ (2)	$\mu = 15.30$ cm^{-1}
$\gamma = 89.29$ (2)	transm coeff = 0.781–0.866
$V = 1122$ (1) Å^3	$R(F_o) = 0.0585$
$Z = 2$	$R_w(F_o^2) = 0.0620$

Reaction of $[Cp_2Ti(\mu\text{-}SMe)_2Cu(NCMe)_2]PF_6$ with PCy_3. To a 20-mL THF solution of $[Cp_2Ti(\mu\text{-}SMe)_2Cu(NCMe)_2]PF_6$ (30 mg, 0.053 mmol) was added PCy_3 (0.15 mg, 0.05 mmol). The solution changed from dark red-orange to bright orange immediately, and an orange solid precipitated. The solid was isolated by filtration, washed with 2 × 10 mL of pentane, and dried in vacuo. $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 30.39 (s), −143.80 (septet).

Reaction of $[Cp_2Ti(\mu\text{-}SMe)_2Cu(NCMe)_2]PF_6$ with PMe_3. To a 20-mL THF solution of $[Cp_2Ti(\mu\text{-}SMe)_2Cu(NCMe)_2]PF_6$ (30 mg, 0.053 mmol) was added PMe_3 (0.08 mg, 0.10 mmol). The color of the solution immediately changed from dark red-orange to purple. $^{31}P\{^1H\}$ NMR (THF): δ −45.88 (br s), −143.80 (septet).

Preparation of $[Cp_2V(\mu\text{-}SEt)_2CuL]PF_6$ (L = PPh_3 (5), L = PCy_3 (6)). To a 30-mL THF suspension of $[Cu(NCMe)_4]PF_6$ (123 mg, 0.33 mmol) was added 2 equiv of the appropriate phosphine and the mixture stirred for 5 min. To the clear, colorless solution was added dropwise a green-black THF solution of $Cp_2V(SEt)_2$ (100 mg, 0.33 mmol), which resulted in an immediate color change to dark brown. The solution was stirred for 20 min and the volume then reduced to 5 mL. The product was precipitated by addition of *n*-hexane and isolated by filtration. The brown microcrystalline product was washed with 2 × 10 mL portions of pentane and dried in vacuo. Yield of **5**: 153 mg, 60%. EPR of **5** (THF): $g = 1.998$, $a\langle^{51}V\rangle = 58.9$. Yield of **6**: 170 g, 65%. EPR of **6** (THF): $g = 2.001$, $a\langle^{51}V\rangle = 60.0$ G.

Preparation of $[Cp_2V(\mu\text{-}SR)_2Cu(NCMe)_2]PF_6$ (R = Me (7), R = Et (8)). To $[Cu(NCMe)_4]PF_6$ (136 mg, 0.36 mmol) in 20 mL of MeCN was added dropwise $Cp_2V(SMe)_2$ (100 mg, 0.36 mmol) or $Cp_2V(SEt)_2$ (100 mg, 0.33 mmol) in 10 mL of MeCN, which resulted in a color change from blue-black to brown. After the mixture was stirred for 10 min, a brown solid was precipitated with diethyl ether and collected by filtration. The solid was washed with 2 × 20 mL portions of pentane and dried in vacuo. Yield of **7** 106 mg, 57%. EPR of **7** (MeCN): $g = 1.996$, $a\langle^{51}V\rangle = 67.5$ G. Yield of **8**: 97 mg, 50%. EPR of **8** (MeCN): $g = 1.999$, $a\langle^{51}V\rangle = 60.0$ G.

X-ray Data Collection and Reduction. Diffraction experiments were performed on a four-circle Syntex $P2_1$ diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71069$ Å). The initial orientation matrix for **2** was obtained from 15 machine-centered reflections selected from rotation photographs. These data were used to determine the crystal system. Partial rotation photographs around each axis were consistent with a triclinic crystal system. The final lattice parameters and the final orientation matrix were determined from 64 high-angle reflections (20° < 2θ < 25°). Machine parameters, crystal data, and data collection parameters are summarized in Table I. The observed extinctions were consistent with the space group $P\bar{1}$, and $\pm h,\pm k,+l$ data were collected (4.5° < 2θ < 45.0°). Three standard reflections were recorded every 197 reflections with no statistically significant change in their intensities over the duration of the data collection. The data were processed by using the SHELX-76 program package. An empirical absorption correction was applied to the data by employing a locally modified version of ABSORB.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[24-26] The heavy atom positions were determined by using direct methods. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinement was carried out by using full-matrix least-squares techniques on F, minimizing the function $w(|F_o| - |F_c|)^2$ where the weight, w, is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitude. In the final cycles of refinement, all the non-hydrogen atoms were assigned anisotropic temperature factors. Hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C–H bond length of 0.95 Å. Hydrogen atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the carbon atom to which they are bonded. In all cases the hydrogen atom contributions were calculated, but not refined. Listings of positional parameters (Table II) and selected bond distances and angles (Table III) are given; thermal parameters, hydrogen atom parameters and observed and calculated structure factors have been deposited as supplementary material.

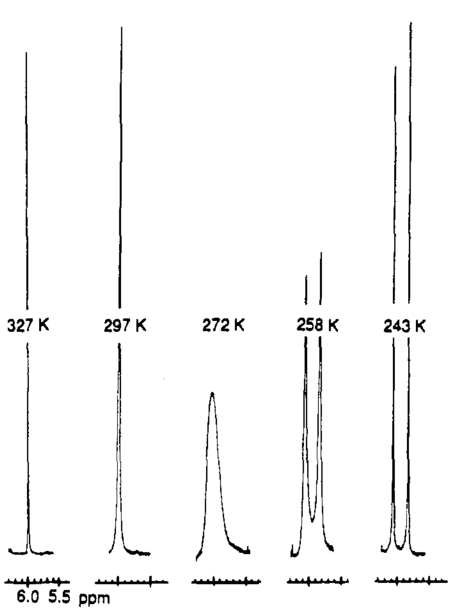

Figure 1. Variable-temperature ^1H NMR spectrum of **2**. The cyclopentadienyl region is shown.

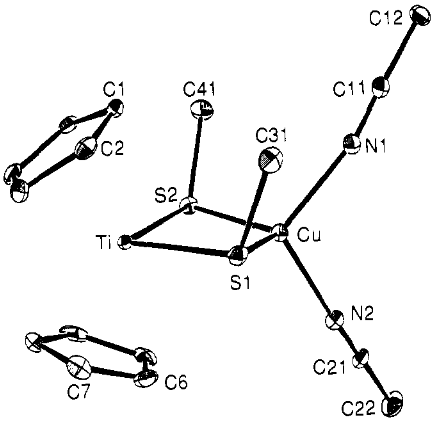

Figure 2. ORTEP drawing of cation of molecule **2**. The 20% thermal ellipsoids are shown. Hydrogen atom are omitted for clarity.

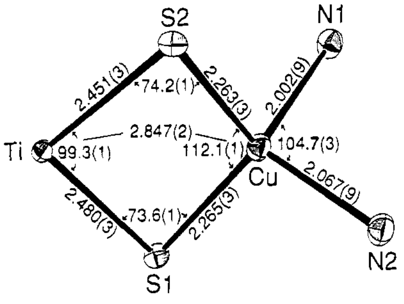

Figure 3. ORTEP drawing of the TiS_2CuN_2 core of **2**.

Results

The reactions involving Ti species are summarized in Scheme I. The results of a crystallographic study of **2** are presented in Tables I–III and in Figures 2 and 3. A variable-temperature ^1H NMR study of **2** is shown in Figure 1. EPR data for the related V(IV) species **6** are shown in Figure 4. The structural and spectral parameters and electrochemical data, presented in the

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Table II. Positional Parameters[a]

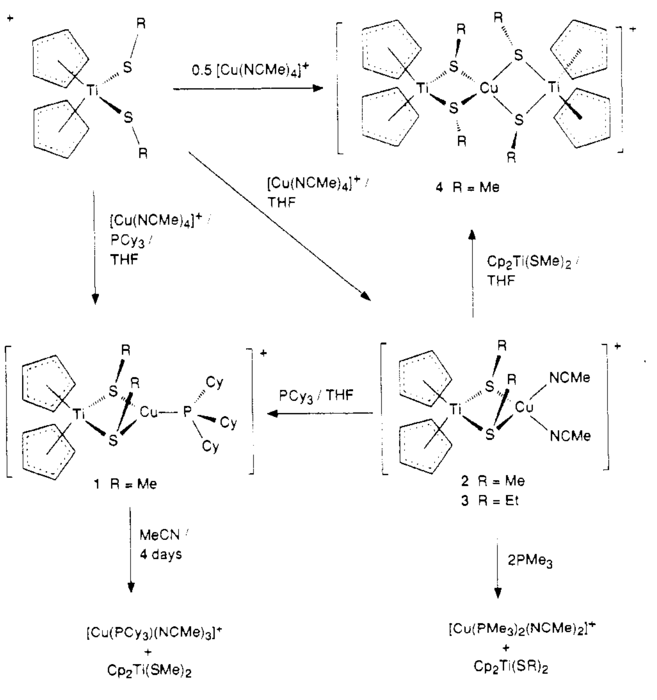
atom	x	y	z	atom	x	y	z
Ti	3436 (2)	7338 (1)	7479 (1)	Cu	2350 (1)	5631 (1)	8166 (1)
S1	482 (3)	6674 (2)	7329 (2)	S2	5159 (3)	6242 (2)	8625 (2)
N1	1980 (12)	5617 (6)	9779 (9)	N2	2124 (11)	4020 (7)	7059 (8)
P	1617 (4)	9208 (2)	12842 (2)	F1	1262 (13)	9579 (8)	11723 (7)
F2	3009 (13)	10129 (7)	13487 (9)	F3	173 (12)	8323 (8)	2141 (13)
F4	355 (10)	9917 (7)	13387 (8)	F5	2094 (17)	8833 (12)	13958 (10)
F6	2839 (11)	8504 (7)	12240 (10)	C1	3550 (13)	8680 (7)	9417 (9)
C2	2428 (14)	8993 (7)	8479 (10)	C3	3391 (17)	9197 (8)	7744 (11)
C4	5106 (16)	9003 (8)	8244 (11)	C5	5204 (13)	8700 (7)	9267 (9)
C6	2275 (21)	6131 (14)	5380 (11)	C7	2472 (19)	7077 (13)	5300 (11)
C8	4135 (21)	7407 (10)	5663 (10)	C9	5096 (16)	6610 (15)	6067 (9)
C10	3869 (29)	5775 (10)	5866 (12)	C11	1992 (14)	5742 (8)	10779 (11)
C12	1965 (15)	5894 (8)	12069 (10)	C21	2263 (14)	3152 (9)	6598 (10)
C22	2512 (17)	1997 (10)	6036 (13)	C31	−383 (13)	7409 (9)	8633 (11)
C41	5871 (14)	6805 (9)	10338 (9)				

[a] Parameters multiplied by 10^4.

Table III. Selected Bond Distances and Angles

		Distances (Å)			
Ti–S1	2.480 (3)	Ti–S2	2.451 (3)	Cu–S1	2.265 (3)
Cu–S2	2.263 (3)	Cu–N1	2.002 (9)	Cu–N2	2.067 (9)
S1–C31	1.832 (11)	S2–C41	1.818 (10)	N1–C11	1.127 (12)
C11–C12	1.465 (15)	N2–C21	1.111 (12)	C21–C22	1.481 (16)
		Ti···Cu	2.847 (2)		
		Angles (deg)			
S2–Ti–S1	99.3 (1)	S2–Cu–S1	112.2 (1)	Cu–S1–Ti	73.6 (1)
Cu–S2–Ti	74.2 (1)	C31–S1–Ti	115.9 (3)	C31–S1–Cu	102.7 (4)
C41–S2–Ti	117.7 (4)	C41–S2–Cu	103.9 (4)	N1–Cu–S1	110.6 (3)
N1–Cu–S2	106.9 (3)	N2–Cu–S1	115.5 (3)	N2–Cu–S2	106.3 (3)
N2–Cu–N1	104.7 (3)	C11–N1–Cu	168.5 (9)	C12–C11–N1	179 (1)
C21–N2–Cu	168 (1)	C22–C21–N2	177 (1)		

Scheme I



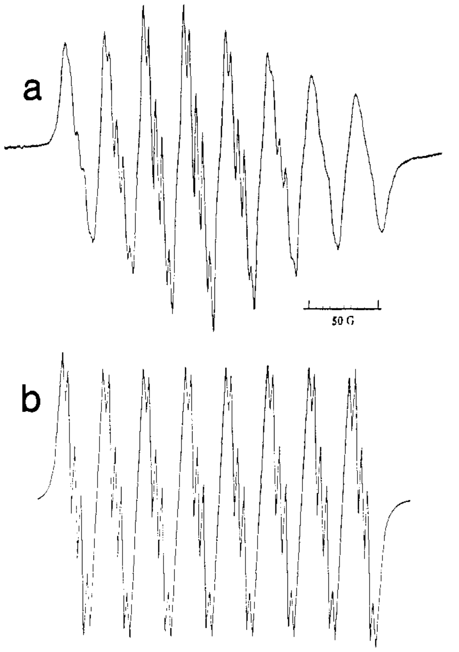


Figure 4. (a) EPR spectrum and (b) computer simulation of EPR spectrum of **6**.

Experimental Section and the tables and figures indicated above, will be introduced at the appropriate places in the Discussion.

Discussion

Addition of the purple metalloligand $Cp_2Ti(SMe)_2$ to a colorless, THF solution of $[Cu(NCMe)_4]PF_6$ and PCy_3 affords a red-orange solution. The bright orange solid **1** precipitated after 10 min and was isolated by filtration. The similarity of the color of **1** to that of the previously reported complexes $[Cp_2Ti(\mu\text{-}SEt)_2CuL]PF_6$ suggests a similar formulation.[6] The $^{31}P\{^1H\}$ NMR spectrum for **1** shows two resonances; a singlet with a chemical shift corresponding to coordinated phosphine and the characteristic septet due to the PF_6 anion. In the ^1H NMR spectrum of **1**, there are the expected singlets due to the cyclopentadienyl and methyl groups and a multiplet corresponding to the cyclohexyl groups. Integration of the both the $^{31}P\{^1H\}$ and the ^1H spectra are consistent with the formulation for **1** as $[Cp_2Ti(\mu\text{-}SMe)_2CuPCy_3]PF_6$. The complex is similar to the complexes $[Cp_2Ti(\mu\text{-}SEt)_2CuL]PF_6$, which we have previously described.[6]

Reaction of $Cp_2Ti(SMe)_2$ or $Cp_2Ti(SEt)_2$ with $[Cu(NCMe)_4]PF_6$ in acetonitrile results in red-orange solutions. Removal of the solvent and trituration with diethyl ether affords red-orange microcrystalline solids **2** and **3**, respectively. ^{1}H NMR spectra for each of these products show singlets in the cyclopentadienyl region and resonances attributable to the respective sulfur substituents. In both cases, a multiplet at about 1.93 ppm is observed and attributed to two Cu-bound acetonitriles. On the basis of the integrations of the NMR data, the structures of **2** and **3** were assigned as $[Cp_2Ti(\mu\text{-}SR)_2Cu(NCMe)_2]PF_6$ (R = Me (**2**), R = Et (**3**)).

The temperature dependence of the ^{1}H NMR spectra of complexes **1** and **2** (Figure 1) was studied in the range from 327–243 K. In both cases, the cyclopentadienyl resonances are singlets at 327 K. These signals broaden as the temperature is lowered, and at 243 K, each becomes two sharp singlets. The cyclopentadienyl environments at low temperature are consistent with a cisoid arrangement of the alkyl groups on the bridging sulfurs for both complexes. Averaging of these environments at ambient temperatures may occur via a simultaneous, pyramidal inversion at the sulfurs. Alternatively, a mechanism involving sequential inversion at one sulfur at a time would require the presence of an intermediate transoid isomer; however, no evidence for this is seen in the ^{1}H NMR spectrum. It may be that steric interactions of the alkyl substituents on sulfur with the ligands on Cu destabilize the transoid isomer and thus facilitate the inversion at the second sulfur. A third possible mechanism for averaging of the cyclopentadienyl environments involves cleavage of a S–Cu bond, rotation, and bond re-formation. Line-shape analyses revealed the activation energies for the averaging process to be 77 and 80 kJ/mol for **1** and **2**, respectively. These values are similar in magnitude to those found for related thiolate-bridged heterobimetallic complexes where the averaging process has been proposed to involve simultaneous pyramidal inversion at the bridging sulfurs.[5,6,21] These data indicate that the thermodynamically preferred conformations for both **1** and **2** in solution are ones in which the alkyl substituents adopt cis dispositions. These geometries have also been observed in the crystallographic studies of $[Cp_2Ti(\mu\text{-}SEt)_2CuL]PF_6$ (L = PPh_3, PCy_3)[6] and **2** (vide infra).

Reaction of 2 equiv of the metalloligand $Cp_2Ti(SMe)_2$ with $[Cu(NCMe)_4]PF_6$ leads to the trimetallic complex $[(Cp_2Ti(\mu\text{-}SMe)_2)_2Cu]PF_6$ (**4**). The dark, red-brown solid precipitates from THF and is isolated by filtration. The ^{1}H NMR data and elemental analyses are consistent with the above formulation (Scheme I). Although a structural study of **4** was not carried out, it is expected that the structure of **4** is similar to that reported for the isoelectronic complex $(Cp_2Ti(\mu\text{-}SMe)_2)_2Ni$.[7] Thus, the Cu center of **4** is expected to occupy a pseudotetrahedral coordination sphere, where the methyl groups on the bridging sulfurs from each metalloligand adopt a transoid disposition. This geometry would permit a minimization of steric interactions between the substituents of the metalloligands about Cu.

The isolation of **2–4** establish that pseudotetrahedral coordination spheres at Cu can be attained in these thiolate-bridged heterobimetallics. We have previously reported the related complex $[Cp_2Ti(\mu\text{-}SCH_2CH_2PPh_2)_2Cu]BF_4$ in which the chelating phosphinethiolate provides a similar pseudotetrahedral environment for Cu.[3] Attempts to employ the sterically less demanding phosphine PMe_3 to synthesize the analogous heterobimetallic $[Cp_2Ti(\mu\text{-}SMe)_2Cu(PMe_3)_2]PF_6$ was not successful. Instead, complex **4** is obtained when 1 equiv of $Cp_2Ti(SMe)_2$ is reacted with $[Cu(NCMe)_4]PF_6$ and 2 equiv of PMe_3 in THF. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture is consistent with the formation of $[Cu(PMe_3)_2(NCMe)_2]PF_6$, leaving the remaining half of the $[Cu(NCMe)_4]PF_6$ to react with the $Cp_2Ti(SMe)_2$ affording **4**. Similarly, addition of PMe_3 to solutions of **2** or **3** does not yield the substituted heterobimetallic but rather $[Cu(NCMe)_2(PMe_3)_2]PF_6$ and the free metalloligand $Cp_2Ti(SMe)_2$. The basicity and small steric demands of PMe_3 presumably facilitate disubstitution at Cu yielding displacement of the metalloligand from Cu. In contrast, addition of PCy_3 to **2** in THF affords the heterobimetallic **1**. The reverse reaction, that is, the formation of **2** by addition of acetonitrile to complex **1**, does not proceed. In fact, the phosphine complex **1** is stable even in MeCN, for 3–4 days, eventually degrading to $Cp_2Ti(SMe)_2$ and $[Cu(PCy_3)(NCMe)_3]PF_6$. These reactions are summarized in Scheme I.

X-ray quality crystals of **2** were obtained by anaerobic diffusion of diethyl ether into an acetonitrile solution of **2**. A crystallographic study shows the crystal is made up of monoclinic unit cells containing four discrete anions and cations. The closest approach between any anion and any cation is 2.511 Å (H4–F2). The cation of **2** is depicted in the ORTEP drawing in Figure 2. The pseudotetrahedral coordination sphere of Ti is comprised of two π-bonded cyclopentadienyl rings and two methanethiolate moieties. The Cu coordination sphere is also pseudotetrahedral consisting of the two sulfurs of the metalloligand and two nitrogens of the coordinated acetonitriles. The alkyl substituents on the bridging sulfur atoms adopt a cis disposition, consistent with the low-energy conformation indicated from the solution studies. The Ti–C, S–C, N–C, and C–C bond lengths are typical.[3-7]

Details of the TiS_2CuN_2 core are shown in Figure 3. The Ti–S bond lengths of 2.451 (3) and 2.480 (3) Å are similar to those found in $[Cp_2Ti(\mu\text{-}SEt)_2CuL]PF_6$ (L = PPh_3, PCy_3).[6] Angles at the bridging sulfur atoms are 74.2 (1) and 73.6 (1)°. These angles are similar to those found in $[Cp_2Ti(\mu\text{-}SEt)_2CuL]PF_6$ (L = PPh_3, PCy_3)[6] and $(Cp_2Ti(\mu\text{-}SMe)_2)_2Ni$[7] and some 4° smaller than the corresponding angles found in $[Cp_2Ti(\mu\text{-}SCH_2CH_2PPh_2)_2Cu]BF_4$.[3] The S1–Ti–S2 angle of 99.3 (1)° is 5° larger than the S–Ti–S angle observed in the free metalloligand $Cp_2Ti(SMe)_2$.[13] The S1–Cu–S2 angle is 112.1°. The angles about the core are similar to those found in other Ti/late-metal, thiolato-bridged heterobimetallics.[3-7] In these cases, the closing down of the M–S–M′ angles and opening up of the S–M–S angles compared to those in related monometallic species have been cited as evidence for metal–metal interaction. The TiS_2Cu core of **2** is puckered, with an angle of 11° between the S1–Cu–S2 and the S1–Ti–S2 planes. In contrast, the TiS_2Cu core of $[Cp_2Ti(\mu\text{-}SCH_2CH_2PPh_2)_2Cu]BF_4$ is planar.[3] The Ti–Cu distance of 2.847 Å in **1** is similar to that seen in $[Cp_2Ti(\mu\text{-}SEt)_2CuL]PF_6$ (L = PPh_3, PCy_3)[6] and substantially less than the 3.024-Å separation found in $[Cp_2Ti(\mu\text{-}SCH_2CH_2PPh_2)_2Cu]BF_4$.[3] The puckering of the TiS_2Cu core accommodates the closer proximity of the metal centers. Dative donation from the electron-rich late-metal center to the Lewis acidic early metal may account for the structural distortion of the TiS_2M cores in **2** and related heterobimetallics.

The possibility of reversible redox chemistry of complexes **1–4** was investigated by cyclic voltammetry. In contrast to the complexes $[Cp_2Ti(\mu\text{-}SCH_2CH_2PPh_2)_2Cu]BF_4$ and $[Cp_2Ti(\mu\text{-}SCH_2CH_2CH_2PPh_2)_2Rh]BF_4$, where reversible electrochemical waves attributable to a formally Ti(IV)/Ti(III) redox couple were observed,[3,4] the complexes **1–4** showed no electrochemically reversible waves. Instead, only irreversible waves were observed at about −0.9 to −1.0 V vs Ag/AgCl in THF by using a Pt electrode and $[NBu_4]BF_4$ as the supporting electrolyte. The inaccessibility of Ti(III)/Cu(I) reduction products of complexes **1–4** precludes a spectroscopic investigation of metal–metal coupling in the reduced complexes by EPR spectroscopy. As such information would be pertinent to the nature and degree of the metal–metal interactions, we pursued the syntheses of electronic analogues of these inaccessible species, namely V(IV)/Cu(I) complexes.

The vanadium metalloligands $Cp_2V(SR)_2$ were prepared as previously described.[7] These species exhibit EPR spectra consisting of eight-line patterns, resulting from coupling of an unpaired electron to a ^{51}V nucleus. Bimetallic complexes analogous in formulaation to **1** were prepared by a similar procedure. Upon addition of green $Cp_2V(SEt)_2$ or blue $Cp_2V(SMe)_2$ THF solutions to a solution containing $[Cu(NCMe)_4]PF_6$ and a trisubstituted phosphine, the reaction mixtures became brown. Addition of *n*-hexane and filtration gave the heterobimetallic complexes $[Cp_2V(\mu\text{-}SEt)_2CuL]PF_6$ (L = PPh_3 (**5**), L = PCy_3 (**6**)). Similarly, complexes of the formulation $[Cp_2V(\mu\text{-}SR)_2Cu(NCMe)_2]PF_6$ (R = Me (**7**), R = Et (**8**)) were prepared by addition of the appropriate $Cp_2V(SR)_2$ to $[Cu(NCMe)_4]PF_6$ in MeCN. Isolation of these complexes was achieved by addition of diethyl ether followed by filtration. These complexes proved to be very difficult to characterize. The products are stable for only short periods of time, even in the solid state under rigorously anaerobic conditions. The nature of the decomposition pathway is not clear; however, the ability of vanadocene dithiolates species to undergo facile reduction to vanadocene and disulfide has been previously described.[27] Despite these difficulties, the thiolato-bridged V(IV)/Cu(I) complexes were characterized by EPR spectroscopy. Each spectrum shows an eight-line pattern due to coupling of the unpaired electron to the vanadium nucleus with additional hyperfine coupling. The observed *g* values were typical of V(IV) species. Computer simulations of the spectra were consistent with the presence of hyperfine couplings of 9.5 G to Cu and 8.0 G to P for both **5** and **6** (Figure 4). The simulations fit well for the central lines. Broadening observed for the outer lines is typical of V(IV) compounds and arises from the anisotropy in the hyperfine interactions as a result of inhibited molecular tumbling caused by solute-solvent interactions.[27] Nonetheless, the spectral are clearly consistent with V-Cu-P couplings. We have previously reported similar coupling between the Ti(III) d^1 metal center and the Rh and P nuclei of $[Cp_2Ti(\mu\text{-}SCH_2CH_2CH_2PPh_2)_2Rh]^0$.[4] Although the line widths of the eight resonances for **7** and **8** are comparable to those of **5** and **6**, distinct hyperfine couplings are not resolved for **7** or **8**. Presumably, additional coupling to the quadrupolar N atoms of the coordinated acetonitriles contributes to the diminished resolution. The mechanism by which V-Cu-L couplings occur is not fully understood. However, molecular orbital considerations for d^1 Cp_2M systems suggest that the unpaired electron occupies the $1a_1$ orbital.[28] Interactions between this orbital and the transannular Cu center may be mediated by the bridging sulfur atoms or may result from direct interactions between the unpaired electron and the Cu. In a related study, we have favored a direct transannular mechanism to explain the larger coupling observed for $Cp_2Ti(S_2PR_2)$ than for $Cp_2Ti(SPR_2)$.[29] This suggestion was also supported by the MO calculations of Lorenz and Wasson.[30] A vehicle for direct electronic communication between V and Cu in the present compounds may arise from a dative donation from Cu to V similar to that inferred from the structural studies of **2**.

In summary, the data presented herein support the notion of electronic communication between disparate metal centers. Such interactions are not regarded as formal bonds; however, their influence on the structural and spectral properties of mixed-metal complexes is apparent. The effects of such interactions on the chemistry of mixed-metal systems is the subject of ongoing investigations.

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Supplementary Material Available: Tables of crystallographic, thermal, and hydrogen atom parameters (5 pages); a table of values of $10F_o$ and $10F_c$ (8 pages). Ordering information is given on any current masthead page.

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Stable Cationic 17-Electron $[LM(CO)_3]^+$ Species (L = 1,4,7-Tribenzyl-1,4,7-triazacyclononane; M = Cr, Mo, W): Synthesis, Spectroscopic Properties, and Reactivity. Crystal Structure of $[LMo(CO)_3](PF_6)\cdot$dmf

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The neutral 18-electron complexes $LM(CO)_3$, where L, represents the tridentate capping ligand 1,4,7-tribenzyl-1,4,7-triazacyclononane and M is Cr, Mo, or W, were prepared from $M(CO)_6$ and L in dimethylformamide (dmf) at 150 °C. Oxidation of these diamagnetic complexes in CH_2Cl_2 with ferrocenium hexafluorophosphate affords the cationic 17-electron species $[LM(CO)_3]PF_6$ in good yields. Magnetic susceptibility measurements and ESR spectroscopy confirm the presence of one unpaired electron per cation in these materials. The crystal structure of $[LMo(CO)_3](PF_6)\cdot$dmf has been determined by X-ray crystallography (trigonal, space group $R\bar{3}$; $a = 18.299$ (4), $c = 24.852$ (7) Å; $Z = 9$). The molybdenum atom is in a pseudooctahedral environment comprising three facially coordinated amine nitrogen atoms and three carbonyl ligands. The cation possesses crystallographically imposed C_3 symmetry. Cyclic voltammetry reveals a reversible one-electron oxidation of $LM(CO)_3$ species in dmf at -0.52 V vs Fc^+/Fc for the chromium complex, at -0.23 V vs Fc^+/Fc for the molybdenum complex, and at -0.305 V vs Fc^+/Fc for the tungsten complex. At more anodic potentials a second irreversible oxidation wave has been observed. The reactivity of the $LM(CO)_3$ species has been briefly investigated.

Introduction

In recent years neutral organotransition-metal, 17-electron, metal-centered radicals[2] such as $CpCr(CO)_3$,[3] $Cp^*Cr(CO)_3$,[3] $TpMo(CO)_3$,[4] and $Tp'Mo(CO)_3$[4] (Cp represents the η^5-cyclopentadienyl anion and Cp* is its pentamethylated derivative, Tp is hydridotris(pyrazolyl)borate(1-), and Tp' is hydridotris(3,5-dimethylpyrazolyl)borate(1-)) have been characterized either as reactive intermediates[3] or in one instance as relatively stable species in the solid state.[4] $CpCr(CO)_3$ exists in solution in equilibrium with its dimer $[CpCr(CO)_3]^2$,[3] which undergoes homolytic dissociation of its weak Cr-Cr bond.[3] The molybdenum and tungsten analogues $[CpM(CO)_3]_2$ are thermally more stable, but homolytic M-M bond cleavage has been shown to occur photochemically.[5] The neutral $CpM(CO)_3$ radical species (M = Mo, W) have also

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