

tetramethylethylenediamine salt but has not been characterized structurally. Related $(\text{CH}_3)_3\text{AuY}$ ($\text{Y} = \text{ylides, e.g. CH}_2\text{PR}_3 \text{ and CH}_2\text{S(O)R}_2$) complexes also have been prepared^{7a} that show considerably decreased reactivity to air and moisture. The increased stability has been attributed to the polar nature of the ylide ligand. The stability of $[\text{Au}(\text{C}_6\text{F}_5)_4]^-$ presumably arises from the electron-withdrawing properties of C_6F_5 .

Two additional structural features in **7** require further discussion, (a) the relative orientation of the pentafluorophenyl rings (along with the Au-C bond distance) and (b) the Au...F distance compared with interactions seen in other group 11 polynuclear complexes.

Fehlhammer and Dahl²⁸ have described a Au(III) homoleptic carbon-bound ring system that is in many ways quite similar to **7**. In this tetrakis(1-isopropyltetrazol-5-ato)aurate(III) anion, $[\text{Au}(\text{CN}_4\text{R})_4]^-$ ($\text{R} = i\text{-C}_3\text{H}_7$), Dahl argues that the Au-carbon bonds primarily reflect single-bond character. This is due to the lack of any significant metal to ligand or ligand to metal π -bonding as the delocalized tetrazolato ring is (a) nearly parallel with the filled d_{xy} gold orbitals and (b) is nearly orthogonal to the empty p_z gold orbital, precluding any orbital overlap. It seems that this same argument could be applied to the tetrakis(pentafluorophenyl)aurate(III) anion (**7**) described here. In both the tetra-

kis(tetrazolato)aurate(III) anion and the tetrakis(pentafluorophenyl)aurate(III) anion, the plane of the coordinated ligand ring and the plane of the four atoms coordinated to the Au(III) center from a dihedral angle between 76 and 71°. In **7** the gold-carbon bond distances range from 2.075 (11) to 2.084 (11) Å, with interaxial angles ranging from 88.2 (6) to 90.1 (7)°. Note that these distances are ~ 0.08 Å longer than in the Dahl structure.

Uson et al.²⁹ report a Ag...F interaction (2.60 and 2.69 Å) in a Pt/Ag tetranuclear complex containing the pentafluorophenyl moiety. This arises from favorable electronic and steric relationships. In complex **7** the steric relationships observed do not show any interaction (Au...F range 3.17-3.22 Å) between the *o*-fluorine of the pentafluorophenyl group and the Au center.

Acknowledgment. This work is supported by National Science Foundation Grant CHE 8408414, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Welch Foundation. L.C.P. is supported by a Welch Fellowship.

Supplementary Material Available: Full listings of anisotropic displacement parameters and H atom positions for **5-7** (6 pages); tables of observed and calculated structure factors for **5-7** (80 pages). Ordering information is given on any current masthead page.

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Synthesis, Characterization, and Structural Studies of Thiolato-Bridged Titanium(IV)-Copper(I) Species: Heterobimetallic Complexes Containing $d^{10} \rightarrow d^0$ Dative Bonds

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Received July 17, 1986

Heterobimetallic complexes of the form $[(\text{C}_6\text{H}_5)_2\text{Ti}(\mu\text{-SCH}_2\text{CH}_3)_2\text{CuL}]\text{PF}_6$, where $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$ (**4**), $\text{P}(\text{C}_6\text{H}_{11})_3$ (**5**), $\text{P}(\text{CH}_2\text{CH}_3)_3$ (**6**), $\text{P}(\text{CH}_2\text{C}_6\text{H}_5)_3$ (**7**), NC_5H_5 (**8**), and $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ (**9**), have been prepared and spectroscopically characterized. In solution at low temperature, the bridging ethanethiolato groups are cisoid (*syn*). At higher temperatures, a dynamic process that allows the averaging of the cyclopentadienyl ring environments takes place. Possible mechanisms of this averaging process involve either Cu-S bond cleavage or pyramidal inversion of the bridging S atoms. **4** crystallizes as the 1.62 THF solvate in the monoclinic space group $P2_1/c$, with $a = 15.157$ (4) Å, $b = 15.809$ (6) Å, $c = 18.527$ (7) Å, $\beta = 100.86$ (3)°, and $Z = 4$. Compound **5** crystallizes in the monoclinic space group $P2_1/n$, with $a = 9.389$ (2) Å, $b = 36.333$ (6) Å, $c = 11.584$ (3) Å, $\beta = 107.81$ (3)°, and $Z = 4$. In each case, the TiS_2Cu core is not planar; the angle between the TiS_2 and the CuS_2 planes is 13.02° for **4** and 17.92° for **5**. The Cu-Ti distances are 2.803 (3) and 2.840 (2) Å for **4** and **5**, respectively. The crystallographic and spectroscopic data are consistent with $d^{10} \rightarrow d^0$ dative bonds.

Introduction

The synthesis and study of heterobimetallic complexes have been the subject of active research over the past few years. Initial studies focused on species containing two different metal atoms usually from the same or neighboring groups.¹⁻⁴ More recently, interest has developed in complexes that contain widely divergent transition metals.⁵⁻⁵⁴ Interest in such compounds arises for several reasons. The combination of an electron-deficient and an electron-rich metal in a single complex presents the possibility of Lewis acid activation of a substrate molecule bound to the electron-rich metal center. This type of cooperative heterobimetallic activation holds potential for applications in catalysis.

A second reason for interest in heterobimetallic complexes stems from studies of heterogeneous catalysts in which electron-rich metals (e.g., Pt, Rh, Co, Ru, Fe) are supported on Lewis acidic supports (e.g., TiO_2 , Al_2O_3).⁵⁵⁻⁵⁹ Activity and surface studies

of these catalysts imply that the support not only serves to maintain a dispersion of the electron-rich metal centers but also may play

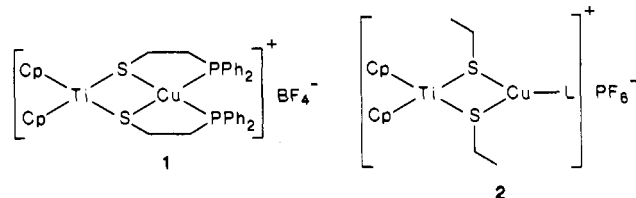
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a more direct role in the catalytic process. The nature of this role is not well understood. It may be that the support alters the

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resulting chemistry by interaction with the substrate or the electron-rich metal center. In an effort to understand the types and nature of the interactions possible between electron-rich and electron-poor metal centers, we are investigating the chemistry and properties of discrete complexes in which early and late transition metals are brought into close proximity.⁴⁴⁻⁴⁷ In particular, we have previously reported the synthesis of the Ti-Cu species **1**.⁴⁶ The structural, spectroscopic, and chemical data for



1 suggest the electron-rich Cu(I) center can interact with the electron-deficient Ti(IV) center via a $d^{10} \rightarrow d^0$ dative bond.⁴⁶ In this paper, we report the synthesis of a series of related Ti-Cu heterobimetallics of the form $[(C_5H_5)_2Ti(\mu-SCH_2CH_3)_2CuL]PF_6$ (**2**), where L is one of several phosphines or pyridine. Spectroscopic characterization of these complexes is reported. Crystallographic investigations of the complexes where $L = P(C_6H_5)_3$ and $P(C_6H_{11})_3$ are described. The results of these studies are consistent with the presence of $Cu \rightarrow Ti$ dative interactions. The nature of these $d^{10} \rightarrow d^0$ dative bonds is discussed.

Experimental Section

All preparations were done under an atmosphere of dry O_2 -free N_2 . Solvents were reagent grade and were distilled from the appropriate drying agents under N_2 and degassed by the freeze-thaw method at least three times prior to use. 1H and ^{13}C NMR spectra were recorded on a General Electric QE-300 spectrometer located at Wayne State University, using the trace of protonated solvent (acetone) as the reference. The chemical shifts are reported in ppm relative to $Si(CH_3)_4$ for both the 1H and ^{13}C NMR data. Variable-temperature 1H NMR spectra were recorded on a Bruker WH-400 spectrometer at the Southwestern Ontario Regional NMR Facility at the University of Guelph. ^{31}P NMR spectra were recorded on a General Electric GN-300 spectrometer located at Wayne State University. ^{31}P NMR chemical shifts are reported in ppm relative to external 85% H_3PO_4 . UV-vis data were recorded on a Shimadzu 240 spectrometer or a Hewlett-Packard 8451A diode array spectrophotometer. Cyclic voltammetry experiments were performed with a BAS CV-27 electrochemistry unit employing a platinum electrode. A saturated calomel electrode was used as the reference electrode. The melting points were determined with a Fisher stage melting point apparatus and were not corrected. Combustion analyses were performed by Guelph Chemical Laboratories, Guelph, Ontario, Canada. $(C_5H_5)_2TiCl_2$, $P(C_6H_5)_3$, $P(CH_2CH_3)_3$, and $(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$ were purchased from the Aldrich Chemical Co.; pyridine was purchased from the J. T. Baker Chemical Co.; $P(CH_2C_6H_5)_3$ and $P(C_6H_{11})_3$ were purchased from the Strem Chemical Co. $Cu(CH_3CN)_4PF_6$ was prepared by the literature method.⁶⁰

Preparation of $(C_5H_5)_2Ti(SCH_2CH_3)_2$ (3**).** This compound was prepared by following the published method⁶¹ involving the reaction of $(C_5H_5)_2TiCl_2$ with CH_3CH_2SH in the presence of NEt_3 . Purification of the crude product was achieved by anaerobic chromatography on neutral alumina with elution by benzene. 1H NMR data are consistent with the literature.⁶¹ $^{13}C\{^1H\}$ NMR (C_6D_6): 111.12 (C_5H_5), 39.08 (CH_2), 18.55 (CH_3).

Preparation of $[(C_5H_5)_2Ti(\mu-SCH_2CH_3)_2CuP(C_6H_5)_3]PF_6$ (4**).** $Cu(CH_3CN)_4PF_6$ (633 mg, 1.7 mmol) was suspended in 30 mL of THF. To this was added $P(C_6H_5)_3$ (892 mg, 3.4 mmol) and the solution stirred for 10 min. **3** (500 mg, 1.7 mmol) was then added. The solution became dark red immediately. After 30 min of stirring, the volume was reduced to 15 mL and the solution cooled to $-10^\circ C$. A red-orange microcrystalline solid was evident after 1 h. The solid was collected by filtration and washed with two 5-mL portions of *n*-hexane. The addition of *n*-hexane to the mother liquor caused precipitation of a second crop of

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product, which was also isolated by filtration: combined yield 1.17 g (89%); mp 141–143 °C. $^1\text{H NMR}$ (CD_3COCD_3): 7.59 (m, 15 H), 6.28 (br s, 10 H), 2.90 (q, 4 H), 1.02 (t, 6 H), $|J_{\text{CH}_2-\text{CH}_3}| = 7.2$ Hz. $^{13}\text{C}\{^1\text{H}\}$ NMR (THF, -80 °C): 134.4 (d, $|J_{\text{P}-\text{C}}| = 14.3$ Hz), 132.0 (s), 130.2 ($|J_{\text{P}-\text{C}}| = 9.4$ Hz) (C_6H_5), 112.3 (d), 110.7 (C_6H_5), 34.1 (CH_2), 18.7 (CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (THF): 6.0 (s), -144.5 (septet, $|J_{\text{P}-\text{F}}| = 712.9$ Hz). UV-vis (THF; λ , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 450 (3185), 370 (3923). Anal. Calcd for $\text{C}_{32}\text{H}_{35}\text{S}_2\text{P}_2\text{F}_6\text{TiCu}$: C, 49.84; H, 4.57; S, 8.32. Found: C, 49.49; H, 4.35; S, 8.39.

Preparation of $[(\text{C}_6\text{H}_5)_2\text{Ti}(\mu\text{-SCH}_2\text{CH}_3)_2\text{CuL}]\text{PF}_6$ ($\text{L} = \text{P}(\text{C}_6\text{H}_{11})_3$ (**5**), $\text{P}(\text{CH}_2\text{CH}_3)_3$ (**6**), $\text{P}(\text{CH}_2\text{C}_6\text{H}_5)_3$ (**7**), NC_5H_5 (**8**), $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ (**9**)). These compounds were prepared in a manner analogous to that used for **2** utilizing the appropriate phosphine or pyridine. Isolation was achieved by precipitation with *n*-hexane. **5**: mp 155–157 °C; $^1\text{H NMR}$ (CD_3COCD_3) 6.20 (br s, 10 H), 2.90 (q, 4 H), 2.2–1.3 (br m, 33 H), 1.34 (t, 6 H), $|J_{\text{CH}_2-\text{CH}_3}| = 7.5$ Hz; $^{31}\text{P}\{^1\text{H}\}$ NMR (THF) 27.1 (s), -144.7 (septet, $|J_{\text{P}-\text{F}}| = 720.4$ Hz); UV-vis (THF; λ , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 462 (5580), 354 (5709). Anal. Calcd for $\text{C}_{32}\text{H}_{52}\text{S}_2\text{P}_2\text{F}_6\text{TiCu}$: C, 48.70; H, 6.77; S, 8.12. Found: C, 48.81; H, 7.08; S, 8.49. **6**: mp 147–148 °C; $^1\text{H NMR}$ (CD_3COCD_3) 6.13 (br s, 10 H), 2.91 (q, 4 H), 1.85 (d of q, 6 H), 1.33 (t, 6 H), 1.16 (d of t, 9 H), $|J_{\text{CH}_2-\text{CH}_3}| = 7.5$ Hz, $|J_{\text{CH}_2-\text{P}}| = 7.7$ Hz, $|J_{\text{CH}_2-\text{CH}_3}| = 7.6$ Hz, $|J_{\text{CH}_2-\text{P}}| = 17.1$ Hz; $^{31}\text{P}\{^1\text{H}\}$ NMR (THF) 2.1 (s), -142.9 (septet, $|J_{\text{P}-\text{F}}| = 711.4$ Hz); UV-vis (THF; λ , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 456 (5349), 352 (5858). Anal. Calcd for $\text{C}_{20}\text{H}_{35}\text{S}_2\text{P}_2\text{F}_6\text{TiCu}$: C, 38.31; H, 5.63; S, 10.23. Found: C, 43.68; H, 6.65; S, 10.70. **7**: mp 95 °C dec; $^1\text{H NMR}$ (CD_3COCD_3) 7.4 (m, 15 H), 6.11 (br s, 10 H), 3.49 (d, 6 H), 2.6 (m, 4 H), 1.09 (t, 6 H), $|J_{\text{CH}_2-\text{P}}| = 8.8$ Hz, $|J_{\text{CH}_2-\text{CH}_3}| = 7.5$ Hz; $^{31}\text{P}\{^1\text{H}\}$ NMR (THF) 6.3 (s), -143.2 (septet, $|J_{\text{P}-\text{F}}| = 712.4$ Hz); UV-vis (THF; λ , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 454 (2823), 348 (3547). Anal. Calcd for $\text{C}_{35}\text{H}_{41}\text{S}_2\text{P}_2\text{F}_6\text{TiCu}$: 51.69; H, 5.08; S, 7.88. Found: C, 52.69; H, 5.54; S, 7.74. **8**: mp 128 °C dec; $^1\text{H NMR}$ (CD_3COCD_3) 8.79 (d of d, 2 H), 8.18 (d of t, 1 H), 7.74 (d of d, 2 H), 6.23 (br s, 10 H), 3.05 (q, 4 H), 1.37 (t, 6 H), $|J_{\text{CH}_0-\text{CH}_3}| = 1.3$ Hz, $|J_{\text{CH}_m-\text{CH}_n}| = 7.7$ Hz, $|J_{\text{CH}_0-\text{CH}_n}| = 6.1$ Hz, $|J_{\text{CH}_2-\text{CH}_3}| = 7.4$ Hz; UV-vis (THF; λ , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 470 (3673), 362 (5170). Anal. Calcd for $\text{C}_{19}\text{H}_{25}\text{NS}_2\text{P}_2\text{F}_6\text{TiCu}$: C, 38.81; H, 4.28; S, 10.91. Found: C, 33.01, 32.91; H, 4.21; S, 10.73. **9**: mp 110 °C dec; $^1\text{H NMR}$ (CD_3COCD_3) 7.4–7.2 (m, 20 H), 6.44 (s, 10 H), 2.6 (m, 8 H), 1.18 (t, 6 H), $|J_{\text{CH}_2-\text{CH}_3}| = 7.5$ Hz; $^{31}\text{P}\{^1\text{H}\}$ NMR (THF) 9.2 (br, s), -142.9 (septet, $|J_{\text{P}-\text{F}}| = 709.9$ Hz); UV-vis (THF; λ , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 466 (1190). Anal. Calcd for $\text{C}_{40}\text{H}_{44}\text{S}_2\text{P}_2\text{F}_6\text{TiCu}$: C, 54.95; H, 4.88; S, 7.07. Found: C, 47.09, 46.74; H, 4.84; S, 7.26.

X-ray Data Collection and Reduction. Orange crystals of **4**·1.62THF were obtained by crystallization from a THF solution of **4** cooled to -10 °C. Alternatively, orange crystals of **4** could be obtained by vapor diffusion of *n*-hexane into a THF solution of **4**.⁶³ Orange crystals of **5** were obtained by vapor diffusion of *n*-hexane into a THF solution of **5**.

Diffraction experiments were performed on a four-circle Syntex P₁ diffractometer with graphite-monochromatized Mo K α radiation. The initial orientation matrix for each compound was obtained from 15 machine-centered reflections selected from rotation photographs. These data were used to determine the crystal systems. Partial rotation photographs around each axis were consistent with a monoclinic crystal system in each case. Ultimately, 30 high-angle reflections ($15^\circ < 2\theta < 30^\circ$) were used to obtain the final lattice parameters and the orientation matrices. Machine parameters, crystal data, and data collection parameters are summarized in Table I. The observed extinctions were consistent with the space group $P2_1/c$ for **4**·1.62THF and $P2_1/n$ for **5**. $\pm h, +k, +l$ data for **4**·1.62THF were collected in two shells ($4.5^\circ < 2\theta < 35^\circ$ and $35^\circ < 2\theta < 40^\circ$), while $\pm h, +k, +l$ data for **5** were collected in one shell ($4.5^\circ < 2\theta < 45^\circ$). Three standard reflections, for each species, were recorded regularly throughout data collection. In the case of **4**·1.62THF, decay of the crystal was indicated by the change in the intensities of the standard reflections. After approximately a 12% decay in the average intensities of the standards, a second crystal was employed to collect the higher angle data ($35^\circ < 2\theta < 40^\circ$). Decay of the second crystal of approximately 12% was also seen. This decay is undoubtedly due to partial loss of the THF molecules in the crystal lattice, despite the fact that the crystals were sealed in capillaries. For compound **5**, the stand-

Table I. Crystallographic Parameters

	4·1.62THF	5
formula	$\text{CuTiC}_{32}\text{H}_{35}\text{S}_2\text{P}_2\text{F}_6 \cdot \text{C}_{6.48}\text{H}_{12.96}\text{O}_{1.62}$	$\text{CuTiC}_{32}\text{H}_{35}\text{S}_2\text{P}_2\text{F}_6$
cryst color, form	orange blocks	orange blocks
<i>a</i> , Å	15.157 (4)	9.389 (2)
<i>b</i> , Å	15.809 (6)	36.333 (6)
<i>c</i> , Å	18.527 (7)	11.584 (3)
β , deg	100.86 (3)	107.81 (2)
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
vol, Å ³	4359 (3)	3762 (1)
density, g cm ⁻³	1.35	1.39
<i>Z</i>	4	4
cryst dimens, mm	0.46 × 0.46 × 0.42 0.42 × 0.46 × 0.39	0.50 × 0.27 × 0.62
abs coeff, μ , cm ⁻¹	8.32	9.60
radiation (λ , Å)	Mo K α (0.710 69)	Mo K α (0.710 69)
temp, °C	24	24
scan speed, deg min ⁻¹	2.0–5.0 ($\theta/2\theta$ scan)	2.0–5.0 ($\theta/2\theta$ scan)
scan range, deg	1.0 below K α_1 to 1.0 above K α_2	1.0 below K α_1 to 1.0 above K α_2
bkgd/scan time ratio	0.5	0.5
data collected	4458	5391
no. of unique data with $F_o^2 > 3\sigma(F_o^2)$	2317	3330
no. of variables	285	397
<i>R</i> , %	9.86	6.22
<i>R_w</i> , %	10.55	6.80
max Δ/σ in final	0.001	0.026
least-squares cycle		
largest residual electron density peak, e Å ⁻³	1.20	0.080
atom associated with residual density	Ti	C31, C36

ards showed no statistically significant change over the duration of data collection. The data were processed with the SHELX-76 program package on the computing facilities at the University of Windsor. A decay correction was applied to the data for **4**·1.62THF, and the standard reflection intensities were used to scale the two portions of the data obtained from the two crystals. The total number of reflections with $F_o^2 > 3\sigma F_o^2$, for each compound, are listed in Table I. The absorption coefficients are small ($\mu = 8.32$ cm⁻¹ for **4**·1.62THF and $\mu = 9.60$ cm⁻¹ for **5**). No absorption corrections were applied to the data.

Structure Solutions and Refinements. Non-hydrogen atomic scattering factors were taken from the literature tabulations.^{64,65} The Cu atom position was determined by the heavy-atom (Patterson) method for **4**·1.62THF, while the Cu atom position in **5** was determined by the direct-methods program MULTAN. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. Refinement was carried out by using full-matrix least-squares techniques on *F*, minimizing the function $\sum w(|F_o| - |F_c|)^2$, where the weight, *w*, is defined as $4F_o^2/\sigma^2(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes. In the final cycles, in which a block-diagonal refinement was employed, the Cu, Ti, S, P, F, O, and cyclopentadienyl carbons of **4**·1.62THF were assigned anisotropic temperature factors. The phenyl ring carbons were described by isotropic thermal parameters, and the ring geometries were constrained to that of regular hexagons with C–C bond distances of 1.39 Å. For **5**, all non-hydrogen atoms were assigned anisotropic temperature factors. For both refinements, hydrogen atom positions were allowed to ride on the carbon to which they are bonded with the assumption of a C–H bond length of 0.95 Å. In each case, 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. For compound **4**, the THF molecules of crystallization were not of full site occupancy. After location and refinement of the positional parameters of the THF molecules, the site occupancy factors were refined. Site occupancies of 0.85 and 0.77 were found for the two THF sites. In addition to the fractional occupancy, rotational disordering of the THF molecules was evident. Thus, it was necessary to constrain the geometries of the THF molecules to that of pentagonal structures in

(62) In some instances poor analytical results were obtained despite repeated recrystallizations and repeated analyses. Such discrepancies have been seen with other Ti–S compounds; see: Shaver, A.; McCall, J. M. *Organometallics* **1984**, *3*, 1823. Coutts, R. S. P.; Surtees, J. R.; Swan, J. R.; Wailes, P. C. *Aust. J. Chem.* **1966**, *19*, 1377.

(63) Crystals of **4** obtained in this manner were triclinic, with *a* = 10.832 (3) Å, *b* = 10.994 (3) Å, *c* = 15.146 (4) Å, $\alpha = 97.67$ (2)°, $\beta = 98.40$ (2)°, $\gamma = 77.01$ (2)°, $V = 1729.2$ (8) Å³, and *Z* = 2. Although the crystal quality was poor, the “rough” structure of **4** was established (3141 data with $F_o > 3\sigma F_o$, *R* = 20.39%). Attempts to obtain better quality crystals from THF/hexane were unsuccessful.

(64) (a) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffraction, Theor. Gen. Crystallogr.* **1968** *A24*, 321. (b) *Ibid.* **1968**, *A24*, 390.

(65) Stewart, R. F.; Davidson, F. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

Table II. Positional Parameters ($\times 10^4$)

atom	x	y	z	atom	x	y	z
[(C ₅ H ₅) ₂ Ti(μ-SCH ₂ CH ₃) ₂ CuP(C ₆ H ₅) ₃]PF ₆ ·1.62THF (4·1.62THF)							
Cu	2172 (1)	3965 (1)	463 (1)	Ti	3092 (2)	5453 (2)	3244 (2)
S1	2829 (3)	4157 (3)	2491 (2)	S2	2490 (3)	4972 (3)	4323 (2)
P1	1358 (3)	2835 (3)	3629 (2)	P2	4075 (4)	7407 (5)	737 (4)
F1	3300 (12)	6919 (17)	929 (11)	F2	3855 (19)	8188 (17)	1111 (19)
F3	4874 (9)	7930 (12)	567 (9)	F4	4623 (17)	7110 (19)	1389 (15)
F5	3505 (16)	7682 (20)	43 (14)	F6	4298 (16)	6701 (18)	291 (18)
C1	4517 (11)	4961 (13)	3786 (14)	C2	4575 (11)	5155 (14)	3107 (14)
C3	4441 (12)	6009 (18)	2986 (12)	C4	4299 (12)	6352 (14)	3666 (13)
C5	4362 (13)	5706 (15)	4166 (11)	C6	2629 (23)	6684 (15)	2591 (28)
C7	2260 (21)	6077 (24)	2169 (13)	C8	1610 (21)	5672 (15)	2567 (30)
C9	1644 (17)	6092 (24)	3183 (21)	C10	2203 (32)	6673 (27)	3194 (19)
C11	288 (6)	3100 (7)	3878 (6)	C12	285 (6)	3715 (7)	4418 (6)
C13	-520 (6)	3942 (7)	4628 (6)	C14	-1322 (6)	3555 (7)	4298 (6)
C15	-1318 (6)	2940 (7)	3758 (6)	C16	-514 (6)	2713 (7)	3548 (6)
C21	1951 (6)	2189 (7)	4375 (6)	C22	1523 (6)	1815 (7)	4898 (6)
C23	2017 (6)	1332 (7)	5463 (6)	C24	2938 (6)	1223 (7)	5506 (6)
C25	3366 (6)	1597 (7)	4983 (6)	C26	2872 (6)	2080 (7)	4417 (6)
C31	1084 (8)	2099 (8)	2847 (5)	C32	1067 (8)	1226 (8)	2955 (5)
C33	906 (8)	682 (8)	2351 (5)	C34	762 (8)	1011 (8)	1640 (5)
C35	780 (8)	1884 (8)	1532 (5)	C36	941 (8)	2427 (8)	2136 (5)
C41	3739 (12)	3348 (13)	2652 (11)	C42	3359 (13)	2522 (13)	2296 (11)
C51	3294 (14)	4441 (12)	5079 (11)	C52	2806 (19)	4138 (17)	5649 (15)
O1	4699 (18)	9103 (22)	3417 (18)	C61	3914 (26)	8715 (15)	2986 (19)
C62	3281 (18)	9447 (22)	2727 (16)	C63	3577 (21)	10147 (15)	3285 (19)
C64	4359 (23)	9766 (22)	3823 (14)	O2	360 (16)	9275 (19)	3812 (18)
C71	238 (20)	9041 (32)	4537 (21)	C72	1183 (28)	9006 (32)	4995 (14)
C73	1788 (16)	8859 (29)	4438 (22)	C74	1147 (23)	8820 (25)	3700 (16)
[(C ₅ H ₅) ₂ Ti(μ-SCH ₂ CH ₃) ₂ CuP(C ₆ H ₁₁) ₃]PF ₆ (5)							
Cu	3205 (1)	3635 (1)	6952 (1)	Ti	838 (1)	3117 (1)	6187 (1)
S1	3520 (2)	3016 (1)	7086 (2)	S2	869 (2)	3782 (1)	5783 (2)
P1	4926 (2)	4056 (1)	7878 (2)	P2	5511 (4)	6624 (1)	7530 (3)
F1	6449 (15)	6956 (3)	7390 (12)	F2	4341 (12)	6896 (3)	7730 (12)
F3	6506 (15)	6386 (4)	7118 (19)	F4	4549 (13)	6296 (3)	7697 (9)
F5	6181 (15)	6655 (4)	8856 (8)	F6	4603 (18)	6623 (4)	6190 (9)
C11	4120 (10)	4422 (3)	8613 (8)	C12	2953 (11)	4643 (3)	7694 (10)
C13	2264 (14)	4930 (3)	8339 (14)	C14	1628 (16)	4746 (5)	9284 (18)
C15	7808 (16)	4524 (4)	10175 (13)	C16	3422 (12)	4244 (3)	9535 (10)
C21	5692 (11)	4306 (3)	6806 (9)	C22	6758 (11)	4615 (3)	7304 (10)
C23	7203 (19)	4824 (4)	6322 (16)	C24	7569 (17)	4600 (4)	5426 (15)
C25	6523 (14)	4286 (4)	4930 (11)	C26	6053 (15)	4076 (3)	5900 (11)
C31	6553 (13)	3892 (2)	9011 (10)	C32	7480 (10)	4138 (2)	10024 (9)
C33	8994 (13)	3987 (3)	10761 (14)	C34	9034 (15)	3585 (3)	11127 (10)
C35	8089 (9)	3333 (2)	10142 (8)	C36	6651 (12)	3481 (3)	9263 (13)
C1	943 (11)	3006 (3)	4212 (8)	C2	1193 (11)	2671 (3)	4803 (8)
C3	70 (12)	2569 (3)	5109 (8)	C4	1132 (10)	2850 (3)	4637 (9)
C5	544 (10)	3111 (3)	4106 (8)	C6	909 (13)	2851 (3)	8091 (9)
C7	570 (11)	2842 (3)	7333 (10)	C8	1056 (10)	3210 (3)	7104 (10)
C9	81 (12)	3432 (3)	7732 (9)	C10	1301 (11)	3217 (4)	8346 (9)
C41	4618 (9)	2926 (2)	6051 (8)	C42	5392 (10)	2555 (3)	6337 (10)
C51	1159 (14)	3918 (3)	4315 (9)	C52	1284 (19)	4289 (4)	4161 (11)

which the C–O bond distances were 1.44 Å and the C–C bond distances were 1.52 Å. For compound **5**, a disordering of one of the cyclohexyl rings was evident. The disorder was sufficiently blurred such that no acceptable model involving two conformations of the disordered ring could be obtained. Thus, in order to maintain a chemically reasonable geometry, the C–C bond distances for this ring were fixed at 1.52 Å and markedly anisotropic thermal parameters were accepted as a result. The final values of $R = \sum |F_o| - |F_c| / \sum |F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2)^{1/2}$ for each species and the maximum Δ/σ on any of the parameters in the final cycles of refinement are given in Table I. Final difference Fourier map calculations showed no peaks of chemical significance. The magnitudes and locations of the largest residual peaks are described in Table I. Positional parameters (Table II) and selected bond distances and angles (Table III) are tabulated.

Results and Discussion

The synthesis of **3** is achieved by reaction of (C₅H₅)₂TiCl₂ with ethanethiol in the presence of NEt₃ in benzene. The purple product is purified by column chromatography. This serves to remove any remaining chloro-substituted species. Addition of **3** to THF solutions containing Cu(CH₃CN)₄PF₆ and either 1 or 2 equiv of trisubstituted phosphine or pyridine results in a rapid color change from purple to orange-red. Cooling or slow addition of

hexane causes precipitation of orange-red crystalline solids. The best yields were obtained when 2 equiv of ligand was employed. ¹H NMR spectral integrations and combustion analyses of these products are consistent with the formulation as **2**. These compounds are stable in air in the solid state; however, in solution they are much more air-sensitive. THF or acetone solutions of these compounds are suitable for the acquisition of spectral data. In CH₃CN, ³¹P{¹H} NMR data are consistent with the displacement of the coordinated phosphine, although the CH₃CN adduct has not as yet been isolated. For compounds **4–8**, degradation in THF or acetone solution is seen after several days as the color changes from red-orange to pale yellow. Compound **9** is even more unstable, as decomposition in concentrated solution is evident after several hours, while in dilute solution, decomposition is apparent almost immediately. The products of decomposition are unknown, but loss of the intense color implies cleavage of at least one Ti–S bond, yielding perhaps a Cu(I) phosphine-thiolate species.

The UV–vis spectra of compounds **4–9** show absorptions that are blue shifted relative to those of the previously reported Cu–Ti heterobimetallic complex **1**.⁴⁶ The change in the geometry of the

Table III. Selected Bond Distances and Angles

[(C₅H₅)₂Ti(μ-SCH₂CH₃)₂CuP(C₆H₅)₃]PF₆·1.62 THF, (4·1.62THF)

Distances (Å)			
Cu–Ti	2.803 (3)	Cu–S1	2.238 (5)
Cu–S2	2.240 (5)	Cu–P1	2.226 (5)
Ti–S1	2.470 (5)	Ti–S2	2.468 (5)
Ti–C1	2.34 (2)	Ti–C2	2.36 (2)
Ti–C3	2.36 (2)	Ti–C4	2.33 (2)
Ti–C5	2.35 (2)	Ti–C6	2.33 (3)
Ti–C7	2.36 (3)	Ti–C8	2.38 (3)
Ti–C9	2.40 (3)	Ti–C10	2.35 (5)
S1–C41	1.86 (2)	S2–C51	1.87 (2)
C41–C42	1.53 (3)	C51–C52	1.48 (4)
Angles (deg)			
Cu–S1–Ti	72.9 (1)	Cu–S2–Ti	72.9 (2)
S1–Cu–S2	114.1 (2)	S1–Ti–S2	99.1 (2)
S1–Cu–P1	124.2 (2)	S2–Cu–P1	121.6 (2)
Cu–P1–C11	113.2 (4)	Cu–P1–C21	110.4 (4)
Cu–P1–C31	116.6 (4)	P1–C11–C12	117.8 (7)
P1–C11–C16	122.2 (8)	P1–C21–C22	122.6 (7)
P1–C21–C26	117.4 (9)	P1–C31–C32	121.3 (8)
P1–C31–C36	118.6 (9)	Ti–S1–C41	116.3 (6)
Cu–S1–C41	101.9 (7)	S1–C41–C42	108 (1)
Ti–S2–C51	117.1 (7)	Cu–S2–C51	103.6 (6)
S2–C51–C52	110 (2)	C1–C2–C3	111 (2)
C2–C3–C4	106 (2)	C3–C4–C5	108 (2)
C4–C5–C1	106 (2)	C5–C1–C2	109 (2)
C6–C7–C8	106 (3)	C7–C8–C9	107 (3)
C8–C9–C10	108 (4)	C9–C10–C6	114 (4)
C10–C6–C7	105 (3)		

[(C₅H₅)₂Ti(μ-SCH₂CH₃)₂CuP(C₆H₁₁)₃]PF₆ (5)

Distances (Å)			
Cu–Ti	2.840 (2)	Cu–S1	2.269 (2)
Cu–S2	2.261 (2)	Cu–P1	2.243 (2)
Ti–S1	2.440 (2)	Ti–S2	2.461 (3)
Ti–C1	2.36 (1)	Ti–C2	2.37 (1)
Ti–C3	2.366 (9)	Ti–C4	2.356 (9)
Ti–C5	2.362 (8)	Ti–C6	2.39 (1)
Ti–C7	2.36 (1)	Ti–C8	2.36 (1)
Ti–C9	2.41 (1)	Ti–C10	2.43 (1)
S1–C41	1.84 (1)	S2–C51	1.87 (1)
C41–C42	1.52 (1)	C51–C52	1.37 (2)
Angles (deg)			
Cu–S1–Ti	74.1 (1)	Cu–S2–Ti	73.8 (1)
S1–Cu–S2	110.9 (1)	S1–Ti–S2	99.1 (1)
S1–Cu–P1	125.6 (1)	S2–Cu–P1	123.5 (1)
Cu–P1–C11	111.8 (3)	Cu–P1–C21	112.6 (3)
Cu–P1–C31	117.0 (3)	P1–C11–C12	111.6 (7)
P1–C11–C16	109.4 (7)	P1–C21–C22	117.4 (8)
P1–C21–C26	115.0 (8)	P1–C31–C32	122.0 (6)
P1–C31–C36	117.2 (7)	Ti–S1–C41	117.4 (2)
Cu–S1–C41	102.7 (3)	S1–C41–C42	110.0 (7)
Ti–S2–C51	116.5 (3)	Cu–S2–C51	102.9 (4)
S2–C51–C52	114.9 (9)	C1–C2–C3	109.4 (9)
C2–C3–C4	105.4 (9)	C3–C4–C5	110.3 (9)
C4–C5–C1	107.8 (8)	C5–C1–C2	107.0 (9)
C6–C7–C8	107.2 (9)	C7–C8–C9	107.9 (8)
C8–C9–C10	109 (1)	C9–C10–C6	107.8 (9)
C10–C6–C7	108 (1)		

Cu from pseudotetrahedral in **1** to pseudotrigonal in the present complexes clearly alters the Ti–S chromophore. Previously, it was suggested that the appearance of low-energy bands in related Cu–Ti complexes was attributable to transitions involving both metal centers.⁶⁶ Although such bands are absent in the spectra of **4–8**, this does not eliminate the possibility of metal–metal interactions (vide infra).

The ³¹P{¹H} NMR spectra of the phosphine complexes **4–7** show resonances with chemical shifts indicative of phosphine coordination to a metal atom, as well as the characteristic septet of resonances arising from the PF₆ anions. In the case of compound

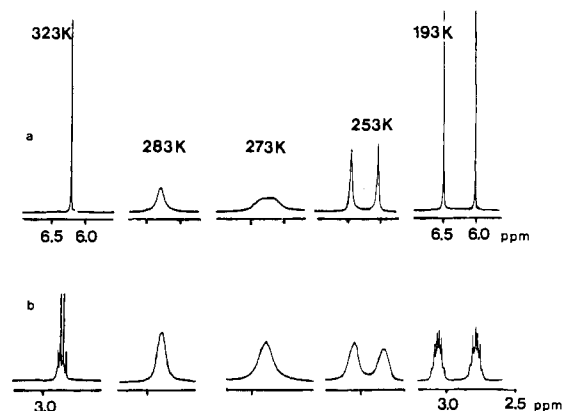


Figure 1. Variable-temperature ¹H NMR spectra of **5**: (a) cyclopentadienyl proton resonances; (b) resonances of the methylene protons of the μ-ethanethiolato groups.

9, the ³¹P{¹H} NMR resonance, arising from the phosphorus coordinated to Cu, was broad at 25 °C (1200 Hz at half-height). At –90 °C, this line width narrows to 300 Hz at half-height. Further, the UV–vis spectrum of **9** is similar to those of the monophosphine complexes **4–7** and markedly dissimilar from the spectral data for **1**.⁴⁶ These data suggest that the diphosphine is not chelating in **9** and that exchange of coordinated and dangling phosphine groups occurs rapidly in solution.

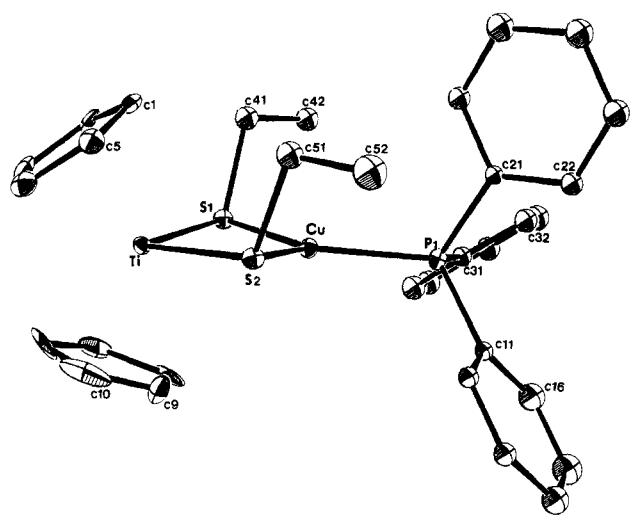
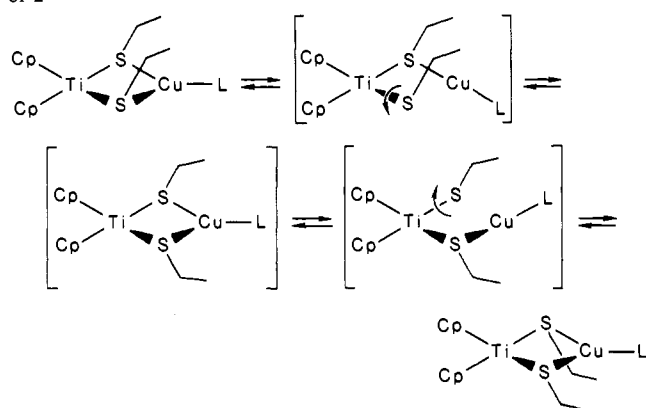
Fluxionality. The ¹H NMR spectra of compounds **4** and **5** were examined over the temperature range +50 to –80 °C. In both cases, the cyclopentadienyl proton resonances are temperature-dependent. At higher temperatures (50 °C), a single resonance is observed at approximately 6.25 ppm. When the system is cooled, this signal broadens and splits into two sharp resonances at about 6.5 and 6.0 ppm (Figure 1). Similarly, the ¹³C{¹H} NMR singlet arising from the cyclopentadienyl carbons becomes two separate resonances at low temperature. At the same time, the quartet in the ¹H NMR spectra that is assigned to the methylene protons of the μ-ethanethiolato groups broadens and splits into two sets of overlapping doublets of quartets. The coalescence temperatures for all of these signals are approximately 10 and 0 °C for **4** and **5**, respectively. The *E_a* values for the signal-averaging processes were determined from line-shape analyses⁶⁷ and were found to be 71 kJ/mol for **4** and 74 kJ/mol for **5**. The low-temperature spectra are assigned to the conformer in which the ethyl substituents of the μ-thiolato moieties are cisoid. This is consistent with the observation of two inequivalent cyclopentadienyl groups. In addition, the methylene protons of the μ-thiolato groups are inequivalent (i.e., exo and endo) and thus geminal coupling is seen at low temperature. At higher temperatures, the dynamic process that results in signal averaging probably involves the interconversion of the cisoid (syn)–transoid (anti)–cisoid (syn) conformers although no direct evidence for the transoid form is observed.⁶⁸ The mechanism for this process may involve metal–sulfur bond cleavage, rotation, and bond re-formation. Cleavage of the Cu–S bond would yield a two-coordinate Cu(I) intermediate, a geometry that is common for Cu(I). Alternatively, the mechanism may involve pyramidal inversion at the bridging S atoms. This mechanism has been proposed for other thiolato-bridged heterobimetallics, and the activation energies for those systems were found to be about 70–77 kJ/mol.^{37,69,70} In the present case, although the value of the activation energy is similar, the process

(67) Intuitively, the chemical shift of the cyclopentadienyl protons of the transoid form could be isochronous with the average chemical shifts for the cyclopentadienyl protons of the cisoid form. However, at no temperature in the range studied were signals attributable to cisoid and transoid forms observed.

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(69) Natile, G.; Maresca, L.; Bor, G. *Inorg. Chim. Acta* 1977, 23, 37.

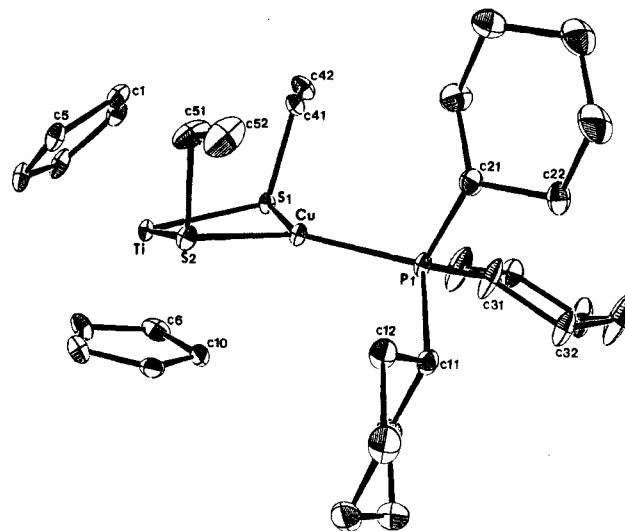
(70) Patel, V. D.; Boorman, P. M.; Kerr, K. A.; Moynihan, K. J. *Inorg. Chem.* 1982, 21, 1383.

Scheme I. Proposed Mechanism for the Cisoid-Cisoid Equilibria of **2****Figure 2.** ORTEP drawing of the cation of **4**, with 20% thermal ellipsoids shown and hydrogen atoms omitted.

of a cisoid-cisoid equilibrium clearly requires consecutive inversions at both S atoms. For this reason we favor the mechanism involving Cu-S bond cleavage (Scheme I). These data imply that the cisoid (syn) form of these complexes is favored thermodynamically. The greater stability of the cisoid form may result from the minimization of steric interactions between the ethyl groups of the μ -thiolato groups and the substituents on the phosphine bound to Cu.

Electrochemistry. The compounds **4-9** were studied by cyclic voltammetry. All show irreversible reductions around -0.8 to -1.0 V vs. SCE. This is in contrast to the case for **1**, where a reversible reduction wave attributable to a formally Ti(IV)-Ti(III) couple is seen.⁴⁶ Apparently, the change from the geometry of the Cu in **1** to that found in the present compounds affects the nature of the LUMO. Preliminary molecular orbital calculations⁷¹ show that for **1** the LUMO is primarily on Ti while for **4-9** the LUMO resides essentially on Cu. Thus, reduction leads to formally Cu(0) species, which undergo decomposition. Reversible oxidation processes are also not observed. Presumably oxidation at Cu or thiolate leads to compound degradation.

Structure Descriptions. Single crystals of **4**·1.62THF were obtained by cooling a saturated THF solution of **4**. An X-ray crystallographic study revealed that the crystals are made up of monoclinic unit cells, each containing discrete cations and anions as well as THF molecules of crystallization. The closest approach of any cation to any anion is 2.542 Å (F4-H3). There are two sites where THF molecules exist in the lattice; however, these sites

**Figure 3.** ORTEP drawing of the cation of **5**, with 20% thermal ellipsoids shown and hydrogen atoms omitted.

are not fully occupied. The closest approach of a THF molecule to either the cation or anion is 2.331 Å (H74B-H33). The geometry of the anion is typical. Selected bond distances and angles within the cation are given in Table III. An ORTEP drawing of the cation is shown in Figure 2. The coordination geometry of Ti is pseudotetrahedral while the Cu atom is in a pseudotrigonal environment. The two π -bonded cyclopentadienyl rings and the two thiolato sulfur atoms comprise the Ti coordination sphere. The Ti-C distances are typical⁴⁶ and average 1.36 (7) Å. The average Ti-S distance observed was 2.469 (1) Å, which is similar to that seen in **1** but significantly longer than the 2.378 (6) Å found for the Ti-S bond distance in $(C_5H_5)_2Ti(SCH_2CH_2CH_2PPh_2)_2$.⁷² The Cu atom coordination sphere consists of the thiolato sulfur atoms and the phosphorus atom of the bound $P(C_6H_5)_3$. The Cu-S bond lengths average 2.239 (1) Å while the Cu-P distance found was 2.226 (5) Å. These values are similar to those seen for **1**.⁴⁶

Crystals of **5** were obtained by anaerobic diffusion of hexane into a THF solution of **5**. The X-ray study of this compound showed the lattice is made up of monoclinic unit cells comprised of discrete anions and cations. The closest approach of a cation to an anion is 2.570 Å (F1-H7). Again, the geometry of the anion is as expected and some selected bond distances and angles for the cation are given in Table III. Figure 3 shows an ORTEP drawing of the cation of **5**. The general structural features of this complex are similar to those found for **4**. The coordination sphere is pseudotetrahedral for Ti and pseudotrigonal for Cu. Ti-C bond distances average 1.39 (2) Å, while Ti-S and Cu-S distances average 2.451 (8) and 2.265 (4) Å, respectively. The Cu-P distance observed was 2.243 (2) Å. The slight lengthening of the Cu-S and Cu-P bonds in **5** compared to the analogous bonds in **4** can be attributed to the increase in the steric demands of $P(C_6H_{11})_3$ vs. those of $P(C_6H_5)_3$. These observations are contrary to those expected from ligand basicity considerations.

The orientation of the substituents of the bridging thiolato groups is cisoid (syn) for both **4** and **5**. In this orientation, the substituents on the phosphine are staggered with respect to the bridging ethanethiolato groups, thereby minimizing any destabilizing steric interactions.

The structural details of the Ti_2CuP core for **4** and **5** are given in Figure 4. The Ti_2Cu cores of **4** and **5** are not planar; rather, they are "butterfly" shaped. The angles between the CuS_2 and the TiS_2 planes are 13.02 and 17.92° for **4** and **5**, respectively. This result is in contrast to that seen for **1**, where the presence of the chelating phosphine-thiolate ligands restricts the four atoms of the Ti_2Cu core to a coplanar geometry.⁴⁶ In the present complexes, the absence of the chelating ligands permits a distortion from coplanarity. The distortion may relieve some of the steric

(71) White, G. S.; Wark, T. A.; Tse, J. S.; Stephan, D. W., manuscript in preparation.

(72) White, G. S.; Stephan, D. W., unpublished results.

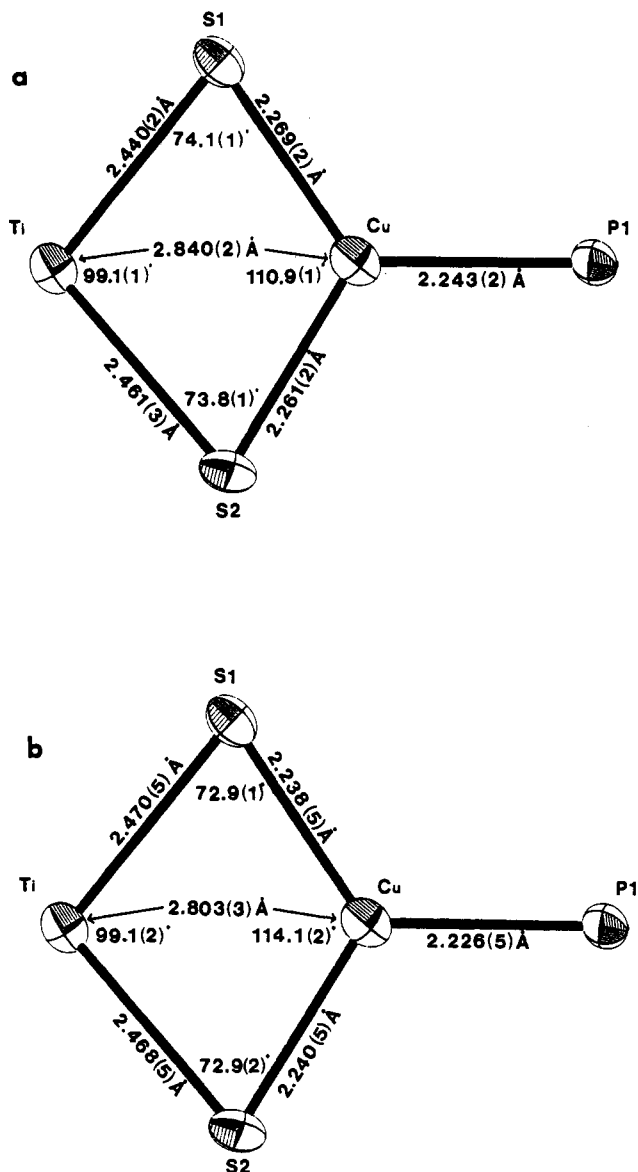
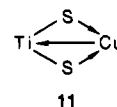


Figure 4. ORTEP drawings of the TiS_2CuP cores of the cations of (a) **5** and (b) **4**.

congestion between the μ -thiolato groups and the substituents on the phosphine. In addition, the distortion may permit Ti to exhibit Lewis acidity toward the electron-rich Cu center. The Cu–S–Ti angles average $72.9(1)$ and $73.9(2)^\circ$ for **4** and **5**, respectively. This is 4 – 6° less than the Cu–S–Ti angles seen in **1**.⁴⁶ In both

compounds the S–Ti–S angles are $99.1(1)^\circ$, while the S–Cu–S angle is $114.1(2)^\circ$ for **4** and $110.9(1)^\circ$ for **5**. Both of the angles at Ti and Cu are larger than the corresponding values seen in **1**.⁴⁶ The Ti–Cu distances in **4** and **5** are $2.803(3)$ and $2.840(2)$ Å, respectively. These values are 0.16 – 0.20 Å shorter than the metal–metal separation found for compound **1**.⁴⁶ It seems clear that the “butterfly” shape of the core, the angles about the CuS_2Ti core, and the Cu–Ti distances are consistent with $d^{10} \rightarrow d^0$ dative interactions in the present compounds. Such interactions, in which Ti(IV) acts as a Lewis acid toward an electron-rich metal center, have been proposed for $(\text{C}_5\text{H}_5)_2\text{Ti}(\mu\text{-SCH}_3)_2\text{Mo}(\text{CO})_4$ ⁷³ (**10**) and compound **1**.⁴⁶ In the present compounds, the Cu–Ti distances are markedly shorter than those of both **10** and **1**, where the Ti–M distances are $3.321(2)$ and $3.024(1)$ Å, respectively. The nature of the metal–metal interactions in these compounds is best described as a $d^{10} \rightarrow d^0$ dative bond. Thus, the core bonding is characterized by **11**. Preliminary results of X α molecular orbital



calculations performed for suitably simplified models are consistent with this interpretation.⁷¹ Furthermore, the calculations show that such a dative interaction has both a σ and a π component. Additional INDO calculations on appropriate models suggest an approximate Ti–Cu bond order of 0.2.

In summary, the use of **3** as a metalloligand offers an alternative and somewhat more versatile method for the synthesis of early- and late-transition-metal heterobimetallics. The crystallographic and spectroscopic data are consistent with dative interactions between electron-poor and electron-rich metal centers. The precise nature of the Cu→Ti dative bonds, as well as the effect such interactions have on the chemistry of the participant metals, is the subject of ongoing research.

Acknowledgment. The NSERC of Canada is thanked for financial support of this work. Drs. O. Mols and R. Hood of Wayne State University are thanked for use of their NMR spectrometers. W. Klimstra of the Southwestern Ontario Regional NMR Facility is thanked for technical assistance in the acquisition of the variable-temperature ^1H NMR data.

Supplementary Material Available: Thermal parameters (Table S1), hydrogen atom parameters (Table S2), and bond distances and angles associated with the cyclohexyl and cyclopentadienyl rings and the PF_6^- anions (Table S3) (9 pages); values of $10|F_o|$ and $10|F_c|$ (Table S4) (22 pages). Ordering information is given on any current masthead page.

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