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Registry No. 1, 83417-55-4; **3**, 79305-76-3; $(C_6H_5)_2C{=}C{=}O$, 525-06-4.

Supplementary Material Available: Listings of thermal parameters (Table I-S) and phenyl-ring least-squares planes (Table II-S), stereoviews showing the packing in one unit cell (Figures 1-S and 2-S), and listings of observed and calculated F^2 values (50 pages). Ordering information is given on any current masthead page.

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Synthesis, Electrochemistry, and Crystal and Molecular Structure of $[(C_5H_5)_2Ti(SCH_2CH_2P(C_6H_5)_2)_2Cu]BF_4$: A Heterobimetallic Species with a Copper to Titanium Dative Bond

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The bifunctional dissymmetric ligand $(C_6H_5)_2PCH_2CH_2SH$ (PSH) was used in the synthesis of a new early-transition-metal/late-transition-metal heterobimetallic species. Initially the Ti complex $(C_5H_5)_2Ti(SCH_2CH_2P(C_6H_5)_2)_2$ (**1**) was prepared. The reaction of **1** with methyl iodide confirms the dangling nature of the phosphine groups. Compound **1** is capable of acting as a tetradentate "metalloligand". The preparation and spectroscopic and electrochemical properties of a copper(I) complex of **1** are reported. The results of an X-ray structural study of this complex are presented. The compound $[(C_5H_5)_2Ti(SCH_2CH_2P(C_6H_5)_2)_2Cu]BF_4$ (**3**) crystallizes in the monoclinic space group $P2_1/c$ with $a = 16.853$ (3) Å, $b = 15.297$ (1) Å, $c = 15.575$ (3) Å, $\beta = 108.90°$, and $Z = 4$. Cyclic voltammetry shows that compound **3** exhibits an electrochemically reversible reduction at -0.99 V vs. SCE. The novel reversibility of this formally Ti(IV)–Ti(III) couple is attributed to the Cu–Ti interaction present in **3**. The details of the structure of this heterobimetallic species are discussed, and the implications of its chemistry are considered.

Introduction

Many studies involving binuclear transition-metal complexes have appeared in the literature.[1] The relevance of bimetallic compounds to bioinorganic systems is one cause for interest.[2,3] Another reason for this interest is the potential application of binuclear organometallic species in catalysis. In this vein, the chemistry associated with water-gas shift catalysis by homonuclear bimetallic rhodium, platinum, and iridium complexes has been studied extensively by the research groups of Eisenberg,[4] Puddephatt,[5] Balch,[6] and Cowie.[7] More recently attention has focused on the activation of small molecules by heterobimetallic systems.[8-21] Compounds containing early-transition-metal/late-transition-metal combinations are expected to exhibit unique reactivity patterns and thus polarize and activate substrates such as CO. This notion is supported by recent work in which early-transition-metal species (i.e., Ti, Zr) act as Lewis acids toward metal carbonyl complexes.[11-13] Despite the potential for applications in catalysis, few early-transition-metal/late-transition-metal species have been synthesized.[1]

We recently reported a monometallic system containing the ligand $(C_6H_5)_2PCH_2CH_2SH$ (PSH).[22] We felt that this bifunctional dissymmetric ligand could be used to link two metal centers together, thus providing a new synthetic route to heterobimetallic species. The use of PSH is attractive for several reasons: group 4[33] metals form stable thiolato complexes, group 8[33] and coinage metals have a well-established phosphine chemistry, and the possibility of sulfur bridges between metal centers offer conceivable metal–metal interactions that could lead to species with new and unique reactivity patterns. In this paper we report our initial work in this area. The preparation of the titanium complex $(C_5H_5)_2Ti(SCH_2CH_2P(C_6H_5)_2)_2$ (**1**) is described. The reaction product of **1** with methyl iodide confirms the nature of this species. Compound **1** is capable of acting as a tetradentate "metalloligand". The preparation and spectroscopic and electrochemical properties of a copper(I) complex of **1**, i.e. $[(C_5H_5)_2Ti(SCH_2CH_2P(C_6H_5)_2)_2Cu]BF_4$ (**3**), are presented. An

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X-ray structural study of **3** was performed. The structure of this heterobimetallic species is discussed, and the implications of these results are considered below.

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 Bruker CXP-80 and Varian EM 360 spectrometers using $Si(CH_3)_4$ as the reference. ^{31}P NMR spectra were recorded on a Bruker CXP 100 spectrometer operating at 36.5 MHz with broad-band proton decoupling. Additional ^{31}P NMR spectra were recorded on a Bruker WH-400 spectrometer operating at 161.98 MHz at the Southwestern Ontario Regional NMR facility at the University of Guelph. Samples were sealed in 5-mm tubes under a N_2 atmosphere. The ^{31}P chemical shifts are reported relative to 85% H_3PO_4. UV-Vis data were recorded by a Shimadzu 240 spectrometer. Cyclic voltammetry was performed with use of a PAR electrochemistry unit in the laboratory of Dr. M. J. Stillman, University of Western Ontario. Melting points were recorded on a Fisher stage melting point apparatus and were not corrected. Combustion analyses were performed by Guelph Chemical Laboratories, Guelph, Ontario. $(C_5H_5)_2TiCl_2$ and CH_3I were purchased from Aldrich Chemical Co. Ph_2PH was purchased from Strem Chemical Co. Ethylene sulfide,[23] $Cu(CH_3CN)_4BF_4$,[24] and the ligand, (diphenylphosphino)ethanethiol,[23] PSH, were prepared by literature methods.

Preparation of $(C_5H_5)_2Ti(SCH_2CH_2P(C_6H_5)_2)_2$ (1). $(C_5H_5)_2TiCl_2$ (300 mg, 1.20 mmol) was dissolved in 50 mL of freshly distilled, degassed benzene along with PSH (595 mg, 2.41 mmol). Triethylamine (245 mg, 2.41 mmol) was added dropwise to the mixture with stirring. The characteristic red of $(C_5H_5)_2TiCl_2$ gradually became deep violet with the addition of base. Stirring for 4 h was followed by filtration using Schlenk techniques to remove triethylamine hydrochloride. The crude product was chromatographed on a column of neutral aluminum using freshly distilled, degassed benzene as eluant. Removal of solvent under vacuum afforded a dark purple viscous oil. Trituration with three, 20-mL portions of dry degassed hexane, followed by evaporation of solvent, yielded the deep purple solid product: 320 mg (40%); mp 160–170 °C dec. ^1H NMR (C_6D_6): δ 7.7 (m, 20 H), 6.3 (s, 10 H), 4.5 (m, 8 H). $^{31}P\{^1H\}$ NMR (C_6H_6): δ −16.5 (s). UV–Vis (CH_3CN; λ, nm (ϵ, M^{-1} cm^{-1})): 535 (3500), 368 (3550), 243 (36 000).

Preparation of $(C_5H_5)_2Ti(SCH_2CH_2P(C_6H_5)_2(Me)I)_2$ (2). **1** (500 mg, 0.75 mmol) was dissolved in a minimum amount of freshly distilled, degassed THF. Iodomethane (300 mg, 2.10 mmol) was added dropwise with stirring. The solution was stirred 2 h and concentrated. Deep red-purple crystalline solid formed as the volume was reduced. This material was isolated by filtration and washed with several portions of THF; yield 430 mg (60%). Anal. Calcd for $C_{40}H_{44}I_2P_2S_2Ti$: C, 50.44; H, 4.66. Found: C, 50.11; H, 4.88. ^1H NMR ($CDCl_3$): δ 7.8 (m, 20 H), 5.9 (s, 10 H), 3.3 (br m, 8 H), 2.85 (d, 6 H, $|J_{P-CH}|$ = 13.8 Hz). $^{31}P\{^1H\}$ NMR (CH_3CN): δ 22.1 (s).

Preparation of $[(C_5H_5)_2Ti(SCH_2CH_2P(C_6H_5)_2)_2Cu]^+BF_4^-$ (3). $Cu(CH_3CN)_4BF_4$ (370 mg, 1.18 mmol) was dissolved in 20 mL of acetonitrile. An acetonitrile solution of **1** (787 mg, 1.18 mmol in 20 mL) was added slowly with stirring to the solution of $Cu(CH_3CN)_4BF_4$. The solution became a dark green-black color in a matter of minutes, and 50 mL of degassed diethyl ether was slowly added. Dark green-black crystals were formed. The crystals were washed with three 50-mL portions of ether and were isolated by filtration: 530 mg (55%); mp 220–224 °C. Anal. Calcd for $C_{38}H_{38}P_2S_2TiCuBF_4$: C, 55.73; H, 4.68. Found: C, 55.02; H, 4.77. ^1H NMR ($CDCl_3$): δ 7.2 (br m, 20 H), 5.7 (br s, 10 H), 3.0 (br m, 8 H). $^{31}P\{^1H\}$ NMR (CH_3CN): δ 4.8 (s). UV–Vis (CH_3CN; λ, nm (ϵ, M^{-1} cm^{-1})): 562 (1300), 440 (6700), 405 (7800), 280 (17 800).

X-ray Data Collection and Reduction. Dark green-black plates of **3** were obtained by vapor diffusion of diethyl ether into a CH_3CN solution of **3**. Diffraction experiments were performed on a four-circle Syntex $P2_1$ diffractometer with a graphite-monochromatized Mo Kα radiation. The initial orientation matrix was obtained from 15 machine-centered reflections selected from a rotation photograph. These data were used to determine the crystal system. Partial rotation photographs around each axis were consistent with a monoclinic crystal system. Ultimately, 35 high-angle reflections ($15 < 2\theta < 35°$) were used to obtain the final lattice parameters and the orientation matrix. Machine parameters, crystal data, and data collection parameters are summarized in Table I. The observed extinctions were consistent with the space group $P2_1/c$. $\pm h, \pm k, +l$ data were collected in one shell ($4.5 < 2\theta < 45.0°$). Three standard reflections were recorded every 197 reflections; their intensities show no statistically significant change over the duration of data collection. The data were processed by using the SHELX-76 program package on the computing facilities at the University of Windsor. A total of 3218 reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. No absorption correction was applied to the data.

Table I. Summary of Crystal Data, Intensity Collection, and Structure Solution

formula	$CuTiS_2P_2C_{38}H_{38}BF_4$
cryst color, form	green-black, plates
a, Å	16.853 (3)
b, Å	15.297 (1)
c, Å	15.575 (3)
β, deg	108.90 (1)
cryst syst	monoclinic
space group	$P2_1/c$
V, Å^3	3798.9 (9)
d(calcd), g cm^{-3}	1.43
Z	4
cryst dimens, mm	0.19 × 0.34 × 0.38
cryst faces	(100), (−1,0,0), (010), (0,−1,0), (001), (0,0,−1), (0,−1,−1)
abs coeff (μ), cm^{-1}	9.46
radiation (λ, Å)	Mo Kα (0.710 69) (graphite monochromator)
temp, °C	24
scan speed, deg/min	2.0–5.0 ($\theta/2\theta$ scan)
scan range, deg	1.0 below Kα_1, 1.1 above Kα_2
bkgd/scan time ratio	0.5
data collcd	2θ of 4.5–45.0° ($\pm h, \pm k, +l$)
total no. of data collcd	7772
no. of unique data ($F_o^2 > 3\sigma F_o^2$)	3218
no. of variables	442 (2 blocks)
R, %	5.61
R_w, %	5.70

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the tabulation of Cromer and Waber.[25,26] The Ti and Cu positions were determined by a direct-methods technique using the 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. The refinement in which all non-hydrogen atoms were assigned isotropic temperature factors gave $R = \sum ||F_o| - |F_c|/\sum |F_o|| = 9.22\%$. Hydrogen atom contributions for the cyclopentadienyl, phenyl, and alkyl hydrogens were included. C–H bond lengths of 0.95 Å were assumed, and hydrogen atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the bonded carbon atom. In the final cycles of blocked-diagonal refinement in which all non-hydrogen atoms were assigned anisotropic temperature factors and all the hydrogen atom contributions were included but not refined, $R = 5.61\%$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2} = 5.70\%$ were obtained. The maximum Δ/σ on any of the parameters in the final cycles was 0.002 for the cation and 0.015 for the anion. A final difference Fourier map calculation showed no peaks of chemical significance; the largest peak was 0.78 electron/Å^3 and was associated with the BF_4 anion. The following data are tabulated: positional parameters (Table II); interatomic distances and angles (Table III).

Temperature factors (Table S-I), hydrogen atom parameters (Table S-II), angles and distances associated with the phenyl and cyclopentadienyl rings (Table S-III), and values of $10|F_o|$ and $10|F_c|$ (Table S-IV) have been deposited as supplementary material.

Results and Discussion

The reaction of $(C_5H_5)_2TiCl_2$ with 2 equiv of PSH in the presence of base (NEt_3) resulted in an intensely purple solution. Formation of NEt_3HCl with nucleophilic displacement of chloride by thiolate on titanium is apparent. Purification of the crude product was achieved by column chromatography. Small amounts of red-brown and orange materials remained on the alumina

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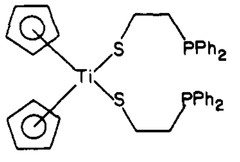
Table II. Positional Parameters ($\times 10^4$)

atom	*x*	*y*	*z*
Ti	4432 (1)	2151 (1)	7456 (1)
Cu	2766 (1)	2382 (1)	5972 (1)
S1	4099 (1)	2563 (1)	5847 (1)
S2	2968 (1)	1985 (1)	7461 (1)
P1	2346 (1)	3691 (1)	5295 (1)
P2	1913 (1)	1213 (1)	5428 (1)
C1	5022 (6)	2792 (6)	8914 (6)
C2	4262 (6)	3217 (5)	8507 (6)
C3	4303 (5)	3650 (5)	7739 (6)
C4	5098 (5)	3528 (5)	7672 (5)
C5	5549 (5)	2998 (5)	8404 (6)
C6	4946 (6)	1004 (6)	6746 (6)
C7	4325 (6)	648 (5)	7025 (6)
C8	4585 (6)	694 (5)	7984 (6)
C9	5358 (6)	1049 (6)	8278 (6)
C10	5587 (6)	1267 (6)	8893 (6)
C11	2273 (5)	4645 (5)	5945 (5)
C12	2167 (5)	4531 (6)	6792 (6)
C13	2100 (6)	5255 (7)	7310 (7)
C14	2158 (6)	6069 (7)	7009 (8)
C15	2268 (5)	6199 (6)	6172 (8)
C16	2319 (5)	5509 (5)	5650 (6)
C21	2409 (5)	3739 (5)	4305 (5)
C22	767 (5)	4335 (6)	4211 (7)
C23	58 (7)	4316 (8)	3450 (10)
C24	−26 (7)	3704 (9)	2784 (9)
C25	593 (7)	3111 (8)	2859 (6)
C26	1324 (6)	3122 (7)	3628 (6)
C31	848 (5)	1328 (5)	4649 (6)
C32	521 (6)	856 (6)	3861 (6)
C33	−297 (7)	1011 (7)	3302 (7)
C34	−783 (6)	1616 (8)	3527 (8)
C35	−461 (6)	2103 (7)	4307 (8)
C36	340 (5)	1955 (6)	4858 (6)
C41	2369 (5)	276 (5)	5032 (5)
C42	3069 (5)	440 (5)	4774 (5)
C43	3465 (6)	−235 (7)	4510 (6)
C44	3176 (8)	−1072 (7)	4497 (7)
C45	2474 (8)	−1259 (6)	4738 (7)
C46	2073 (6)	−572 (5)	5004 (6)
C51	4040 (5)	3722 (5)	5525 (5)
C52	3189 (5)	3936 (5)	4822 (5)
C53	2501 (5)	879 (5)	7299 (5)
C54	1712 (5)	826 (5)	6462 (5)
B	3182 (10)	8522 (9)	8669 (10)
F1	3324 (10)	8237 (6)	9499 (7)
F2	3245 (8)	7913 (6)	8149 (7)
F3	2464 (6)	8856 (10)	8519 (7)
F4	3685 (7)	9182 (6)	8761 (10)

column. These were presumed to be starting material $(C_5H_5)_2TiCl_2$ and monosubstitution product $(C_5H_5)_2TiCl(SCH_2CH_2P(C_6H_5)_2)$, respectively. The purple compound, which was eluted quickly from the column with benzene, was isolated as a viscous oil. Attempts to crystallize this material were unsuccessful although purple solid could be obtained by trituration of the oil with hexane. This compound is stable for short periods of time in halogenated solvents. It readily decomposes on exposure to air, presumably decaying to uncharacterized Ti–O species. The $^{31}P\{^1H\}$ NMR spectrum of this product shows a singlet at −16.5 ppm. This signal is consistent with equivalent uncoupled phosphorus atoms. The chemical shift is similar to that of the free ligand,[22] PSH (−17.8 ppm). This observation is consistent with a formulation in which dangling phosphine moieties are present. The UV–vis spectrum of this compound is similar to those described for $(C_5H_5)_2Ti(SR)_2$ type species. Thus, this purple product is formulated as the disubstitution product **1**.



1

Table III. Selected Bond Distances and Angles

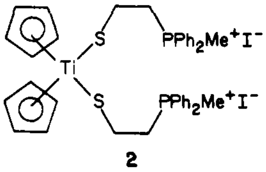
Distances (A)

Ti-Cu	3.024 (1)	Ti-C1	2.376 (8)
Ti-S1	2.465 (2)	Ti-C2	2.392 (9)
Ti-S2	2.484 (3)	Ti-C3	2.358 (8)
Cu-S1	2.332 (2)	Ti-C4	2.358 (8)
Cu-S2	2.314 (2)	Ti-C5	2.367 (8)
Cu-P1	2.279 (2)	Ti-C6	2.382 (10)
Cu-P2	2.267 (2)	Ti-C7	2.386 (8)
S1-C51	1.837 (8)	Ti-C8	2.362 (8)
S2-C53	1.848 (8)	Ti-C9	2.371 (9)
P1-C52	1.838 (9)	Ti-C10	2.349 (10)
P2-C54	1.848 (9)	P1-C11	1.802 (8)
C51-C52	1.532 (9)	P1-C21	1.817 (7)
C53-C54	1.534 (9)	P2-C31	1.821 (7)
		P2-C41	1.826 (9)

Angles (deg)

Ti-S1-Cu	78.1 (1)	S1-Cu-P1	91.2 (1)
Ti-S2-Cu	78.0 (1)	S1-Cu-P2	124.8 (1)
S1-Ti-S2	97.5 (1)	S2-Cu-P1	128.3 (1)
S1-Cu-S2	106.4 (1)	S2-Cu-P2	92.1 (1)
Ti-S1-C51	119.8 (3)	P1-Cu-P2	117.1 (1)
Cu-S1-C51	99.7 (3)	Ti-C1-C2	73.6 (5)
Ti-S2-C53	118.2 (3)	Ti-C1-C5	72.4 (5)
Cu-S2-C53	100.7 (2)	Ti-C2-C1	72.4 (5)
S1-C51-C52	110.9 (5)	Ti-C2-C3	71.7 (5)
P1-C52-C51	109.6 (6)	Ti-C3-C2	74.4 (5)
S2-C53-C54	112.2 (5)	Ti-C3-C4	72.9 (5)
P2-C54-C53	111.7 (6)	Ti-C4-C3	72.8 (5)
P1-C21-C22	123.4 (7)	Ti-C4-C5	73.1 (5)
P1-C21-C26	117.7 (6)	Ti-C5-C1	73.1 (5)
Cu-P2-C54	101.5 (2)	Ti-C5-C4	72.4 (4)
Cu-P2-C31	122.6 (3)	Ti-C6-C7	73.5 (6)
C54-P2-C31	101.0 (4)	Ti-C6-C10	71.7 (6)
Cu-P2-C41	117.3 (3)	Ti-C7-C6	73.1 (5)
C54-P2-C41	105.0 (4)	Ti-C7-C8	71.7 (4)
C31-P2-C41	106.4 (4)	Ti-C8-C7	73.6 (5)
Cu-P1-C52	101.6 (2)	Ti-C8-C9	73.8 (5)
Cu-P1-C21	119.0 (3)	Ti-C9-C8	73.1 (5)
C52-P1-C21	102.9 (4)	Ti-C9-C10	71.7 (5)
Cu-P1-C11	121.5 (3)	Ti-C10-C6	74.3 (6)
C52-P1-C11	105.2 (4)	Ti-C10-C9	73.5 (6)
C21-P1-C11	104.2 (4)		
P1-C11-C12	118.8 (6)		
P1-C11-C16	123.8 (7)		
P2-C31-C32	124.5 (7)		
P2-C31-C36	117.3 (6)		
P2-C41-C42	116.5 (6)		
P2-C41-C46	124.0 (8)		

Reaction of **1** with 2 equiv of methyl iodide was performed in THF. A purple solid was isolated. The ^{31}P NMR spectrum of this material shows a singlet at 22.1 ppm. The ^1H NMR spectrum shows a doublet in the methyl region at 2.85 ppm with $|J_{P-CH_3}| = 13.8$ Hz. These data are suggestive of phosphonium salt formation. Combustion analysis data are consistent with the formulation of this product as **2**.



2

The formation of **2**, a simple derivative of **1**, is additional proof for the dangling nature of the PS ligands in **1**. Previous studies involving phosphorus–sulfur chelate complexes reveal alkylation occurs at sulfur when both thiolate and phosphine are coordinated to a metal.[27] Alkylation at the phosphorus occurs here presumably because of the greater basicity and accessibility of the dangling phosphine groups.

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(27) Roundill, D. M.; Roundill, S. G. N.; Beaulieu, W. B.; Bagchi, U. *Inorg. Chem.* **1980**, *19*, 3365.

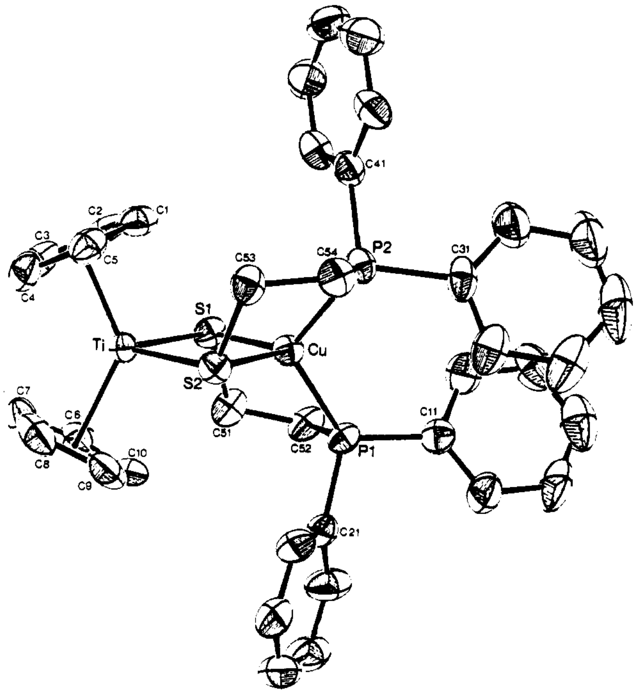
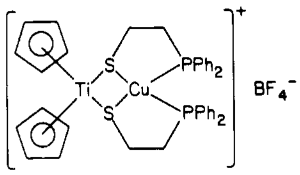


Figure 1. ORTEP drawing of the cation $[(C_5H_5)_2Ti(SCH_2CH_2P(C_6H_5)_2)_2Cu]^+$. 50% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity.

Reaction of $Cu(CH_3CN)_4BF_4$ with **1** was performed in CH_3CN. The solution becomes green-black immediately on addition of a solution of **1** to the solution of the Cu(I) salt. The product is isolated by precipitation with diethyl ether. The $^{31}P\{^1H\}$ NMR spectrum at −40 °C of this material shows a singlet with a chemical shift of 4.8 ppm, consistent with two equivalent P atoms. The downfield shift of the signal indicates coordination to Cu. The UV–vis spectrum reveals absorbances at 562, 440, 405, and 280 nm. The appearance of new low-energy bands in this compound suggest transitions involving both metal atoms,[28] thus inferring a certain Ti/Cu proximity. Combustion analysis data were consistent with the formulation of the product as **3**.



3

The ^{31}P NMR spectrum of **3** shows a temperature dependence. When the mixture is warmed above −40 °C, the singlet begins to broaden and shift to lower field. At 60 °C the signal is approximately 580 Hz wide at half-height and is centered at 5.3 ppm. This broadening is attributed to the presence of two conformers. Two conformations of the SP chelate rings are possible: transoid and cisoid. Examination of molecular models reveals that the transoid form offers less steric interaction between the PS ligands and less ring strain. In fact, a cisoid geometry can only be obtained by a deformation of geometries of at least two atoms of the TiS_2Cu core. Thus, we believe the complex is present in predominantly the transoid form. Similar conclusions were made for $(C_5H_5)_2Ti(SC_6H_5)_2Mo(CO)_4$.[29] Further thermochemical analysis of the inversion process was precluded by the nature of the solvent.

Single crystals of **3** were obtained from an anaerobic vapor diffusion of diethyl ether into a CH_3CN solution of **3**. An X-ray crystallographic study of this species revealed that the crystals were made of unit cells each containing discrete cations and anions as is evident from the Cu–B and Ti–B distances of 10.220 and 10.274 Å, respectively. The closest nonbonded contact between cation and anion is 2.422 Å (F4–H8). Selected interatomic dimensions are given in Table III. An ORTEP drawing of the cation is shown in Figure 1. The geometries of Ti and Cu are both pseudotetrahedral. Two π-bonded cyclopentadienyl rings and two sulfurs of the PS ligands are bonded to Ti. The Ti–C distances average 2.370 (13) Å. Ti–S distances of 2.465 (2) and 2.484 (3) Å were observed. These are in the range of those seen in other Ti(IV)–S species.[30] The Cu coordination sphere consists of the two sulfur and two phosphorus atoms of the PS chelates. Cu–S and Cu–P distances are typical.[18] The bite angles of the PS chelates are similar, averaging 91.7°, typical for five-membered chelate rings.[31] The conformation of the PS chelate rings is confirmed as a transoid arrangement with respect to the TiS_2Cu core.

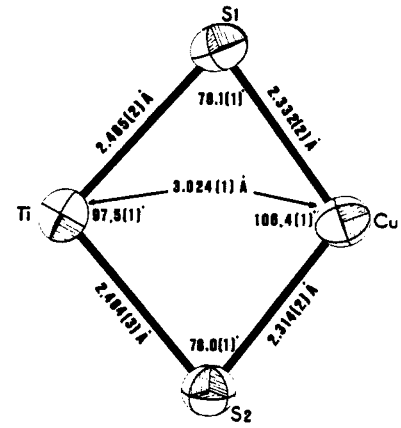
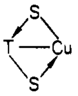


Figure 2. ORTEP drawing of the TiS_2Cu core.

The four atoms of the core are coplanar. The detailed geometry of the core is illustrated in Figure 2. The angles at sulfur (i.e., Cu–S–Ti) are constrained to 78.0 (1)° while those at Ti and Cu are 97.5 (1) and 106.4 (1)°, respectively. Distortion of the angles at bridging atoms to less than 80° have been described as evidence for a metal–metal interaction in other systems.[30] The Cu–Ti distance is 3.024 (1) Å, considerably shorter than the Mo–Ti distance of 3.321 (2) Å seen in the related sulfur-bridged species $(C_5H_5)_2Ti(SCH_3)_2Mo(CO)_4$.[29] Thus, these data support the notion of a Cu→Ti dative bond. The Ti–S and Cu–S bond lengths although chemically equivalent exhibit a small yet distinct long–short alteration about the TiS_2Cu core. The cause of this deformation is not clear. Although the magnitude of the differences is in the range attributable to packing phenomena, the alternation of the bond lengths is suggestive of at least a partial bonding character as illustrated by **4**.



4

Other systems in which Ti(IV) and other transition metals act as a Lewis acid toward electron-rich centers have been documented.[10,30] In this case the Lewis acid/Lewis base interaction occurs between two metals centers. The Cu→Ti interaction is best described as a d^{10}→d^0 dative bond.

Compound **3** was studied by cyclic voltammetry. Attempts to oxidize **3** electrochemically resulted in only irreversible processes, presumably arising from oxidation of Cu(I) or thiolate. It is not surprising that the pseudotetrahedral Cu(I) species **3** does not undergo a reversible oxidation. The products of such an oxidation, that is tetrahedral Cu(II) species, have been to date synthetically illusive. A cyclic voltammogram of **3** showing a reversible re-

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(28) Braterman, P. S.; Wilson, V. A. *J. Organomet. Chem.* **1971**, *31*, 131.

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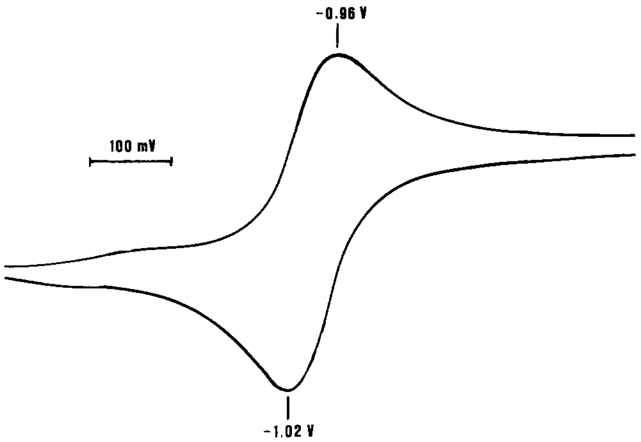

Figure 3. Cyclic voltammogram of 3 in CH_3CN with $N(C_4H_9)_4PF_6$ as the supporting electrolyte. Potentials shown are vs. SCE.

duction is illustrated in Figure 3. The reduction potential is -0.99 V vs SCE. The peak separation of 60 mV is consistent with a one-electron process. Electrochemical studies have demonstrated the general irreversibility of Ti(IV) reductions.[32] The metal-metal interaction present in **3** presumably results in the novel reversibility of this formally Ti(IV)-Ti(III) couple.

The synthetic route established here, and confirmed by the crystallographic data, provides a new and direct route to novel heterobimetallic species. Interactions between early and late transition metals are forced by the geometry of the "metalloligand" **1**. Novel reactivity patterns are expected for such new heterobimetallic species and are exemplified by the novel electrochemical properties of compound **3**. The nature of the product of the reduction of **3** as well as the chemistry of other complexes (specifically Rh) of the "metalloligand" **1** are the subject of current work. The result of these studies will be reported in due course.

Acknowledgment. The NSERC of Canada is thanked for financial support of this research. G.S.W. is grateful for the award of an NSERC postgraduate scholarship. Dr. J. P. Oliver and Dr. M. Rahman of Wayne State University are thanked for the use of their diffractometer and fruitful discussions regarding structure solution. Dr. M. J. Stillman of the University of Western Ontario is thanked for the use of his PAR electrochemistry unit.

Registry No. **1**, 95616-02-7; **2**, 95616-03-8; **3**, 95616-05-0; PSH, 3190-79-2; $(C_5H_5)TiCl(SCH_2CH_2P(C_6H_5)_2)$, 95616-06-1; $(C_5H_5)_2TiCl_2$, 1271-19-8; $Cu(CH_3CN)_4BF_4$, 15418-29-8; Cu, 7440-50-8; Ti, 7440-32-6; iodomethane, 74-88-4.

Supplementary Material Available: Tables S-I-S-IV listing temperature factors, hydrogen atom parameters, angles and distances associated with phenyl and cyclopentadienyl rings, and observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

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(32) Dessy, R. E.; King, R. B.; Waldrop, M. *J. Am. Chem. Soc.* **1966**, *88*, 5112.

(33) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III→3 and 13.)

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Synthesis of New CO Complexes of Palladium[1]

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The palladium(II) complexes $Pd(NO_2)_2L_2$ (L = PPh_3, $PMePh_2$, PMe_2Ph, PEt_3) react with CO to form $Pd_4(CO)_5L_4$. These reaction products have been characterized by IR and ^{31}P, ^1H, and ^{13}C NMR spectroscopy. $Pd_4(CO)_5(PPh_3)_4$ crystallized in the monoclinic space group $C2/c$ with $Z = 4$, $a = 24.957$ (5) Å, $b = 16.138$ (3) Å, $c = 17.758$ (3) Å, and $\beta = 103.47$ (2)°. The palladium atoms are at the corners of a distorted tetrahedron in which five of the six edges are bridged by the carbonyl ligands. The unbridged edge has a Pd-Pd distance of 3.209 (1) Å, indicating the absence of a metal-metal bond. The average bonding Pd-Pd distances are 2.753 (1) and 2.758 (13) Å. The average Pd-P distance is 2.318 (2) Å, and the average Pd-C-Pd angle is 82.0°. $Pd(NO_2)_2(PEt_2Ph)_2$ and $PdCl(NO_2)(PEt_2Ph)_2$ react with CO to form the novel Pd(I) dimer $Pd_2(CO)Cl_2(PEt_2Ph)_3$, which was also structurally characterized by X-ray crystallography. The compound crystallized in the monoclinic space group $P2_1/a$ with $Z = 4$, $a = 20.041$ (3) Å, $b = 11.353$ (3) Å, $c = 19.920$ (5) Å, and $\beta = 129.16$ (1)°. The molecule is dimeric with a Pd-Pd bond and is the first example of a semibridging carbonyl ligand in palladium complexes. Pd2 has roughly square-planar geometry with two phosphines, one chloride, and Pd1 comprising its coordination sphere. One phosphine, one chloride, Pd2, and the carbonyl ligand comprise the coordination sphere of Pd1. The semibridging carbonyl produces severe distortion in the coordination geometry of both Pd1 and Pd2. Some important distances and angles include Pd1-Pd2 = 2.6521 (3) Å, Pd1-C = 1.874 (3) Å, Pd2-C = 2.110 (3) Å, and Pd1-C-Pd2 = 83.3 (1)°.

Introduction

The synthesis of low-valent palladium complexes is of interest because of their importance in catalysis and organic synthesis.[2-5] Relatively few general methods for their preparation are available that permit their derivatization. Among them are the reduction of Pd(II) complexes with hydrazine and CO reduction of palladium acetate in acetic acid[6] in the presence of tertiary phosphine and isonitrile ligands. In our continuing studies of NO_2 ligands as oxidants, we have recently reported[7] the synthesis of $Pd_4(CO)_5(PMePh_2)_4$ from the reaction between CO and Pd-

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(1) Presented at the 2nd IUPAC Symposium on Organometallic Chemistry Directed toward Organic Synthesis, Dijon, France, Aug 1983.

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