Synthesis and Structural Studies of Ti–Rh Heterobimetallic Complexes. Characterization and Electrochemistry of the Redox Partners [Cp₂Ti(SCH₂CH₂CH₂PPh₂)₂Rh]BF₄ and [Cp₂Ti(SCH₂CH₂CH₂PPh₂)₂Rh]⁰

Graham S. White and Douglas W. Stephan*

*Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario, Canada N9B 3P4*

The metalloligand $Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2$ (3) was prepared by reaction of Cp_2TiCl_2 with $HSCH_2CH_2CH_2PPh_2$ in the presence of base. 3 crystallizes in the monoclinic space group $P2_1/n$ with $a = 21.794 (6)$ Å, $b = 13.596 (4)$ Å, $c = 11.998 (4)$ Å, $\beta = 91.87 (3)°$, $V = 3553 (2)$ Å³, and $Z = 4$. Reaction of 3 with $[(NBD)_2Rh]BF_4$ yields $[Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2Rh]BF_4$ (4). 4 crystallizes from acetone as $4 \cdot C_3H_6O$ in the monoclinic space group $P2_1/c$ with $a = 18.451 (7)$ Å, $b = 13.355 (9)$ Å, $c = 17.442 (7)$ Å, $\beta = 95.62 (4)°$, $V = 4277 (4)$ Å³, and $Z = 4$. 4 exhibits fluxional behavior as evidenced by the temperature-dependent ¹H NMR spectra. This is attributed to an equilibrium between the two conformers of 4 in which the alkyl substituents on the bridging sulfur atoms adopt either a cisoid or a transoid orientation. 4 exhibits an electrochemically reversible one-electron reduction at −0.87 V vs. SCE. This is attributed to a formally Ti(IV)–Ti(III) redox couple. The reaction of 4 with Cp_2Co yields the reduced neutral species $[Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2Rh]^0$ (5). This extremely air-sensitive species exhibits an EPR spectrum with $g = 1.979$, $a(^{47}Ti/^{49}Ti) = 9.0$ G, $a(^{103}Rh) = 1.8$ G, and $a(^{31}P) = 2.8$ G. The implications of the spectral and structural results on the nature of the bonding in these heterobimetallic complexes are discussed. The possibility of a direct through-space dative interaction between the d⁸ Rh center and the electron-deficient Ti center is considered.

Introduction

Heterobimetallic complexes have been the subject of numerous recent studies.[1,2] Of particular interest are species that combine early, electron-deficient and late, electron-rich metal centers.[3-12] Such complexes have potential for applications in homogeneous catalytic processes. The presence of the Lewis acidic metal offers the possibility of cooperative activation of a substrate molecule bound to the late transition metal. Alternatively, interactions between the two proximate metal centers may lead to unique reactivity patterns. Evidence of enhanced activity has been observed for heterogeneous catalysts where electron-rich metals are dispersed on Lewis acidic supports.[13-23] In an effort to probe the nature and effects of interactions between proximate early and late transition metals, we are investigating several types of discrete early–late heterobimetallic complexes.[4-12] In one aspect of this work, we have previously reported syntheses of the Ti–Cu heterobimetallic compounds, 1 and 2, in which ti-

1   2
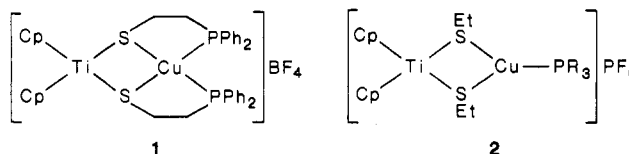
tanium-thiolate complexes act as metalloligands for Cu-(I).[8-11] Spectroscopic, theoretical, and crystallographic data for these Ti–Cu species suggest the presence of dative d¹⁰→d⁰ metal–metal interactions.[8-11] In attempts to explore similar interactions in cases where applications in catalysis might arise, Rh was incorporated as the late transition metal. In this paper we describe the use of the

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metalloligand $Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2$ (3) in the synthesis of the Ti–Rh heterobimetallic complex [Cp_2Ti-$(SCH_2CH_2CH_2PPh_2)_2Rh$]BF_4 (4). In order to achieve this synthesis the new metalloligand 3 was prepared. A three-carbon alkyl chain between the S and P atoms was required as shorter alkyl chains cannot accommodate a square-planar coordination geometry about the Rh atom. The structures of 3 and 4 have been elucidated by X-ray methods. The spectral and electrochemical properties of 4 were studied. 4 undergoes a reversible one-electron reduction yielding the reduced species [Cp_2Ti-$(SCH_2CH_2CH_2PPh_2)_2Rh$]^0 (5) which was characterized by EPR spectroscopy. These results are presented and discussed herein.

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. ^{1}H NMR spectra were recorded on a Bruker CXP-100 spectrometer, using the trace of protonated solvent as the reference. The chemical shifts are reported in parts per million relative to $Si(CH_3)_4$. $^{31}P\{^1H\}$ NMR spectra were recorded on a General Electric GN-300 spectrometer located at Wayne State University. $^{31}P\{^1H\}$ NMR chemical shifts are reported in parts per million relative to external 85% H_3PO_4. UV–vis data were recorded on a Hewlett-Packard 8451A diode array spectrophotometer. Cyclic voltammetry experiments were performed by using a BAS CV-27 electrochemistry unit employing a platinum electrode and [Bu_4N]PF_6 as the supporting electrolyte. Either a saturated calomel or a Ag/AgCl electrode was used as the reference electrode; however, the potentials reported are given vs. the SCE. In the CV experiments scan speeds of 200–500 mV/s were employed. The melting points were determined by using a Fisher stage melting point apparatus and were not corrected. Combustion analyses were performed by Guelph Chemical Laboratories, Guelph, Ontario, and Galbraith Laboratories Inc., Knoxville, TN. Cp_2TiCl_2, $HSCH_2CH_2CH_2Cl$, norbornadiene (NBD), and $RhCl_3 \cdot xH_2O$ were purchased from the Aldrich Chemical Co.; Ph_2PH was purchased from the Pressure Chemical Co. [(NBD)$_2$Rh]BF_4 and Cp_2Co were prepared by the literature methods.[24,25]

Preparation of $HSCH_2CH_2CH_2PPh_2$ (6). This compound was prepared by a modification of a published method.[26] Ph_2PH (10.0 g, 53.7 mmol) was dissolved in 50 mL of THF. To this was added 32.0 mL of a 1.67 M ethereal MeLi solution. $HSCH_2C$-H_2CH_2Cl (5.9 g, 53.3 mmol) was then added via an addition funnel over a period of 0.5 h, discharging the orange color. The mixture was refluxed for 12 h, cooled, and then washed with two 15-mL portions of degassed H_2O. The organic layer was isolated and fractionally distilled in vacuo, yielding 6.56 g (47%) of a colorless oil: bp 160–168 °C (0.5–0.7 mm); ^{1}H NMR (CDCl$_3$) δ 7.7 (m, 4 H), 7.1 (m, 6 H), 2.25 (d of t, |$J_{CH_\alpha-SH}$| = 7.4 Hz, |$J_{CH_\alpha-CH_\beta}$| = 7.4 Hz, 2 H), 1.9 (m, 2 H), 1.5 (m, |$J_{CH_\beta-P}$| = 40 Hz, 2 H), 0.92 (t, 1 H); $^{31}P\{^1H\}$ NMR (C$_6$H$_6$) δ –17.4 (s).

Preparation of $Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2$ (3). This compound was prepared by reaction of Cp_2TiCl_2 with 6 in the presence of NEt_3 in a manner directly analogous to that previously published.[8] Purification of the crude product was achieved by anaerobic chromatography on neutral alumina with elution by a 50:50 benzene/acetonitrile mixture. Evaporation of the solvent yielded a purple oil. Upon trituration with several portions of hexane, a purple solid formed and was isolated in 69% yield: mp 105–108 °C dec; UV–vis (CH$_3$CN, λ, nm (ε, M^{-1} cm^{-1})) 535 (3500), 368 (3550), 243 (36 000); ^{1}H NMR (CDCl$_3$) δ 7.3 (m, 20 H), 6.05 (s, 10 H), 3.07 (t, |$J_{CH_\alpha-CH_\beta}$| = 7.0 Hz, 4 H), 1.9 (m, 4 H), 1.5 (br m, 4 H); $^{31}P\{^1H\}$ NMR (C$_6$H$_6$) δ –16.5 (s). Anal. Calcd for $C_{40}H_{42}P_2S_2Ti$: C, 68.96; H, 6.08. Found: C, 69.50; H, 6.08.

Preparation of [$Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2Rh$]$BF_4$ (4). 3 (300 mg, 0.43 mmol) was added to a suspension of 160 mg (0.43

mmol) of [(NBD)$_2$Rh]BF_4 in 50 mL of THF and 10 mL of CH_3CN. The solution darkened to a brown-black color in a few minutes. The solution was stirred for 2 h, and the volume was then reduced under vacuum to ca. 10 mL. Slow addition of 40 mL of hexane led to precipitation of 4. The product was isolated by filtration: yield 230 mg (60%); mp >300 °C. Recrystallization from acetone at –10 °C yielded blocks of 4·C_3H_6O: CV (CH$_3$CN) $E^{o\prime}$ = –0.87 V; UV–vis (CH$_3$CN, λ, nm (ε, M^{-1} cm^{-1})) 315 (11 250), 520 (1090); ^{1}H NMR (CD$_3$CN) δ 7.3 (m, 20 H), 5.82 (s, 10 H), 3.1 (m, 4 H), 2.3 (br m, 4 H), 2.1 (m, 4 H), 2.0 (s, 6 H); $^{31}P\{^1H\}$ (CH$_3$CN) δ 24.8 (d, |J_{Rh-P}| = 162 Hz). Anal. Calcd for $C_{40}H_{42}BF_4P_2RhS_2Ti \cdot C_3H_6O$: C, 54.68; H, 5.12; S, 6.79. Found: C, 53.69; H, 5.46; S, 6.93.

Generation of [$Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2Rh$]^0 (5). A 2-mL benzene solution of 11 mg of Cp_2Co was slowly added to a 10 mL CH$_3$CN solution of 4 (47 mg). The solution became amber, and a yellow precipitate ([Cp_2Co]BF_4) formed. The solution was filtered and the filtrate sealed in an EPR tube or UV–vis cell. Alternatively, supporting electrolyte was added and the solution examined by cyclic voltammetry. Both CV and EPR spectroscopy confirmed the presence of 5: EPR (THF/C$_6$H$_6$) g = 1.979, $a\langle^{47}Ti/^{49}Ti\rangle$ = 9.0 G, $a\langle^{31}P\rangle$ = 2.8 G, $a\langle^{103}Rh\rangle$ = 1.8 G; CV (CH$_3$CN) $E^{o\prime}$ = –0.87 V; UV–vis (C$_6$H$_6$, λ, nm (ε, M^{-1} cm^{-1})): 320 (3450).

X-ray Data Collection and Reduction. Violet crystals of 3 were obtained by crystallization from a THF solution of 3 cooled to –10 °C. On standing at –10 °C, brown-black crystals of 4·C_3H_6O were obtained from an acetone solution of 4.

Diffraction experiments were performed on a four-cycle Syntex P2$_1$ diffractometer using either Nb-filtered or graphite-monochromatized Mo Kα 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° < 2θ < 30°) 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 $P2_1/n$ for 3 and $P2_1/c$ for 4·C_3H_6O. ±h,+k,+l data for 3 (4.5° < 2θ < 40.0°) and ±h,+k,+l data for 4·C_3H_6O (4.5° < 2θ < 45.0°) were collected. Three standard reflections, for each species, were recorded regularly throughout data collection. The standards showed 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. 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 (μ = 4.24 cm^{-1} for 3 and μ = 7.14 cm^{-1} for 4·C_3H_6O). No absorption corrections were applied to the data.

Structure Solutions and Refinements. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[27,28] The Ti atom position for 3 and the Rh atom position for 4 were determined by using the heavy-atom (Patterson) method. 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, respectively. In the final cycles of least-squares refinement the metal atoms, S, P, cyclopentadienyl, and alkyl carbon atoms were assigned anisotropic temperature factors. 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 1.395 Å. For 4, the B–F bond distances were constrained to 1.300 Å. For both refinements, hydrogen atom positions were allowed to ride on the carbon to which they are bonded assuming a C–H bond length of 0.95 Å. In each case, hydrogen atom temperature factors were fixed at 1.10 times the isotropic tem-

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Table I. Crystallographic Parameters

	3	4
formula	$C_{40}H_{42}P_2S_2Ti$	$BC_{40}F_4H_{42}P_2RhS_2Ti\cdot$ C_3H_6O
cryst color, form	violet prisms	brown-black blocks
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a (Å)	21.794 (6)	18.451 (7)
b (Å)	13.596 (4)	13.355 (9)
c (Å)	11.998 (4)	17.442 (7)
β (deg)	91.87 (3)	95.62 (4)
V (Å^3)	3553 (2)	4277 (4)
D (g cm^{-3})	1.30	1.47
Z	4	4
cryst dimens (mm)	0.62 × 0.30 × 0.20	0.35 × 0.35 × 0.35
abs coeff μ (cm^{-1})	4.24	7.14
radiatn (λ (Å))	Mo Kα (0.710 69), Nb filter	Mo Kα (0.710 69), graphite monochromator
temp (°C)	24	24
scan speed (deg/min)	2.0–5.0 ($\theta/2\theta$ scan)	2.0–5.0 ($\theta/2\theta$ scan)
scan range (deg)	1.0 below Kα_1, 1.0 above Kα_2	1.0 below Kα_1, 1.0 above Kα_2
bkgd/scan time ratio	0.5	0.5
data collected	3737	6147
2θ range	4.5–40.0° ($\pm h,k,l$)	4.5–45.0° ($\pm h,k,l$)
no. of unique data ($F_o^2 > 3\sigma(F_o^2)$)	1717	3307
no. of variables	238	328 (2 blocks)
R	10.01	6.53
R_w	10.41	7.14
max Δ/σ in final cycle	0.002	0.001
largest residual electron density (e/Å^3)	0.77	1.46
atom associated with residual density	P2	Rh

Figure 1. Variable-temperature ^{1}H NMR spectra of 4 (only the Cp proton resonances are shown).

perature factor of the carbon atom to which they are bonded. In all cases, the hydrogen atom contributions were calculated, but not refined. The final values of $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$ 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. Thermal parameters (Table S1), hydrogen atom parameters (Table S2), bond distances and angles associated with the cyclopentadienyl rings, the BF_4 anion, and the acetone of crystallization (Table S3), and the values of $10|F_o|$ and $10|F_c|$ (Table S4) have been deposited as supplementary material.

Results and Discussion

We have previously reported the preparation of **1** utilizing the metalloligand $Cp_2Ti(SCH_2CH_2PPh_2)_2$ (**7**).[8] Initial attempts to prepare Rh complexes of this metalloligand led only to an uncharacterized mixture of products. An examination of molecular models indicated that **7** is not able to act as a tetradentate ligand for Rh without considerable strain in the pseudo-square-planar coordination sphere of Rh. One method of reducing the strain is to extend the alkyl chain between the S and P atoms. To this end, the ligand $HSCH_2CH_2CH_2PPh_2$ (**6**) was prepared by nucleophilic displacement of chloride from $HSCH_2CH_2CH_2Cl$ by diphenylphosphide. The ^{1}H and $^{31}P\{^1H\}$ NMR spectra of **6** are consistent with the formulation. Reaction of **6** with Cp_2TiCl_2 in the presence of base yields the purple metalloligand **3**. Purification of **3** can be achieved by chromatography on neutral alumina, in a manner similar to that used for the metalloligand **7**.[8] An orange-brown band remaining on the column presumably results from the binding of Cp_2TiCl_2 and the monosubstitution product $Cp_2TiCl(SCH_2CH_2CH_2PPh_2)$ to the
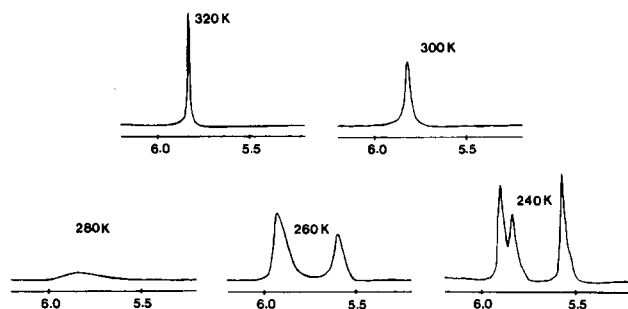
column, while **3** is eluted by a 50:50 benzene/acetonitrile mixture. Once the product is free of impurities, **3** crystallizes as purple crystals. ^{1}H and $^{31}P\{^1H\}$ NMR data as well as combustion analyses are consistent with the formulation of **3**. The UV–vis spectrum is similar to that reported for **7**[8] and other titanocenedithiolate complexes.[29] The $^{31}P\{^1H\}$ NMR spectrum of **3** shows a single resonance at –16.5 ppm. This chemical shift is similar to that of **6**, suggesting dangling phosphine groups. This was confirmed by an X-ray crystallographic study of **3** (vide infra).

Reaction of **3** with $[(NBD)_2Rh]BF_4$ in THF results in a rapid color change from purple to brown-black. The brown-black crystalline solid **4** is isolated from the reaction mixture by precipitation with diethyl ether. The ^{1}H NMR spectrum shows resonances attributable to the presence of the metalloligand **3**. The $^{31}P\{^1H\}$ NMR spectrum of the product shows only a doublet which is indicative of equivalent phosphorus nuclei coupled to Rh. The UV–vis spectrum shows relatively strong absorptions at 520 and 315 nm. In other related bimetallic systems such low-energy bands have been attributed to transitions involving proximate metal centers.[8,30,31] These data as well as the elemental analyses of the product are consistent with the formulation of **4** as $[Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2Rh]BF_4$. This formulation was confirmed by a crystallographic study (vide infra).

Fluxionality. The ^{1}H NMR spectra of **4** were examined over the temperature range 47 to –33 °C. The cyclopentadienyl proton resonances are temperature-dependent (Figure 1). At higher temperature (47 °C) a single sharp resonance is observed at 5.83 ppm. On cooling, the signal broadens and then sharpens to yield the limiting spectrum at –33 °C which consists of three distinct resonances at 5.91, 5.84, and 5.57 ppm. These spectra are attributable to a nondegenerate intramolecular process[32] involving the equilibrium between the cisoid and transoid conformers of **4**. At 47 °C, the chemical shift of the time-averaged resonance indicates that the more abundant species in solution is the transoid conformer. The equilibrium constant (K_{eq} = [transoid]/[cisoid]) is approximately 9. At low temperature (–33 °C), the three resonances are attributable to the two conformers of **4**. For the cisoid conformer, two Cp resonances are observed as the Cp rings are magnetically inequivalent. The additional resonance observed at –33 °C is attributable to the magnetically equivalent Cp rings of the transoid conformer. From the integration, an approximate value of K_{eq} is estimated to be 0.3 at –33 °C. Thus, at low temperature the cisoid

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Table II. Positional Parameters[a]

atom	x	y	z	atom	x	y	z
			Molecule 3				
Ti	449.0 (1)	614.5 (2)	300.9 (3)	S1	456.0 (2)	673.1 (4)	115.0 (4)
S2	551.1 (2)	551.4 (4)	306.1 (4)	P1	504.3 (3)	829.2 (4)	−226.8 (5)
P2	666.9 (2)	298.8 (4)	248.7 (5)	C1	523.0 (8)	751 (2)	104 (2)
C2	538.6 (9)	765 (2)	−15 (2)	C3	489.9 (8)	827 (2)	−80 (2)
C4	561.7 (8)	470 (2)	189 (2)	C5	628 (1)	474 (2)	153 (2)
C6	675 (1)	430 (2)	237 (2)	C01	405 (1)	485 (2)	193 (2)
C02	359 (1)	548 (2)	211 (3)	C03	350 (1)	549 (2)	320 (3)
C04	392 (1)	487 (2)	377 (2)	C05	424 (1)	443 (2)	291 (2)
C06	486 (2)	681 (2)	468 (2)	C07	503 (1)	745 (2)	384 (3)
C08	451 (2)	786 (2)	341 (2)	C09	404 (1)	746 (2)	398 (3)
C10	423 (1)	684 (2)	474 (2)	C11	716.4 (6)	255 (1)	139.6 (9)
C12	774.3 (6)	213 (1)	158.2 (9)	C13	808.2 (6)	182 (1)	68.2 (9)
C14	784.2 (6)	192 (1)	−40.4 (9)	C15	726.3 (6)	234 (1)	−59.0 (9)
C16	692.4 (6)	265 (1)	31.0 (9)	C21	715.6 (6)	270.7 (9)	372 (1)
C22	713.8 (6)	171.9 (9)	403 (1)	C23	747.7 (6)	139.4 (9)	497 (1)
C24	783.4 (6)	205.8 (9)	559 (1)	C25	785.2 (6)	304.6 (9)	528 (1)
C26	751.4 (6)	337.1 (9)	435 (1)	C31	574.4 (7)	899.7 (9)	−227 (1)
C32	621.7 (7)	869.5 (9)	−295 (1)	C33	675.9 (7)	924.0 (9)	−298 (1)
C34	682.8 (7)	1008.6 (9)	−233 (1)	C35	635.5 (7)	1038.8 (9)	−165 (1)
C36	581.3 (7)	984.3 (9)	−162 (1)	C41	450.7 (6)	921 (1)	−2797 (8)
C42	412.4 (6)	979 (1)	−216.1 (8)	C43	374.2 (6)	1049 (1)	−267.9 (8)
C44	374.2 (6)	1060 (1)	−383.5 (8)	C45	412.5 (6)	1002 (8)	−447.1 (8)
C46	450.8 (6)	932 (1)	−395.3 (8)				
			Molecule 4				
Rh	2108 (1)	4649 (1)	6662 (1)	Ti	863 (1)	4841 (1)	7747 (1)
S1	992 (1)	3755 (2)	6666 (1)	S2	2011 (2)	5735 (2)	7706 (1)
P1	2293 (1)	3385 (2)	5828 (1)	P2	3039 (1)	5622 (2)	6359 (1)
F1	1078 (5)	8014 (8)	10400 (6)	F2	1747 (4)	6813 (7)	9967 (7)
F3	567 (5)	6632 (8)	9884 (6)	F4	1055 (8)	7683 (10)	9242 (6)
B	1113 (4)	7263 (6)	9925 (6)	C01	512 (8)	3560 (10)	8604 (7)
C02	748 (9)	4372 (10)	9047 (7)	C03	1452 (9)	4550 (10)	8978 (6)
C04	1701 (6)	3825 (9)	8510 (6)	C05	1112 (9)	3201 (9)	8284 (6)
C06	−219 (7)	5222 (13)	6962 (8)	C07	−391 (7)	5166 (13)	7722 (9)
C08	−41 (8)	5941 (11)	8130 (8)	C09	354 (8)	6456 (11)	7656 (8)
C10	259 (9)	6036 (12)	6922 (8)	C51	574 (6)	4083 (9)	5698 (6)
C52	827 (6)	3307 (9)	5127 (6)	C53	1626 (5)	3361 (8)	4986 (5)
C54	1999 (7)	7055 (8)	7433 (7)	C55	2728 (7)	7373 (8)	7197 (7)
C56	2889 (7)	6991 (7)	6406 (6)	C12	2476 (4)	2053 (4)	7063 (3)
C13	2486 (4)	1113 (4)	7412 (3)	C14	2263 (4)	269 (4)	6980 (3)
C15	2030 (4)	366 (4)	6198 (3)	C16	2020 (4)	1306 (4)	5849 (3)
C11	2243 (4)	2150 (4)	6281 (3)	C22	3201 (3)	3112 (6)	4596 (3)
C23	3861 (3)	2882 (6)	4310 (3)	C24	4481 (3)	2706 (6)	4813 (3)
C25	4439 (3)	2760 (6)	5611 (3)	C26	3779 (3)	2990 (6)	5897 (3)
C21	3160 (3)	3166 (6)	5389 (3)	C32	2637 (3)	5761 (5)	4814 (4)
C33	2727 (3)	5803 (5)	4030 (4)	C34	3417 (3)	5673 (5)	3781 (4)
C35	4016 (3)	5500 (5)	4317 (4)	C36	3926 (3)	5458 (5)	5101 (4)
C31	3236 (3)	5588 (5)	5349 (4)	C42	4000 (4)	4684 (5)	7454 (4)
C43	4653 (4)	4555 (5)	7919 (4)	C44	5224 (4)	5230 (5)	7873 (4)
C45	5142 (4)	6034 (5)	7361 (4)	C46	4489 (4)	6163 (5)	6896 (4)
C41	3918 (4)	5488 (5)	6943 (4)	C57	3785 (7)	5923 (9)	10047 (8)
C58	3526 (9)	6603 (12)	9421 (9)	C59	3671 (12)	4838 (12)	9947 (13)
O1	4062 (6)	6281 (8)	10638 (6)				

[a] Multiplied by 10^4.

conformer is more abundant in solution. The mechanism of this interconversion probably involves pyramidal inversion at sulfur. This mechanism has been proposed for other sulfur-bridged bimetallic complexes.[33-35] These data imply that the cisoid form of 4 is thermodynamically favored. The reason for this is not clear, but it is noteworthy that similar thermodynamic favoring of the cisoid form of other thiolato-bridged bimetallics has been observed.[9,33-35]

Structure Descriptions. Single purple crystals of 3 were obtained by cooling a THF solution of 3. The X-ray diffraction study showed that the crystals are made up of monoclinic unit cells each containing four molecules. The closest approach between two molecules is 2.856 Å (S1–

H16). An ORTEP drawing of a single molecule of 3 is shown in Figure 2. Selected bond distances and angles are included in Table III. There are two cyclopentadienyl rings and two sulfur atoms comprising the pseudotetrahedral coordination sphere about Ti. The phosphine groups are indeed dangling as the closest Ti⋯P distance is 6.448 Å. The Ti–C distances are typical.[8] The Ti–S bond distances average 2.381 (6) Å which is shorter than those reported in other mononuclear Ti complexes where Ti–S distances in the range 2.403–2.611 Å were found.[8-10,12,36-41] The

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Table III. Selected Bond Distances and Angles

Molecule 3

Distances (Å)

Ti-S1	2.378 (6)	Ti-S2	2.384 (6)
S1-C1	1.81 (2)	S2-C4	1.81 (2)
C1-C2	1.49 (2)	C4-C5	1.51 (3)
C2-C3	1.55 (3)	C5-C6	1.54 (3)
C3-P1	1.80 (2)	C6-P2	1.79 (2)
P1-C31	1.80 (2)	P2-C11	1.82 (1)
P1-C41	1.81 (2)	P2-C21	1.83 (1)
Ti-C01	2.37 (2)	Ti-C06	2.32 (2)
Ti-C02	2.38 (2)	Ti-C07	2.34 (2)
Ti-C03	2.36 (2)	Ti-C08	2.37 (2)
Ti-C04	2.33 (2)	Ti-C09	2.37 (2)
Ti-C05	2.40 (2)	Ti-C10	2.36 (2)

Angles (deg)

S1-Ti-S2	93.3 (2)	Ti-S1-C1	109.7 (6)
Ti-S2-C4	110.0 (6)	S1-C1-C2	110 (1)
S2-C4-C5	110 (1)	C1-C2-C3	113 (2)
C4-C5-C6	115 (2)	C2-C3-P1	111 (1)
C5-C6-P2	112 (2)	C3-P1-C31	100.5 (8)
C6-P2-C11	102.0 (9)	C3-P1-C41	102.8 (7)
C6-P2-C21	102.5 (9)	C31-P1-C41	99.9 (7)
C11-P2-C21	99.8 (6)		

Molecule 4

Distances (Å)

Ti-S1	2.409 (3)	Ti-Rh	3.127 (2)
Ti-S2	2.438 (3)	Rh-S1	2.380 (3)
Ti-C01	2.41 (1)	Rh-S2	2.349 (3)
Ti-C02	2.38 (1)	Rh-P1	2.276 (3)
Ti-C03	2.34 (1)	Rh-P2	2.259 (3)
Ti-C04	2.37 (1)	S1-C51	1.84 (1)
Ti-C05	2.41 (1)	C51-C52	1.54 (2)
Ti-C06	2.36 (1)	C52-C53	1.52 (2)
Ti-C07	2.35 (1)	S2-C54	1.83 (1)
Ti-C08	2.37 (2)	C54-C55	1.51 (2)
Ti-C09	2.35 (2)	C55-C56	1.53 (2)
Ti-C10	2.36 (2)	C53-P1	1.822 (9)
P1-C11	1.836 (6)	C56-P2	1.85 (1)
P1-C21	1.862 (7)	P2-C31	1.832 (7)
P2-C41	1.838 (4)		

Angles (deg)

S1-Ti-S2	96.8 (1)	S1-Rh-S2	100.1 (1)
Ti-S1-Rh	81.5 (1)	S1-Rh-P1	79.3 (1)
Ti-S2-Rh	81.6 (1)	S2-Rh-P2	86.8 (1)
Ti-S1-C51	120.7 (4)	S1-Rh-P2	165.4 (1)
Ti-S2-C54	119.5 (4)	S2-Rh-P1	168.9 (1)
S1-C51-C52	107.9 (7)	P1-Rh-P2	96.4 (1)
S2-C54-C55	110.8 (8)	Rh-S1-C51	99.4 (4)
C51-C52-C53	115.6 (9)	Rh-S2-C54	113.2 (4)
C54-C55-C56	114 (1)	C53-P1-C11	105.9 (4)
C52-C53-P1	117.4 (7)	C53-P1-C21	101.9 (4)
C55-C56-P2	114.4 (7)	C56-P2-C31	96.4 (4)
C11-P1-C21	96.7 (3)	C56-P2-C41	101.5 (4)
C31-P2-C41	106.5 (3)		

S1-Ti-S2 angle of 93.3 (2)° is similar to that found in Cp$_2$TiS$_5$[39] and Cp$_2$*Ti (SH)$_2$ (8).[40] This value is substantially greater than that seen in Cp$_2$Ti(S$_2$C$_2$H$_2$)[37] and Cp$_2$Ti(S$_2$C$_6$H$_4$)[38] in which the chelating ligands restrict the S-Ti-S angle to ca. 82°. The alkyl substituents on the sulfur atoms are on opposite sides of the TiS$_2$ plane. The angles between the TiSC planes and the TiS$_2$ plane are 53.4 and 53.6°. The Ti-S-C angles are 109.7 (6) and 110.0 (6)°. This geometry about sulfur suggests some degree of π bonding between the pπ orbital on sulfur and the 1a$_1$ orbital on Ti.[42] The shorter Ti-S bond lengths in 3, as compared to those in 8 (2.381 (6) vs. 2.413 (3) Å), reflect

(40) Bottomley, F.; Drummond, D. F.; Egharevba, G. O.; White, P. S. *Organometallics* **1986,** *5,* 1620.
(41) Zank, G. A.; Rauchfuss, T. B. *Organometallics* **1984,** *3,* 1191.
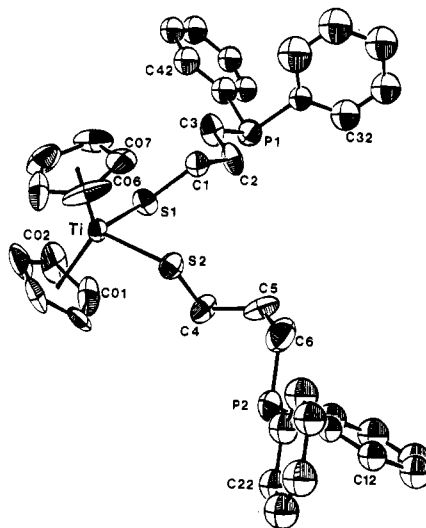(42) Lauher, J. W.; Hoffman, R. *J. Am. Chem. Soc.* **1976,** *98,* 1729.

Figure 2. ORTEP drawing of 3 (50% thermal ellipsoids are shown; hydrogens are omitted for clarity).
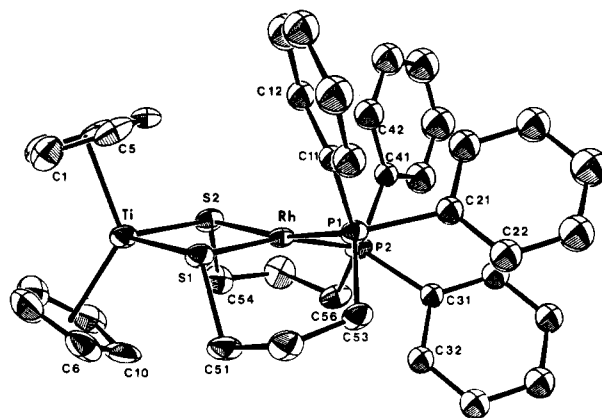

Figure 3. ORTEP drawing of the cation of 4 (30% thermal ellipsoids are shown; hydrogens are omitted for clarity). Note the cisoid conformation of the alkyl substituents on the sulfur atoms.

an increase in the strength of the Ti-S π interaction. This is consistent with the presence of the electron-donating alkyl substituent on sulfur and the poorer electron-donating Cp rings in 3.

Single brown-black crystals of 4·C$_3$H$_6$O were obtained by recrystallization from acetone. The X-ray diffraction study showed that the crystals are made up of monoclinic unit cells each containing four discrete cations and anions as well as four molecules of acetone. The closest approach between anions and cations is 2.451 Å (F3···H08). The acetone molecule does not interact with either the cation or anion as the closest approach to either is 2.589 Å (O1···H24). An ORTEP drawing of the cation of 4 is shown in Figure 3. Selected bond distances and angles are included in Table III. In the cation there are two cyclopentadienyl rings and two sulfur atoms comprising the pseudotetrahedral coordination sphere about Ti. The two sulfur atoms also bind to Rh. The two phosphine groups complete the distorted square-planar coordination sphere of the Rh. The Ti-C distances are typical and similar to those observed in 3. The Ti-S bond distances, 2.409 (3) and 2.438 (3) Å, are longer than those found in 3 which is consistent the bridging nature of the sulfur atoms. The alkyl substituents on the sulfur atoms adopt a cisoid configuration about the TiS$_2$Rh core. Rh-S and Rh-P distances are typical.[43] The geometry about Rh is that

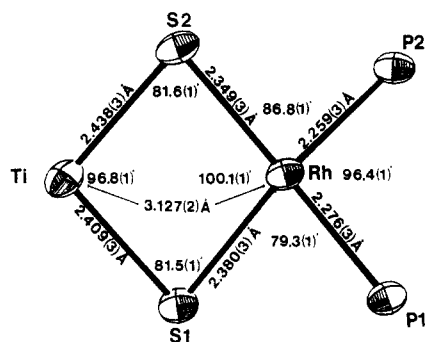(43) Dick, D. G.; Stephan, D. W. *Can. J. Chem.* **1986,** *64,* 1870.

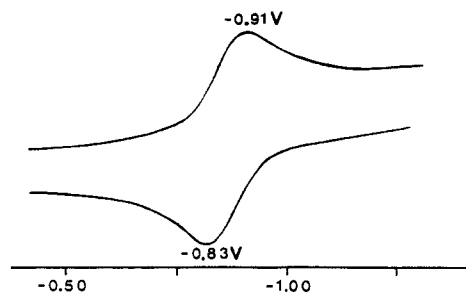**Figure 4.** ORTEP drawing of the core of the cation of 4.

Figure 5. Cyclic voltammogram of **4** in CH_3CN using a Pt electrode and $[Bu_4N]PF_6$ as the supporting electrolyte. Potentials shown are vs. SCE.
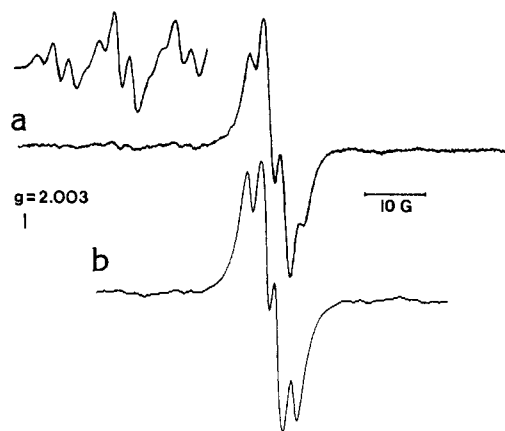

Figure 6. (a) EPR spectrum of **5** in benzene/CH_3CN solution at 50 °C. (b) Computer simulation of the EPR spectrum of **5**.

of a distorted square plane. The trans S–Rh–P angles are 165.4 (1) and 168.9 (1)°, and thus the P1 and P2 atoms are 0.44 and 0.51 Å above and below the RhS_2 plane, respectively. These deviations are similar to those observed in the complex $[(MeSCH_2CH_2PPh_2)_2Rh]BF_4$ (**9**).[43] The six-membered chelate rings formed by the sulfur–phosphorus ligation to Rh in **4** adopt chair conformations. The bite angles at Rh (i.e., the S–Rh–P angles) for these chelates are 86.8 (1) and 79.3 (1)°. While the former is typical[43] of such chelate rings, the latter is substantially smaller. This effect may result from steric interaction of the phenyl substituents on phosphorus (H42···H26 = 2.462 Å). However, the P–Rh–P angle is similar to that seen in **9**, suggesting that these steric effects are not responsible for the small S1–Rh–P1 bite angle. The S–Rh–S angle in **4** is 100.1 (1)°, which is considerably larger than the S–Rh–S angle found in **9** (90.0 (1)°). Thus, the geometrical constraints imposed by the formation of the four-membered TiS_2Rh ring may be the primary cause of the closing down of the S1–Rh–P1 angle.

The atoms of the TiS_2Rh core are coplanar. The detailed geometry of the core is illustrated in Figure 4. The angles at sulfur (Ti–S–Rh) are 81.5 (1)°, which is slightly larger than the corresponding Ti–S–Cu angle in **1** (78.1 (1)°). Angles at bridging atoms of less than 80° have been used as criteria for evidence of a metal–metal interaction.[44] The Ti–Rh distance is 3.127 (2) Å, which is slightly longer than the Cu–Ti distance[8] of 3.024 (1) Å seen in **1** and shorter than the Mo–Ti distance of 3.321 (2) Å seen in the related species $Cp_2Ti(\mu$-SMe$)_2Mo(CO)_4$.[30] The Ti–S and Rh–S bond lengths exhibit a short–long alternation about the TiS_2Rh core similar to that seen in **1**. This suggests at least some degree of bonding character as illustrated in **10**. Thus, although the structural data are not conclusive, there is some suggestion of a dative $d^8 \rightarrow d^0$ interaction between the Rh and Ti centers.

10
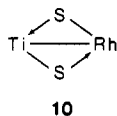
Electrochemistry. The electrochemical properties of **3** and **4** were studied by cyclic voltammetry using acetonitrile as the solvent, $[Bu_4N]PF_6$ as the supporting electrolyte, a SCE as the reference electrode, and a Pt working electrode. No reversible oxidation processes were observed for either compound. The irreversible oxidations presumably arise from oxidation of the thiolate ligands. Irreversible reduction of **3** was observed at a potential of ca. –1.5 V vs. SCE. This feature is typical for $Cp_2Ti(SR)_2$ complexes.[8–10] A reversible one-electron reduction process is observed at $E^{\circ\prime}$ of –0.87 V (initial applied potential, E_i

= 0.00 V vs. SCE). This potential is 120 mV less reducing than that seen for an analogous wave assigned to the formally Ti(IV)/T(III) redox couple of **1**.[8] Substitution by the d^8 Rh for the d^{10} Cu presumably leads to diminished electron density on the Ti atom and thus the lower reduction potential. The peak separation of 80 mV is consistent with a one-electron process. The reversibility of the process is suggested by the ratio of i_{pa}/i_{pc} = 1 for scan rates between 200 and 500 mV/s. This was confirmed by the successful chemical generation of the reduced species **5**. Reaction of **4** with Cp_2Co in acetonitrile/benzene

4   **5**
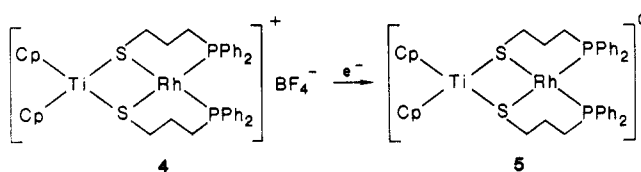
yielded an amber solution of **5** with precipitation of $[Cp_2Co]BF_4$. Cyclic voltammetry of this solution gave a reversible wave at potentials indentical with that seen for **4** ($E^{\circ\prime}$ = –0.87 V vs. SCE, E_i = –1.50 V, scan rate = 200–500 mV/s).

The EPR spectrum of **5** is slightly anisotropic at 25 °C, while at 50 °C an isotropic spectrum is obtained (Figure 6). Presumably, the anisotropic at room temperature arises from inhibited molecular tumbling. Spectral parameters were obtained by computer simulation. Although the possibility of an equilibrium in solution between the cisoid and transoid conformers of **5** exists, we have no means of ascertaining the position of the equilibrium. Thus, the question of the conformation of **5** was not addressed. However, it seems likely that as with **4**, the transoid conformer of **5** will predominate in solution at 50 °C. Furthermore, it is unlikely that differences in the EPR parameters for the two possible conformers would be discernible given the observed linewidths.

(44) Davies, G. R.; Kilbourn, B. T. *J. Chem. Soc. A* **1971**, 87.

The *g* value of 1.979 and the $a\langle^{47}Ti/^{49}Ti\rangle$ value of 9.0 G are typical for Ti(III) species;[12] thus the reduction is formally attributed to a Ti(IV)/Ti(III) redox couple. Hyperfine couplings to two chemically equivalent phosphorus and a Rh nuclei of 2.8 and 1.8 G, respectively, were observed. Molecular orbital calculations on the related complexes 1 and 2 indicate that the LUMO is primarily Ti d_{z^2} in character (where the *z* axis is the Ti–Cu vector). If the situation is similar for 4, then occupation of this orbital upon formation of 5 would account for the typical Ti(III) *g* and $a\langle^{47}Ti/^{49}Ti\rangle$ values. Furthermore, it suggests that the mechanism of coupling to Rh may involve a direct through-space interaction rather than a Fermi contact or through-bond process. Similar trans-annular interactions across four-membered rings have been postulated in Ti(III) dithiophosphinate complexes[12,45] and supported by extended Hückel MO calculations.[45] Single-crystal EPR experiments and MO calculations are underway to clarify the nature of the coupling mechanism in 5.

Summary. The preparative route described herein demonstrates that use of a metalloligand such as 3 can provide a facile method for the synthesis of heterobi-

metallic complexes. The present report shows that such metalloligands can accommodate late metals in pseudo-square planar environments. Characterization of the reduced and oxidized forms of the Rh–Ti species 4 suggests the possibility of metal–metal interactions in these heterobimetallics. The reactivity and chemistry of these and related species are the subject of ongoing research and will be reported in due course.

Registry No. 3, 109863-51-6; 4, 109863-53-8; 5, 109863-54-9; 6, 109863-55-0; Cp_2TiCl_2, 1271-19-8; [(NBE)$_2$Rh]BF$_4$, 36620-11-8; Cp$_2$Co, 1277-43-6; HSCH$_2$CH$_2$CH$_2$Cl, 17481-19-5; Ph$_2$PH, 829-85-6.

Supplementary Material Available: Tables of thermal parameters, hydrogen atom parameters, and bond distances and angles associated with the cyclopentadienyl rings, the BF$_4$ anion, and the acetone of crystallization (9 pages); listings of 10|F_o| and 10|F_c| (21 pages). Ordering information is given on any current masthead page.

(45) Lorenz, D. R.; Wasson, J. R. *J. Inorg. Nucl. Chem.* **1975**, *37*, 2265.

Asymmetric Induction in the Nucleophilic Cyclopropane Ring Cleavage Reaction with Vitamin B$_{12s}$

Hisanobu Ogoshi,* Yasuaki Kikuchi, Taro Yamaguchi, Hiroo Toi, and Yasuhiro Aoyama*

Department of Materials Science and Technology, Technological University of Nagaoka, Kamitomioka, Nagaoka, Niigata 940-21, Japan

Vitamin B$_{12s}$ reacts with cyclopropane derivatives having electron-withdrawing substituents such as acetyl, methoxycarbonyl, and cyano groups to give 3-substituted propyl–cobalt complexes. The alkylation with prochiral 1-acetyl-1-alkylcyclopropanes results in an asymmetric induction (ee 24–33%) at carbon 3 in the resulting alkyl ligands. Examination of the ^{1}H NMR spectra of the alkylation products indicates that (1) two prochiral methyl groups in 3,3-diacetylpropyl– and 3,3-bis(methoxycarbonyl)propyl–cobalt complexes are rendered diastereotopic by the presence of the chiral B$_{12}$ and are observed to be spectroscopically nonequivalent and (2) enantiomeric methyl groups in 3-acetyl-3-alkylpropyl– and 3-acetyl-3-(methoxycarbonyl)propyl–cobalt complexes having an asymmetric center at carbon 3 are also rendered diastereotopic and spectroscopically distinguishable in a similar manner.

Introduction

An interest in vitamin B$_{12}$ from the viewpoint of synthetic organic chemistry lies in its potentiality as a naturally occurring, chiral catalyst in asymmetric organic synthesis. Scheffold et al. have recently shown that vitamin B$_{12}$ can be used as a catalyst for C–C bond formation processes.[1] Fischli et al. also found that B$_{12}$ catalyzes enantioselective reduction of α,β-unsaturated carbonyl compounds.[2] Both catalytic reactions involve alkyl-cobalt complexes as the key intermediates. The most common procedure for preparing organometallic B$_{12}$ derivatives utilizes the "supernucleophilicity" of the Co(I) species or B$_{12s}$ toward alkylating agents such as alkyl halides and

Michael olefins.[3] In order to achieve a high degree of enantioselectivity, the conformational flexibility of alkylating agent should be minimized at the transition state of alkylation. These considerations, coupled with our previous finding on the facile cyclopropane ring cleavage by anionic Rh(I) porphyrin complexes,[4] prompted us to investigate the hitherto unknown reaction of B$_{12s}$ with cyclopropane derivatives.[5] We report here that cyclopropanes having electron-withdrawing groups readily react with B$_{12s}$ to give 3-substituted propyl–cobalt complexes and that the alkylation with prochiral cyclopropane de-

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