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Synthesis, Electrochemistry, Reactivity, and Structural Studies of the Early/Late-Transition-Metal Heterobimetallic Complex [$Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2Ni$]

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The metalloligand $Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2$ (1) reacts with $(COD)_2Ni$ to yield the heterobimetallic complex [$Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2Ni$] (5) in which 1 acts as a tetradentate ligand. The "inside" complex 5 crystallizes in the space group $P2_1/c$ with a = 15.993 (3) Å, b = 8.957 (2) Å, c = 24.794 (4) Å, β = 94.19 (2)°, and Z = 4. The structural study confirms that 1 provides a pseudotetrahedral S_2P_2 coordination sphere for the Ni(0) center. Distortion of the geometry about the TiS_2Ni core, as well as the Ti···Ni distance of 2.852 (3) Å, is consistent with a $d^{10} \rightarrow d^0$, Ni(0)→Ti(IV) dative interaction. Complex 5 can be converted to an "outside" complex, where 1 acts in a bidentate fashion, by reaction with carbon monoxide. The resulting macrocyclic complex $Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2Ni(CO)_2$ (6) crystallizes as $6 \cdot 0.5C_6H_6$ in the space group $P\bar{1}$ with a = 12.450 (4) Å, b = 19.741 (7) Å, c = 13.763 (5) Å, α = 76.81 (3)°, β = 138.24 (2)°, γ = 109.77 (3)°, and Z = 2. The Ti···Ni separation in this species is 6.889 Å. Compound 5 exhibits two, one-electron, electrochemically reversible oxidations to yield the formally Ni(I) and Ni(II) analogues 7 and 8, respectively. Attempts to prepare 8 by reaction of 1 with $[Ni(CH_3CN)_6][BF_4]_2 \cdot 0.5CH_3CN$ led to the formation of $[Ni_3(SCH_2CH_2CH_2PPh_2)_4][BF_4]_2$ (9). Similarly, chemical or electrochemical oxidation of 5 led to the formation of 9. Compound 9 is a linear, centrosymmetric nickel trimer that crystallizes in the space group $P2_1/n$ with a = 18.709 (5) Å, b = 16.422 (6) Å, c = 10.586 (3) Å, β = 104.05 (2)°, and Z = 2. The terminal nickel atoms are coordinated to two sulfur and two phosphorus atoms. The four sulfur atoms also bind to the central nickel yielding a NiS_4 coordination sphere. Although the oxidation product of 5 could not be isolated, the related Ti(IV)–Pd(II) heterobimetallic complex 10 can be prepared by reaction of 1 with $[Pd(CH_3CN)_4][BF_4]_2$. The chemistry of these heterobimetalic species are discussed in the light of the structural and spectroscopic data.

Introduction

Recently, interest has focused on heterobimetallic complexes that contain both early, electron-deficient and late, electron-rich metal centers.[1-40] The potential of such systems to promote activation of a substrate molecule by the two constituent metals is the basic reason for interest in such species. Lewis acid type interactions of early metals with the oxygen of a substrate bound to a later metal atom has been demonstrated by Casey and others.[1,2,10,15,19] In addition to potential applications in catalysis, interest in heterobimetallics also arises because of the phenomenon of "strong metal-support interactions" (SMSI) that occurs in heterogeneous catalysis.[41] SMSI have been observed for catalysts in which late transition metals are deposited on early-transition-metal supports. For example, SMSI have been observed for methanation catalysts derived from Ni deposited on TiO_2.[42,43] Although

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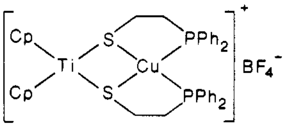
such SMSI are not well-understood, the enhanced catalytic activity of these heterobimetallic systems has been attributed to these interactions.

In our attempts to develop related chemistry involving early transition metal/late transition metal heterobimetallic complexes, our research focused initially on the establishment of convenient synthetic routes to such species. We have previously described several systems in which the functionalized early-transition-metal complexes $Cp_2Ti(S(CH_2)_nPPh_2)_2$ (n = 2, 3),[35,37,38] $Cp_2Ti(SEt)_2$,[36,38] and $Cp_2M(PR_2)_2$[32-34,40] (M = Zr, Hf; R = Ph, Cy) act as metalloligands to bind later transition-metal atoms. Complexes **2–4** exhibit novel electrochemical and/or structural features that are attributed to the proximity of the early and late transition metals. Dative interactions between the electron-rich and electron-deficient metal centers of these heterobimetallic complexes have been proposed on the basis of chemical, structural and theoretical data.[32-40]



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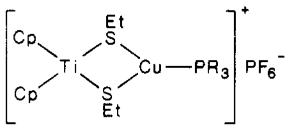

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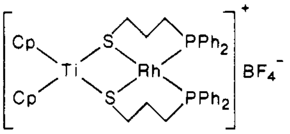

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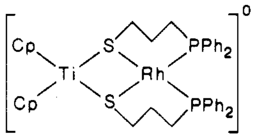

4b

In this paper, we extend the chemistry of these types of heterobimetallics and describe the synthesis and characterization of $[Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2Ni]$ (**5**). Reaction of **5** with CO yields $Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2Ni(CO)_2$ (**6**). **5** exhibits two, one-electron, electrochemically reversible oxidations implying the formation of $[Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2Ni][BF_4]$ (**7**) and $[Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2Ni][BF_4]_2$ (**8**). Attempts to prepare the Ni(II) complex by direct chemical or electrochemical syntheses led to the formation of $[Ni_3(SCH_2CH_2CH_2PPh_2)_4][BF_4]_2$ (**9**). Although the oxidation product of **5** could not be isolated, the Ti(IV)–Pd(II) complex $[Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2Pd][BF_4]_2$ (**10**), which is isoelectronic to **8**, was obtained. Crystallographic data for complexes **5**, **6**, and **9** are presented. The chemistry of these heterobimetallic systems is discussed in the light of the structural data.

Experimental Section

All preparations were done under an atmosphere of dry, O_2-free N_2. Solvents were reagent grade, were distilled from the appropriate drying agents under N_2, and were degassed by the freeze–thaw method at least three times prior to use. ^1H NMR spectra were recorded on a Bruker AC-300 spectrometer, using the trace of protonated solvent as the reference. The chemical shifts are reported in parts per million (ppm) relative to $Si(CH_3)_4$ for the ^1H NMR data. $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AC-200 spectrometer. ^{31}P 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 voltammograph employing a platinum disk electrode and $[Bu_4N]PF_6$ or $[Bu_4N]BF_4$ as the supporting electrolyte. A Ag/AgCl electrode was used as the reference electrode; however, potentials are reported versus the SCE. Combustion analyses were performed by Galbraith Laboratories Inc., Knoxville, TN. $Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2$ (**1**) was prepared as previously reported.[37] $[Ni(CH_3CN)_6][BF_4]_2\cdot0.5CH_3CN$, $[Pd(CH_3CN)_4][BF_4]_2$, and $[Cp_2Fe]BF_4$ were prepared by literature methods.[44-46] $(COD)_2Ni$ was purchased from the Strem Chemical Co.

Preparation of $[Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2Ni]$ (5). To a 40-mL THF solution containing 300 mg (0.43 mmol) of **1** was added 120 mg (0.43 mmol) of $(COD)_2Ni$. The initially dark purple solution became dark green-black after a few minutes. The mixture was stirred for 2 h. The volume of solvent was reduced to 5 mL, and a dark green-black solid precipitated upon slow addition of 50 mL of hexane. The solid was isolated by filtration to yield 225 mg (70%) of **5**: ^1H NMR (C_3D_6O) δ 7.2 (br m, 20 H(Ph)), 6.27 (s, 10 H(Cp)), 2.3 (br m, 12 H(6CH_2)); $^{31}P\{^1H\}$ NMR (C_6H_6) δ 6.4 (s); UV–vis (C_6H_6; λ, nm (ϵ, M^{-1} cm^{-1})) 555 (1400), 443 (7200), 400 (7250), 290 (20 600). Anal. Calcd for $C_{40}H_{42}NiP_2S_2Ti$: C, 63.67; H, 5.60. Found: C, 60.32; H, 5.93.[47]

Preparation of $Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2Ni(CO)_2$ (6). To 60-mL benzene solution containing 600 mg (0.86 mmol) of **1** was added 237 mg (0.86 mmol) of $(COD)_2Ni$, generating complex **5**. After the solution was stirred for 2 h, carbon monoxide was bubbled through the solution for 20 min. The solution gradually changed color from green-black to purple. Evaporation of the solvent, followed by trituration with three 10-mL portions of hexane, yielded a crude solid product. Recrystallization from benzene/hexane yielded 480 mg (70%) of microcrystalline **6**$\cdot0.5C_6H_6$: mp 148–160 °C dec; ^1H NMR (C_3D_6O) δ 7.3 (m, 20 H(Ph)), 6.2 (s, 10 H(Cp)), 3.3 (m, 4 H(2CH_2)), 2.5 (br m, 8 H(4CH_2)); $^{31}P\{^1H\}$ NMR (C_6H_6) δ 25.1 (s); IR (KBr, cm^{-1}) ν_{CO} 1995, 1936; UV–vis (CH_3CN; λ, nm (ϵ, M^{-1} cm^{-1})) 530 (4000), 372 (3550), 245 (40 500). Anal. Calcd for $C_{45}H_{45}NiO_2P_2S_2Ti$: C, 63.55; H, 5.33; S, 7.54. Found: C, 64.62; H, 5.20; S, 7.92.[47]

Preparation of $[Ni_3(SCH_2CH_2CH_2PPh_2)_4][BF_4]_2$ (9). A 10-mL, dark blue acetonitrile solution containing 100 mg (0.20 mmol) of $[Ni(CH_3CN)_6][BF_4]_2\cdot0.5CH_3CN$ was added dropwise to a purple suspension of 140 mg (0.20 mmol) of **1** in 10 mL of acetonitrile. The reaction mixture turned dark brown after a few minutes. The solution was stirred for 4 h. Addition of diethyl ether caused precipitation of a dark brown powder that was recrystallized from acetonitrile/diethyl ether yielding 70 mg (75%): mp 215–230 °C dec; ^1H NMR (C_3D_6O) δ 7.5 (m, 40 H(Ph)), 2.6 (br m, 24 H(12CH_2)); $^{31}P\{^1H\}$ NMR (CH_3CN) δ 12.3 (s). Anal. Calcd for $C_{60}H_{64}B_2F_8Ni_3P_4S_4$: C, 51.96; H, 4.65; S, 9.24. Found: C, 51.72; H, 4.94; S, 9.14.

Preparation of $[Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2Pd][BF_4]_2$ (10). A 10-mL, yellow acetonitrile solution of 142 mg (0.32 mmol) of $[Pd(NCCH_3)_4][BF_4]_2$ was added dropwise to a purple suspension of 222 mg (0.32 mmol) of **1** in 20 mL of acetonitrile. In minutes the mixture became a bright orange solution which was stirred overnight. Addition of diethyl ether resulted in the precipitation of a yellow-orange powder which, upon recrystallization from acetonitrile/diethyl ether, yielded 120 mg (39%) of the pale orange compound: mp 275–280 °C dec; ^1H NMR (CD_3CN) δ 7.5 (m, 20 H(Ph)), 6.40 (s, 10 H(Cp)), 3.32 (m, 4 H(2CH_2)), 2.66 (m, 4 H(2CH_2)), 2.36 (m, 4 H(2CH_2)); $^{31}P\{^1H\}$ NMR (CH_3CN) δ 13.2 (s); UV–vis (CH_3CN; λ, nm (ϵ, M^{-1} cm^{-1})) 456 (4380), 360 (4800). Anal. Calcd for $C_{40}H_{42}B_2F_8PdP_2S_2Ti$: C, 49.19; H, 4.33; S, 6.56. Found: C, 48.02; H, 4.53; S, 6.48.[47]

X-ray Data Collection and Reduction. Dark green-black crystals of **5** were obtained by vapor diffusion of pentane into a benzene solution of **5**. Purple crystals of **6**$\cdot0.5C_6H_6$ were obtained by vapor diffusion of hexane into a benzene solution of **6**. Brown crystals of **9** were obtained by diffusion of diethyl ether into an acetonitrile solution of **9**. Diffraction experiments were performed on a four-circle Syntex $P2_1$ diffractometer with graphite-monochromatized Mo Kα radiation. The initial orientation matrix for each compound was obtained from 15 machine-centered reflections

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Table I. Crystallographic Parameters

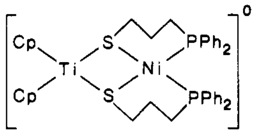
	5	$6 \cdot 0.5C_6H_6$	9
formula	$C_{40}H_{42}NiP_2S_2Ti$	$C_{45}H_{45}NiO_2P_2S_2Ti$	$C_{60}H_{64}B_2F_8Ni_3P_4S_4$
cryst color, form	green-black blocks	purple plates	brown blocks
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a (Å)	15.993 (3)	12.450 (4)	18.709 (5)
b (Å)	8.957 (2)	19.741 (7)	16.422 (6)
c (Å)	24.794 (4)	13.763 (5)	10.586 (3)
α (deg)		76.81	
β (deg)	94.19 (2)	138.24 (2)	104.05 (2)
γ (deg)		109.77 (3)	
V (Å^3)	3542 (1)	2118 (1)	3155 (2)
D (g cm^{-3})	1.42	1.33	1.46
Z	4	2	2
cryst dimens (mm)	0.31 × 0.23 × 0.23	0.62 × 0.35 × 0.11	0.13 × 0.23 × 0.42
abs coeff μ (cm^{-1})	9.27	7.82	11.10
radiatn γ (Å)	Mo Kα (0.71069)	Mo Kα (0.71069)	Mo Kα (0.71069)
temp (°C)	24	24	24
scan speed (deg/min)	2.0–5.0	2.0–5.0	2.0–5.0
scan range (deg)	1.0 below Kα_1 1.0 above Kα_2	1.0 below Kα_1 1.0 above Kα_2	1.0 below Kα_1 1.0 above Kα_2
bdgd/scan time ratio	0.5	0.5	0.5
unique data	3797	5888	4613
data $F_o^2 > 3\sigma(R_o^2)$	1501	3147	1520
no. of variables	237	316 (2 blocks)	194
R (%)	5.75	4.74	6.97
R_w (%)	5.49	5.01	7.09
max Δ/σ in final cycle	0.002	0.002	0.001
largest residual electron	0.43	0.52	0.64
atom associated with residual density	C34	C15	F3

selected from rotation photographs. These data were used to determine the crystal systems. Partial rotation photographs around each axis were consistent with monoclinic crystal systems for **5** and **9** and with a triclinic crystal system for $\mathbf{6}\cdot 0.5C_6H_6$. Ultimately, 30 high-angle reflections (22° < 2θ < 25°) were used to obtain the final lattice parameters and the orientation matrix for **5**, while for $\mathbf{6}\cdot 0.5C_6H_6$ and **9**, 25 such reflections were used. Machine parameters, crystal data, and data collection parameters are summarized in Table I. The observed extinctions were consistent with the space groups $P2_1/c$ for **5**, $P\bar{1}$ for $\mathbf{6}\cdot 0.5C_6H_6$, and $P2_1/n$ for **9**. For **5**, $\pm h,+k,+l$ data were collected in one shell (4.5° < 2θ < 40°). In the case of $\mathbf{6}\cdot 0.5C_6H_6$, $\pm h,\pm k,+l$ data were collected for 4.5° < 2θ < 40.0° while for **9**, $\pm h,+k,+l$ data were collected over the range 4.5° < 2θ < 45.0°. During each data collection three standard reflections were recorded every 197 reflections. For **5**, the intensities of the standards showed a gradual 17% decay over the course of data collection. Thus, corrections based on this decay in intensity were applied to the data. For $\mathbf{6}\cdot 0.5C_6H_6$ and **9** the intensities of the standards showed no statistically significant change over the duration of the data collections. The data were processed by using the SHELX-76 program package on the computing facilities at the University of Windsor. A total of 1501 reflections for **5**, 3147 reflections for $\mathbf{6}\cdot 0.5C_6H_6$, and 1520 reflections for **9** with $F_o^2 > 3\sigma R_o^2$ were used in the respective refinements. In each case the absorption coefficients are small and thus no absorption correction was applied to the data.

Structure Solutions and Refinements. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[48,49] For **5** and $\mathbf{6}\cdot 0.5C_6H_6$, the Ti and Ni atom positions were determined by using direct methods. For **9**, the Ni atom positions were determined via the heavy-atom (Patterson) method. In all cases, the remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were 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. Final cycles of refinement were performed by using full-matrix refinements methods for compounds **5** and **9**, while for $\mathbf{6}\cdot 0.5C_6H_6$ it was necessary to employ a block diagonal refinement. In the final cycles of the refinements, the metal atoms, S, P, O, F, and cyclopentadienyl, alkyl, and carbonyl C atoms were assigned anisotropic temperature factors. A small degree of disordering of the alkyl chain conformation was apparent in the case of **5**. This disorder was best modeled by assigning C52 and C55 isotropic temperature factors. The carbon atoms of all phenyl rings, as well as the B atom of the anion of **9**, were described by isotropic thermal parameters. The phenyl ring geometries were constrained to that of regular hexagons with C–C bond lengths of 1.395 Å. The B–F distances of the BF_4 anions of **9** were constrained to be 1.320 (5) Å. 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. 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. The final values of $R = \sum||F_o| - |F_c|/\sum|F_o||$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$ are given in Table I. The maximum Δ/σ on any of the parameters in the final cycles of the refinements and the locations of the largest peaks in the final difference Fourier map calculations are also given in Table I. The residual electron densities were of no chemical significance. The following data are tabulated: positional parameters (Table II); selected bond distances and angles (Table III). Thermal parameters (Table S1), hydrogen atom parameters (Table S2), bond distances and angles associated with the cyclopentadienyl rings and BF_4 anion (Table S3), and values of $10|F_o|$ and $10|F_c|$ (Table S4) have been deposited as supplementary material.

Results and Discussion

The reaction of **1** with $(COD)_2Ni$ in THF results in the formation of the Ti–Ni heterobimetallic complex **5**. This



5

green-black species is stable only in the strict absence of O_2 and H_2O. The ^1H NMR spectrum of **5** show resonances

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Table II. Positional Parameters[a]

atom	x	y	z	atom	x	y	z
Molecule 5							
Ni	2341 (1)	4884 (2)	3766 (1)	Ti	1047 (2)	3149 (3)	4166 (1)
S1	2344 (3)	2441 (5)	3735 (2)	S2	1258 (2)	5889 (5)	4110 (2)
P1	3446 (3)	5455 (5)	4320 (2)	P2	2275 (3)	5730 (5)	2925 (2)
C1	1603 (22)	1574 (31)	4865 (8)	C2	738 (21)	1653 (32)	4917 (9)
C3	538 (15)	3104 (38)	5059 (8)	C4	1323 (21)	3881 (25)	5098 (7)
C5	1943 (15)	2933 (33)	4984 (8)	C6	585 (13)	1920 (33)	3326 (10)
C7	321 (14)	3396 (28)	3277 (9)	C8	−258 (12)	3648 (29)	3665 (9)
C9	−365 (13)	2301 (36)	3951 (9)	C10	183 (16)	1283 (25)	3739 (12)
C11	4315 (6)	6717 (9)	4135 (4)	C12	4740 (6)	6267 (9)	3691 (4)
C13	5438 (6)	7067 (9)	3546 (4)	C14	5710 (6)	8317 (9)	3845 (4)
C15	5285 (6)	8767 (9)	4289 (4)	C16	4587 (6)	7967 (9)	4434 (4)
C21	3226 (6)	6249 (11)	4991 (3)	C22	2743 (6)	7547 (11)	4977 (3)
C23	2550 (6)	8226 (11)	5459 (3)	C24	2841 (6)	7607 (11)	5954 (3)
C25	3324 (6)	6309 (11)	5967 (3)	C26	3516 (6)	5630 (11)	5486 (3)
C31	2148 (6)	4386 (12)	2358 (3)	C32	2535 (6)	2996 (12)	2427 (3)
C33	2467 (6)	1947 (12)	2010 (3)	C34	2013 (6)	2289 (12)	1524 (3)
C35	1627 (6)	3679 (12)	1455 (3)	C36	1694 (6)	4727 (12)	1871 (3)
C41	3144 (6)	6915 (9)	2711 (4)	C42	3692 (6)	6410 (9)	2338 (4)
C43	4350 (6)	7318 (9)	2196 (4)	C44	4460 (6)	8731 (9)	2427 (4)
C45	3912 (6)	9236 (9)	2799 (4)	C46	3254 (6)	8328 (9)	2941 (4)
C51	3269 (10)	1587 (16)	4127 (6)	C52	4065 (11)	2529 (19)	4104 (7)
C53	4110 (8)	3782 (15)	4521 (6)	C54	593 (10)	6959 (18)	3632 (7)
C55	1049 (11)	7840 (20)	3226 (7)	C56	1363 (10)	6990 (18)	2754 (6)
Molecule 6·0.5C_6H_6							
Ni	9009 (1)	7296 (0)	504 (1)	Ti	8450 (2)	8324 (1)	−5445 (1)
S1	7736 (2)	7146 (1)	−4827 (2)	S2	8861 (2)	8938 (1)	−3843 (2)
P1	9091 (2)	6310 (1)	68 (2)	P2	6754 (2)	7711 (1)	−1297 (2)
O1	8959 (11)	6783 (5)	2632 (8)	O2	11913 (9)	8330 (4)	1330 (10)
C1	6807 (12)	8944 (5)	−7643 (9)	C2	5986 (12)	8761 (5)	−7261 (9)
C3	5437 (10)	8021 (5)	−7349 (9)	C4	5946 (11)	7746 (4)	−7772 (8)
C5	6770 (12)	8312 (5)	−7981 (8)	C6	10943 (12)	7984 (5)	−4063 (14)
C7	11391 (11)	8556 (6)	−3284 (10)	C8	11092 (10)	9162 (4)	−4160 (11)
C9	10502 (12)	8970 (5)	−5393 (11)	C10	10356 (13)	8243 (5)	−5387 (13)
C11	7281 (5)	5516 (2)	−882 (4)	C12	6065 (5)	5493 (2)	−986 (4)
C13	4654 (5)	4911 (2)	−1710 (4)	C14	4458 (5)	4351 (2)	−2329 (4)
C15	5673 (5)	4373 (2)	−2225 (4)	C16	7084 (5)	4955 (2)	−1502 (4)
C21	10776 (5)	5955 (2)	1836 (4)	C22	12376 (5)	6421 (2)	2763 (4)
C23	13705 (5)	6202 (2)	4139 (4)	C24	13434 (5)	5517 (2)	4588 (4)
C25	11834 (5)	5051 (2)	3661 (4)	C26	10505 (5)	5270 (2)	2286 (4)
C31	6936 (4)	8553 (2)	−750 (5)	C32	8529 (4)	9012 (2)	295 (5)
C33	8732 (4)	9667 (2)	702 (5)	C34	7342 (4)	9862 (2)	64 (5)
C35	5749 (4)	9403 (2)	−980 (5)	C36	5546 (4)	8749 (2)	−1388 (5)
C41	4781 (5)	7118 (2)	−1975 (4)	C42	3474 (5)	6798 (2)	−3377 (4)
C43	2073 (5)	6295 (2)	−3799 (4)	C44	1980 (5)	6111 (2)	−2820 (4)
C45	3287 (5)	6431 (2)	−1418 (4)	C46	4688 (5)	6934 (2)	−995 (4)
C51	9321 (9)	7011 (4)	−2874 (7)	C52	8515 (8)	6628 (4)	−2377 (7)
C53	9769 (8)	6417 (4)	−786 (7)	C54	7045 (9)	8564 (4)	−4187 (8)
C55	7547 (9)	8463 (3)	−2776 (8)	C56	6148 (8)	7973 (3)	−2990 (7)
C61	9032 (12)	7017 (5)	1828 (9)	C62	10748 (11)	7938 (5)	999 (11)
C71	5651 (13)	330 (5)	4487 (11)	C72	6580 (11)	472 (5)	5902 (10)
C73	5911 (13)	119 (6)	6416 (10)				
Molecule 9							
Ni1	0 (0)	0 (0)	0 (0)	Ni2	8600 (1)	608 (1)	986 (2)
S1	9815 (2)	758 (3)	1619 (4)	S2	8957 (2)	−521 (3)	162 (5)
P1	8429 (2)	1693 (3)	2117 (5)	P2	7431 (3)	275 (3)	193 (5)
F1	5871 (6)	−1316 (7)	7545 (10)	F2	5082 (7)	−1987 (10)	6021 (14)
F3	6240 (7)	−2155 (9)	6210 (12)	F4	5687 (11)	−1051 (10)	5455 (15)
C11	8691 (6)	1425 (7)	3838 (11)	C12	8844 (6)	616 (7)	4209 (11)
C13	9107 (6)	419 (7)	5522 (11)	C14	9217 (6)	1031 (7)	6464 (11)
C15	9063 (6)	1840 (7)	6093 (11)	C16	8801 (6)	2037 (7)	4780 (11)
C21	7538 (7)	2219 (8)	1868 (12)	C22	7306 (7)	2677 (8)	733 (12)
C23	6647 (7)	3113 (8)	510 (12)	C24	6219 (7)	3089 (8)	1421 (12)
C25	6451 (7)	2630 (8)	2556 (12)	C26	7111 (7)	2195 (8)	2779 (12)
C31	6806 (6)	333 (7)	1264 (13)	C32	6999 (6)	−103 (7)	2428 (13)
C33	6520 (6)	−128 (7)	3253 (13)	C34	5848 (6)	283 (7)	2912 (13)
C35	5655 (6)	719 (7)	1748 (13)	C36	6134 (6)	744 (7)	924 (13)
C41	7057 (6)	809 (6)	−1318 (12)	C42	6371 (6)	586 (6)	−2094 (12)
C43	6115 (6)	934 (6)	−3323 (12)	C44	6546 (6)	1504 (6)	−3776 (12)
C45	7233 (6)	1727 (6)	−3000 (12)	C46	7488 (6)	1380 (6)	−1771 (12)
C51	10049 (10)	1797 (11)	1326 (21)	C52	9830 (10)	2384 (11)	2308 (22)
C53	9006 (9)	2565 (11)	1965 (17)	C54	8364 (10)	−608 (13)	−1487 (18)
C55	7642 (11)	−1042 (13)	−1466 (22)	C56	7337 (10)	−808 (12)	−255 (20)
B	5733 (7)	−1623 (8)	6353 (11)				

[a] Multiplied by 10^4.

Table III. Selected Bond Distances and Angles

Molecule 5							
Distances (Å)							
Ti···Ni 2.825 (3)							
Ti–S1	2.484 (5)	Ni–P1	2.217 (5)	Ti–CO9	2.41 (2)	Ti–C10	2.37 (2)
Ti–S2	2.483 (5)	Ni–P2	2.213 (4)	S1–C51	1.87 (1)	S2–C54	1.81 (2)
Ni–S1	2.189 (5)	Ni–S2	2.182 (4)	C51–C52	1.53 (2)	C54–C55	1.51 (2)
Ti–CO1	2.36 (2)	Ti–CO2	2.38 (2)	C52–C53	1.53 (2)	C55–C56	1.51 (2)
Ti–CO3	2.41 (2)	Ti–CO4	2.41 (2)	P1–C53	1.88 (1)	C2–C56	1.87 (1)
Ti–CO5	2.40 (2)	Ti–CO6	2.42 (2)	P1–C11	1.87 (1)	P2–C31	1.85 (1)
Ti–CO7	2.43 (2)	Ti–CO8	2.39 (2)	P1–C21	1.87 (1)	P2–C41	1.86 (1)
Angles (deg)							
S1–Ti–S2	96.2 (2)	P1–Ni–P2	119.1 (2)	Ni–P1–C11	124.0 (3)	C53–P1–C11	97.5 (6)
S1–Ni–P1	104.4 (2)	S1–Ni–P2	108.0 (2)	Ni–P1–C21	116.5 (3)	C53–P1–C21	101.9 (5)
S2–Ni–P1	106.4 (2)	S2–Ni–P2	104.0 (2)	Ni–P1–C53	112.9 (5)	C56–P2–C31	100.4 (6)
Ti–S1–C51	122.3 (5)	Ti–S2–C54	119.0 (6)	Ni–P2–C31	119.2 (4)	C56–P2–C41	100.3 (6)
S1–C51–C52	113 (1)	S2–C54–C55	115 (1)	Ni–P2–C41	118.7 (3)	C11–P1–C21	100.3 (4)
S51–C52–C53	112 (1)	C54–C55–C56	117 (2)	Ni–P2–C56	113.8 (5)	C31–P2–C41	101.3 (4)
C52–C53–P1	114 (1)	C55–C56–P2	115 (1)				
Molecule **6**·0.5C_6H_6							
Distances (Å)							
Ti–S1	2.398 (2)	Ni–P1	2.218 (3)	Ti–C7	2.388 (7)	C52–C53	1.527 (9)
Ti–S2	2.389 (4)	Ni–P2	2.224 (2)	Ti–C8	2.379 (9)	S2–C54	1.82 (1)
Ti–Cl	2.368 (8)	Ni–C61	1.76 (2)	Ti–C9	2.39 (2)	C54–C55	1.52 (2)
Ti–C2	2.40 (1)	Ni–C62	1.76 (1)	Ti–C10	2.37 (2)	C55–C56	1.51 (1)
Ti–C3	2.414 (9)	C61–O1	1.16 (2)	P1–C53	1.84 (1)	P2–C56	1.83 (1)
Ti–C4	2.376 (7)	C62–O2	1.15 (2)	P1–C11	1.843 (4)	P2–C31	1.855 (6)
Ti–C5	2.38 (1)	S1–C51	1.818 (7)	P1–C21	1.848 (4)	P2–C41	1.846 (6)
Ti–C6	2.39 (1)	C51–C52	1.52 (2)				
Angles (deg)							
Si–Ti–S2	94.3 (1)	P1–Ni–P2	118.5 (1)	C52–C53–P1	113.7 (7)	Ni–C62–O2	177 (1)
Ti–S1–C51	112.6 (2)	P1–Ni–C61	102.4 (4)	C55–C56–P2	114.7 (4)	Ni–P1–C11	120.3 (3)
Ti–S2–C54	108.2 (3)	P2–Ni–C61	105.7 (4)	C53–P1–C11	105.1 (3)	Ni–P1–C21	108.4 (2)
S1–C51–C52	110.6 (5)	P1–Ni–C62	102.3 (5)	C53–P1–C21	99.7 (3)	Ni–P1–C53	117.6 (2)
S2–C54–C55	111.5 (5)	P2–Ni–C62	109.2 (3)	C56–P2–C31	101.2 (3)	Ni–P2–C31	112.4 (1)
C51–C52–C53	112.9 (7)	C61–Ni–C62	119.4 (5)	C56–P2–C41	102.4 (3)	Ni–P2–C41	116.1 (2)
C54–C55–C56	112.2 (5)	Ni–C61–O1	174.5 (8)	C11–P1–C21	102.9 (2)	Ni–P2–C56	119.6 (4)
				C31–P2–C41	102.7 (3)		
Molecule 9							
Distances (Å)							
Ni1···Ni2	3.206 (2)	Ni1–S1	2.213 (5)	P1–C11	1.82 (1)	P2–C56	1.84 (2)
Ni1–S2	2.175 (5)	Ni2–S1	2.222 (5)	P1–C21	1.84 (1)	P2–C31	1.82 (1)
Ni2–S2	2.221 (5)	Ni2–P1	2.212 (5)	P2–C41	1.81 (1)	C51–C5	1.55 (2)
Ni2–P2	2.212 (5)	S1–C51	1.81 (2)	C54–C55	1.53 (3)	C52–C5	1.53 (2)
S2–C54	1.83 (2)	P1–C53	1.82 (2)	C55–C56	1.57 (3)		
Angles (deg)							
S1–Ni1–S2	81.2 (2)	S1–Ni2–S2	80.0 (2)	Ni2–P2–C31	118.4 (5)	C56–P2–C31	100.1 (8)
S1–Ni2–P1	91.1 (2)	S2–Ni2–P1	169.1 (2)	Ni2–P2–C41	110.5 (4)	C56–P2–C41	104.4 (8)
S1–Ni2–P2	170.5 (2)	S2–Ni2–P2	90.5 (2)	C31–P2–C41	110.9 (5)	S1–C51–C52	111 (1)
P1–Ni2–P2	98.3 (2)	Ni1–S1–Ni2	92.6 (2)	C51–C52–C53	112 (2)	P1–C53–C52	114 (1)
Ni1–S1–C51	107.9 (6)	Ni2–S1–C51	109.0 (7)	S2–C54–C55	111 (2)	C54–C55–C56	113 (2)
Ni1–S2–Ni2	93.7 (2)	Ni1–S2–C54	107.6 (7)	P2–C56–C55	115 (1)	P1–C11–C12	119.9 (4)
Ni2–S2–C54	105.6 (7)	Ni2–P1–C53	114.7 (6)	P1–C11–C16	119.9 (4)	P1–C21–C22	117.3 (4)
Ni2–P1–C11	107.9 (4)	C53–P1–C11	104.8 (7)	P1–C21–C26	122.7 (4)	P2–C31–C32	117.2 (4)
Ni2–P1–C21	123.1 (5)	C53–P1–C21	98.9 (7)	P2–C31–C36	122.7 (4)	P2–C41–C42	119.8 (3)
C11–P1–C21	105.8 (5)	Ni2–P2–C56	111.2 (6)	P2–C41C46	119.9 (3)		

attributable to the Cp and phosphino thiolate ligands. Chemical equivalence of the Cp rings on Ti is implied by the single proton resonance (at 6.27 ppm). Unlike the related complexes **3** and **4**, the Cp resonances of **5** do not show a temperature dependence. This is consistent with a relatively rigid molecular geometry in solution. The position of the single resonance observed in the $^{31}P\{^1H\}$ NMR spectrum of **5** (at 6.4 ppm) is consistent with coordination of phosphorus to Ni(0). The features of the UV-vis spectrum of **5** are similar to those seen for the isoelectronic complex **2**.[35] Thus, on the basis of the spectral data, as well as combustion analyses, the structure of **5** was assigned that of an "inside" heterobimetallic in which **1** acts as a tetradentate metalloligand providing a S_2P_2 coordination sphere for the Ni(0) center. This geometry was later confirmed by an X-ray crystallographic study.

An X-ray crystallographic study of **5** revealed that the geometries of the Ti and Ni coordination spheres are both pseudotetrahedral (Figure 1). Two π-bonded cyclopentadienyl rings and two sulfur atoms comprise the Ti coordination sphere. The Ti–C and Ti–S distances are typical.[35,36,40] The Ni coordination sphere contains the two bridging sulfur atoms and two phosphorus atoms. The Ni–S distances are 2.189 (5) and 2.182 (4) Å. Few Ni(0)–S bond distances are reported in the literature; however, these values are similar to those reported for the dication $[(Cp_2Nb(\mu\text{-SEt})_2)_2Ni]^{2+}$.[50] The Ni–P distances that av-

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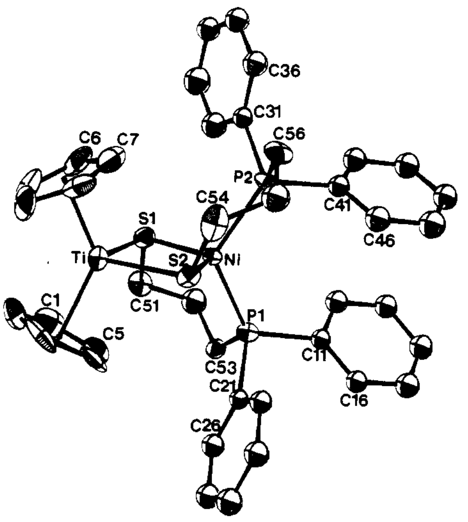


Figure 1. ORTEP drawing of **5** (30% thermal ellipsoids are shown; hydrogen atoms are omitted for clarity).

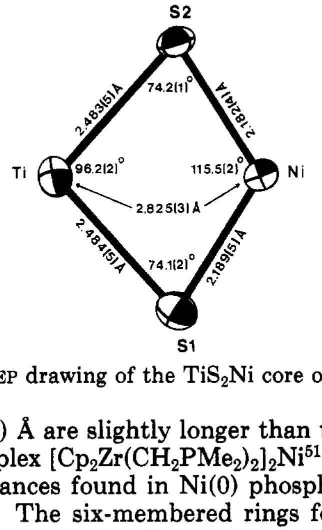


Figure 2. ORTEP drawing of the TiS_2Ni core of **5**.

erage 2.215 (5) Å are slightly longer than those seen for the Ni(0) complex $[Cp_2Zr(CH_2PMe_2)_2]_2Ni$[51] but similar to the Ni–P distances found in Ni(0) phosphine/carbonyl complexes.[52] The six-membered rings formed by the phosphino thiolate on Ni adopt a pseudochair conformation with the alkyl substituents on two sulfur atoms in a *transoid* disposition with respect to each other. The overall geometry is very reminiscent of that of the isoelectronic cation of **2**.[35]

The four atoms of the TiS_2Ni core are coplanar. The structural details of the core are illustrated in Figure 2. Comparison of the isoelectronic species **5** and **2** shows that the Ti–S–M angles are some 4° smaller in **5**. The S–Ti–S angles differ only slightly (96.2 (2)° in **5** versus 97.5 (1)° in **2**) but is substantially greater than those found in $Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2$,[37] Cp_2TiS_5,[53] $Cp^*{}_2Ti(SH)_2$,[54] $Cp_2Ti(S_2C_2H_2)$,[55] or $Cp_2Ti(S_2C_6H_4)$.[56] The angle at Ni, i.e., the S–Ni–S angle of **5**, is dramatically larger than the S–Cu–S of **2** (115.5 (2)° versus 106.4 (1)°, respectively). The Ti···Ni distance of 2.825 (2) Å is much shorter than the Ti···Cu of 3.024 (1) Å in **2**.[35] This Ti···Ni separation is also much shorter than the Ti···Rh separation (3.127 (1) Å) found in **4a**.[37] These data support the notion of a d^{10}→d^{0}, Ni(0)→Ti(IV), dative interaction similar to those we have previously described for related early/late heterobimetallic systems.

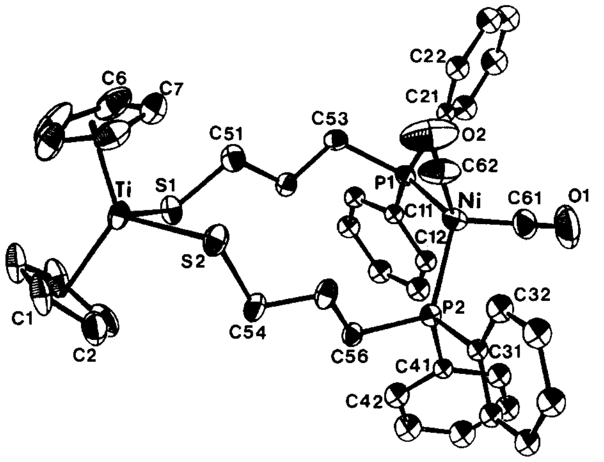
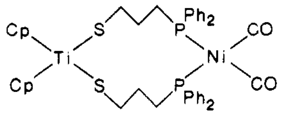


Figure 3. ORTEP drawing of **6** (30% thermal ellipsoids are shown; hydrogen atoms are omitted for clarity).

The shorter Ti–M separation in the d^{10}–d^{0} species **5**, compared to that seen in the d^{8}–d^{0} complex **4a**,[37] is consistent with a strengthening of the dative interaction. This is due to an increase in the number of valence electrons on the late metal, and thus the greater donor ability. Compounds **2** and **5** are isoelectronic d^{10}–d^{0} systems. The longer Ti–M distance in **2** is attributed to the presence of a formal 1+ charge on the Cu(I) center. This decreases the Lewis basicity of the Cu relative to that of the Ni(0) center in **5** in which there is no formal charge. This difference accounts for the greater distortions of the angles at S and Ni, as well as the closer approach of the Ni to the Ti atom in **5**. Thus, these results imply that the strength of the dative interactions between the metals in such heterobimetallic systems follows simple Lewis acid/base principles.

Preliminary molecular orbital calculations[38] have been performed on appropriate models of these thiolate-bridged, early/late heterobimetallic systems. The results suggest that the dative interaction between the metals has a σ component which corresponds to overlap of the d_{z^2} orbitals of the two metals along the metal–metal vector. In addition, there appears to be a π component of the dative interaction corresponding to overlap of the d_{yz} orbitals of the metals. The precise nature of the interaction is the subject of ongoing work and will be reported in detail in due course.



6

Complex **5** reacts with carbon monoxide in THF to yield the purple compound **6**. The ^1H NMR spectrum of **6** shows resonances attributable only to the presence of the metalloligand **1**. The $^{31}P\{^1H\}$ NMR spectrum of **6** consists of a single resonance at 25.1 ppm. The position of this resonance is consistent with the presence of a stronger π acceptor ligand on Ni. The IR spectrum of **6** exhibits two strong absorptions at 1995 and 1936 cm^{-1}. These are attributable to CO bound to Ni(0). The visible spectrum of **6** is markedly similar to that of **1**.[38] This suggests that **6** contains a Cp_2TiS_2 moiety that is unperturbed by the

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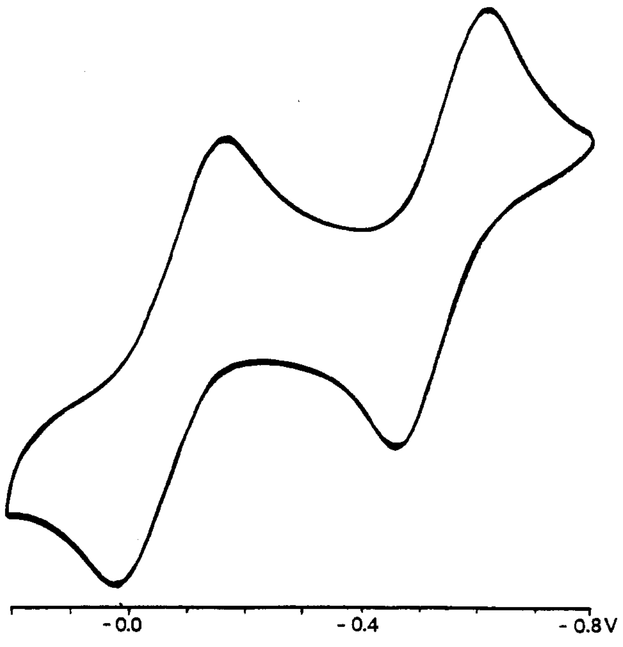
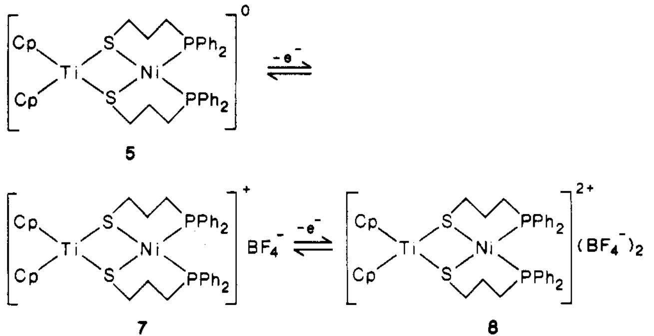


Figure 4. Cyclic voltammogram of 5 in THF using a Pt electrode and $[Bu_4N]PF_6$ as the supporting electrolyte. Potentials shown are vs. SCE.

presence of the Ni. On the basis of these data and elemental analyses, the proposed structure of 6 was that of an "outside" heterobimetallic in which 1 acts in a bidentate fashion generating a macrocyclic structure that contains both a Cp_2TiS_2 and a $P_2Ni(CO)_2$ fragment. This proposition was confirmed by X-ray crystallography.

The crystallographic study of $6{\cdot}0.5C_6H_6$ showed that the coordination spheres about both the Ti and Ni atoms are pseudotetrahedral (Figure 3). The coordination sphere of the Ti in 6, like 5, contains two π-bonded cyclopentadienyl groups and two sulfur atoms. Ti–C and Ti–S distances are typical.[35,36,40] The Ni is bonded to two phosphorus atoms and two CO groups. The Ni–P and Ni–C distances, as well as the geometry about the Ni, are typical of Ni(0) complexes of the form $(R_3P)_2Ni(CO)_2$.[52] The Ti···Ni separation is 6.889 Å, which is substantially longer than the Zr···Ni distance of 4.049 Å found in $Cp^*Zr(OCH_2PPh_2)_3Ni(CO)$.[18] The 12-membered ring formed by the Ti, Ni, and the two phosphino thiolate ligands adopts a "crown-type" conformation in which the alkyl chains bound to the S atoms and to the P atoms are disposed in transoid orientations.

Compound 5 was studied by cyclic voltammetry in THF by using a Pt disk electrode. Reversible waves were seen at −0.06 and −0.51 V versus SCE when $[Bu_4N]PF_6$ was used as the supporting electrolyte. Changing the electrolyte to $[Bu_4N]BF_4$ resulted in a slight, cathodic shift of the waves by about 100 mV. Changes such as these in the redox potentials are known and have been attributed to differences in the strength of the ion pairing with the ions of the supporting electrolyte and changes in the solvation of the ion pairs.[57] The peak separations for the two waves were 160 and 220 mV which suggests that the redox processes being observed are pseudoreversible, one-electron transfers. The two waves maintained their reversible character despite variation of the scan speed from 5 to 600 mV/s. The potentials at which these one-electron transfer processes take place suggest that they can be formally assigned to the stepwise oxidations of the Ni(0) of 5 to Ni(I) and Ni(II) (eq 1).[58] Similar redox chemistry was mentioned briefly in a footnote of a paper by Rigo describing the monometallic complex $Ni(CH_3CH_2SCH_2CH_2PPh_2)_2$; however, the electrochemical data were not reported.[59]



5

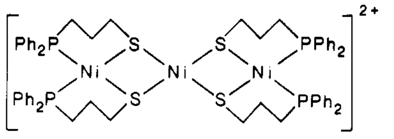
7

8

(1)

The preparation of 8 was attempted by several methods. A direct synthesis of 8 from 1 and $[Ni(CH_3CN)_6]BF_4{\cdot}0.5CH_3CN$ was attempted, as was the chemical oxidation of 5 by $[Cp_2Fe]BF_4$ and electrochemical oxidation of 5 at a Pt electrode in a CV cell. In all cases the compound isolated was not 8 but rather a complex in which Ni was the only constituent metal. The fate of the titanocene moiety in this degradation has not been determined. The apparently poor thermodynamic stability of 8 may arise from the increase in Lewis acidity of Ni upon oxidation to Ni(II) resulting in a substantial weakening of the Ti–S bonds.

The product isolated from the oxidation reactions has a ^1H NMR spectrum that shows resonances attributable only to the protons of the phosphino thiolate ligand. The $^{31}P\{^1H\}$ NMR spectrum of 9 contains a singlet at 12.3 ppm. On the basis of these data and elemental analyses, 9 was formulated as a trinuclear Ni(II) species. This was confirmed by X-ray diffraction experiments.



9

The X-ray crystallographic study of 9 showed the coordination spheres of the nickel atoms to be pseudo square planar. The central nickel atom, which sits on the center of symmetry for the cation, is coordinated to four sulfur atoms (Figure 5). The Ni–S distances are typical for Ni(II)–S bonds.[60–62] The sulfur atoms form bridges to Ni2 and Ni2′ which are centrosymmetrically positioned on either side of Ni1. The coordination spheres of the Ni2 atoms are comprised of two sulfur and two phosphorus atoms. The average Ni–S distance for Ni1–S is 2.194 (5) Å, while the average Ni2–S distance is 2.222 (5) Å. This is in contrast to other sulfur-bridged nickel trimers[60–62] where the Ni1–S distances are longer than the Ni2–S bond lengths. This anomaly may be a result of the trans in-

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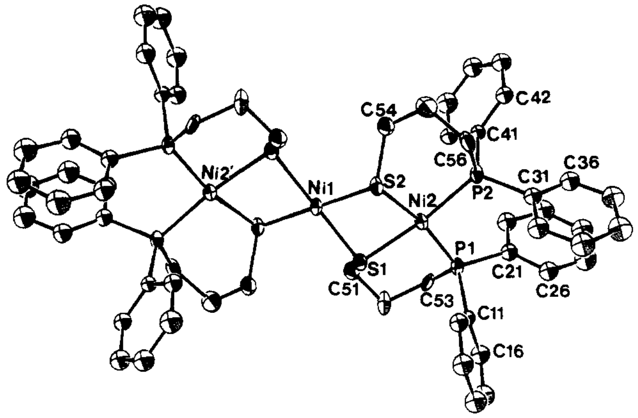
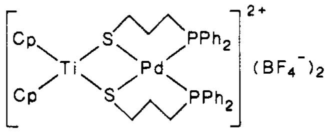


Figure 5. ORTEP drawing of the cation of **9** (30% thermal ellipsoids are shown; hydrogen atoms are omitted for clarity).

fluence of the phosphine ligation to Ni2. The Ni–P bond lengths average 2.212 (5) Å. The bite angles at Ni2 formed by the phosphino thiolate groups are typical of six-membered chelate rings. The Ni···Ni distance of 3.206 (2) Å is substantially larger than those previously reported for $[Ni(Ni(H_2NCH_2CH_2CH_2S)_2)_2]^{2+}$ (2.733 (7) Å),[60] $[Ni(Acac)_2]_3$ (2.882 and 2.896 Å),[61] $[Ni(Ni(O_2CCH(CH_3)CH_2S)_2)_2]^{2-}$ (2.783 Å),[63] and $[(NiSCH_2CH_2S)_3]^{2-}$ (2.856 Å).[63] This difference is attributable to the flexibility of the three carbon alkyl chains in the phosphino thiolate ligands.

The coordination planes about the Ni atoms form a "chair" conformation where the plane about Ni2 and its symmetry-related partner are parallel and are linked by the coordination plane of Ni1. The angle between the NiP_2S_2 (Ni2) plane and the NiS_4 (Ni1) plane is 35.4°. This geometry is similar to that reported for $[Ni(Ni(SCH_2CH_2CH_2NH_2)_2)_2]^{2+}$ and $[Ni(Ni(O_2CCH(CH_3)CH_2S)_2)_2]^{2-}$ where the corresponding angles between the coordination planes are 71°[60] and 65°,[62] respectively.

It is clear that the oxidation product of **5** (i.e., **8**) is not a stable heterobimetallic species; however, a complex that is isoelectronic with **8** can be isolated. Reaction of $[Pd(CH_3CN)_4][BF_4]_2$ with **1** yielded a yellow-orange compound. The ^1H NMR of this material showed resonances attributable to Cp and phosphino thiolate protons. The $^{31}P\{^1H\}$ NMR showed a resonance at 13.2 ppm, consistent with coordination of phosphorus to palladium. These data as well as the combustion analyses are consistent with the formulation of the compound as the heterobimetallic **10**. Presumably, it is the softer nature of Pd that accounts for the greater stability of the Ti(IV)–Pd(II) complex over the isoelectronic Ti(IV)–Ni(II) species.



10

Summary

The Ti–Ni heterobimetallics presented here further illustrate the viability of a synthetic strategy in which functionalized early-transition-metal complexes can be used as metalloligands for the synthesis of such mixed-metal species. Furthermore, these compounds demonstrate that the proximity of the two metals in such species can be controlled. Compounds in which metal–metal interactions occur, such as those observed in the "inside" complex **5**, or compounds with discrete, yet linked, metal centers, such as in the "outside" complex **6**, are possible. The effect of metal atom proximity and metal–metal interactions as well as metal atom oxidation states on the reaction chemistry of these heterobimetallics is the subject of current investigations.

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Registry No. **1**, 109863-51-6; **5**, 112841-04-0; **6**, 112841-02-8; **6**·$0.5C_6H_6$, 112841-03-9; **9**, 112840-99-0; **10**, 112841-01-7; $(COD)_2Ni$, 1295-35-8; $[Ni(CH_3CN)_6[BF_4]_2$, 15170-11-3; $[Pd(NCCH_3)_4][BF_4]_2$, 21797-13-7.

Supplementary Material Available: Thermal parameters (Table S1), hydrogen atom parameters (Table S2), and bond distances and angles associated with the cyclopentadienyl rings or BF_4 anion (Table S3) (11 pages); values of $10|F_o|$ and $10|F_c|$ (Table S4) (25 pages). Ordering information is given on any current masthead page.

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