Organometallic Chemistry of Sulfur/Phosphorus Donor Ligand Complexes of Nickel(II) and Nickel(0)

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The X-ray crystal structures and electrochemical properties as well as chemical reactivity of the thioether complexes $[Ni(Ph_2PCH_2CH_2SEt)_2][BF_4]_2$ (**5**) and $[Ni(Ph_2PCH_2CH_2SCH_2CH_2CH_2SCH_2CH_2PPh_2)][BF_4]_2$ (**6**), $[Ni(PSSP)]^{2+}$, are compared with the thiolate $Ni(Ph_2PCH_2CH_2S)_2$ (**4**). Complex **4** crystallized in the orthorhombic space group *Pbca* (No. 61) with a = 9.204(2) Å, b = 15.766(3) Å, c = 17.177(3) Å, V = 2492.6(8) Å^3, Z = 4, and final R = 0.050 (R_w = 0.050) for 2212 unique reflections. Complex **5** crystallized in the monoclinic space group $P2_1/c$, with a = 10.267(2) Å, b = 13.102(2) Å, c = 13.263(2) Å, β = 93.750(10)°, V = 1780.3(5) Å^3, Z = 2, and final R = 0.076 (R_w = 0.072) for 1777 unique reflections. The square-planar structures of **4** and **5** have sulfur donors in a trans arrangement and show a 0.04-Å lengthening of *both* the Ni—S and Ni—P bonds on going from the thiolate to the thioether complex. Within the CH_3CN solvent window, the cyclic voltammograms of **5** and **6** show two reversible redox events assigned to $Ni^{II/I}$ and $Ni^{I/0}$, whereas the thiolate **4** shows only a sulfur-based irreversible oxidation and no reduction. Complexes **5** and **6** can be chemically reduced to Ni^0 species, **5**^{R} and **6**^{R}, with Na/Hg amalgam. The ^1H NMR spectra of the reduced complexes indicate loss of one thioether donor for **5**^{R} and both for **6**^{R}. Protonation of the reduced species produced a Ni—H and reaction with both CH_3I or $CH_3C({=}O)Cl$ gave rise to $Ni{-}CH_3$ and $NiC(O)CH_3$ functionalities, respectively. The tetradentate derivatives $[HNi(PSSP)]^+$ and $[CH_3Ni(PSSP)]^+$ are more stable than their bidentate analogues and show loss of reversible redox activity; i.e., the cyclic voltammograms find no evidence for stable $Ni^I{-}H$ or $Ni^I{-}CH_3$, or for $Ni^{III}{-}H$ or $Ni^{III}{-}CH_3$ species. The $NiC(O)CH_3$ compounds rapidly and reversibly decarbonylate in solution (at temperatures >-30 °C). A contrast of the abilities of structurally analogous P—SR vs N—SR ligands to stabilize subvalent nickel and organonickel functionalities is made.

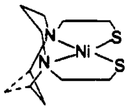
Introduction

Three of the known nickel-containing enzymes catalyze reactions in nature that can be rationalized on the basis of organometallic-type intermediates containing Ni—H or Ni—C (C = CO, CH_3, or $C({=}O)CH_3$) bonds.[1] Nevertheless, molecular model complexes designed to contain the mixed hard (nitrogen or oxygen)/soft (sulfur) donor atom coordination environment of nickel in the native enzymes have proven successful to support stable Ni—C or Ni—H functionalities in only one case, a Ni^{II} complex of a tetradentate, tripod, $N{-}(SR)_3$ ligand.[2] In that example, the synthesis used anion metathesis at Ni^{II}, eq 1, rather than the typical organometallic approach of reduction to Ni^0 followed by oxidative addition, eq 2.

$$Ni^{II}X + R^- \text{ (or } H^-) \rightarrow X^- + Ni^{II}R \text{ (or } Ni^{II}H) \quad (1)$$

$$Ni^{II} + 2e^- \rightarrow Ni^0 \overset{HX \text{ or } RX}{\rightarrow} X^- + Ni^{II}R \text{ (or } Ni^{II}H) \quad (2)$$

The limited access to Ni^0 in a nitrogen/sulfur donor environment is further affirmed by our work with $N_2S_2Ni^{II}$ complexes of the *N,N'*-bis(mercaptoethyl)-1,5-diazacyclooctane ligand and alkylated derivatives: (BME-DACO)Ni^{II} (**1**), [*N,N'*-bis(3-thiabutyl)-1,5-diazacyclooctane]nickel(II) iodide, $[(BTB\text{-}DACO)Ni^{II}][I]_2$ (**2**), and [4,8-dithia-1,11-diazabicyclo[9.3.3]heptadecane]nickel(II) bromide, $[Ni(bicycle)]Br_2$ (**3**).[3,4] Crystal structures of all find an N_2S_2 square plane with cis sulfur and nitrogen donor atoms. Close ion pair interactions with halide anions generate a quasi-square-pyramidal structure of **3** in the solid state; however large counterions or good anion solvating solvents render **3** square planar. Although we have not been able to generate the Ni^0 oxidation state in the N-S complexes, Ni^I complexes are obtained upon reducing **2** or **3** with cobaltocene or metallic zinc.[5] Such metastable complexes are unreactive with alkylating agents but react with acids to produce hydrogen gas. Whether hydrogen production involves an outer-sphere electron transfer or an inner-sphere Ni-H intermediate remains to be determined.



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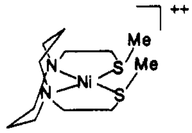

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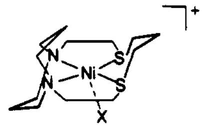

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Similar square-planar phosphino thiolate and thioether chelated nickel(II) complexes, $(Ph_2PCH_2CH_2S)_2Ni^{II}$ (**4**),

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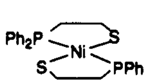
$[(Ph_2PCH_2CH_2SEt)_2Ni]^{2+}$ (dication of **5**), and $[(Ph_2PCH_2CH_2SCH_2CH_2CH_2SCH_2CH_2PPh_2)Ni]^{2+}$, $[(PSSP)Ni]^{2+}$ (dication of **6**), have been reported.[6-8] Complex **6** has been characterized by X-ray crystallography and is an analogue of **3** with iodide or bromide ions set in the apical position of a square pyramid at 2.638(4) and 2.645(4) Å, respectively.[8] The former is within the average of known Ni–I distances (2.71 Å), whereas the latter is beyond that of known Ni–Br distances (2.41 Å).[9] The molecular structures of **4** and **5** were reported as trans isomers;[6,7] however those configurations were not established by crystallography until now (vide infra).



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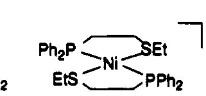

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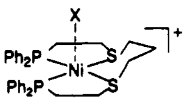

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In contrast to the N_2S_2Ni complexes **2** and **3**, complex **5** was shown by cyclic voltammetry to have two reversible redox events, assigned to $Ni^{II/I}$ and $Ni^{I/0}$.[10] Bulk chemical reduction to Ni^0 followed by addition of acid produced Ni^{II}–H, convincingly characterized as $[HNi(Ph_2PCH_2CH_2SEt)_2]^+$ by IR and NMR spectroscopies as well as its ability to act as an olefin isomerization catalyst.[7]

An understanding of the disparate abilities of phosphorus versus nitrogen donors to stabilize Ni^0 and organometallic functionalities is clearly of importance in further development of the reaction chemistry of "biological" nickel. In this paper we report the molecular structures of **4** and of **5** as a BF_4^- salt. The P—S series (**4–6**) is compared with the N—S series (**1–3**) with respect to electrochemical properties. The chemically reduced complexes $\mathbf{5^R}$ and $\mathbf{6^R}$ have been shown to react with CH_3I and $CH_3C(=O)Cl$, and the resultant Ni—CH_3 and Ni—$C(=O)CH_3$ products were examined with respect to CO migratory insertion/deinsertion reactivity.

Experimental Section

Materials and Methods. All manipulations were performed using standard Schlenk techniques or in an argon atmosphere glovebox. Reagents were obtained from vendors and used as received. Dichloromethane was distilled over phosphorus pentoxide under nitrogen. Acetone was dried using NaI or dried over molecular sieves (4 Å). Acetonitrile was distilled once from CaH_2, once from P_2O_5, and freshly distilled from CaH_2 immediately before use. Toluene, benzene, tetrahydrofuran, diethyl ether, and hexane were distilled from sodium benzophenone ketyl under nitrogen. Infrared spectra were recorded on a Mattson Galaxy 6021 or an IBM IR/32 using 0.1-mm NaCl cells or KBr pellets. ^1H and ^{31}P NMR spectra were obtained on an XL200 Varian spectrometer; all ^{31}P NMR spectra were referenced to external H_3PO_4. Cyclic voltammograms were recorded on a BAS-100A electrochemical analyzer using $AgNO_3$ reference electrodes and Pt^0 or glassy carbon working electrodes with 0.1 M $[n\text{-}Bu_4N][PF_6]$ as electrolyte. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. The ligands, $Ph_2PCH_2CH_2SH$,[11] $Ph_2PCH_2CH_2SEt$,[12] and $Ph_2P(CH_2)_2S(CH_2)_3S(CH_2)_2PPh_2$[13] were prepared as described in the literature with little modification, as was the complex $[Ni(Ph_2PCH_2CH_2SEt)_2][BF_4]_2$.[7]

$Ph_2P(CH_2)_2S(CH_2)_3S(CH_2)_2PPh_2$. The following modification of the reported preparation was used.[13] A 2.46-g (10-mmol) portion of $Ph_2PCH_2CH_2SH$ was dissolved in 50 mL of THF and added dropwise to 0.24 g (10 mmol) of NaH powder in a flask vented to a safety Nujol bubbler for H_2 release. The mixture was stirred for 30 min following which 0.51 mL (5 mmol) of $BrCH_2CH_2CH_2Br$ was added via syringe. This cloudy mixture was refluxed overnight. The solvent was then removed in vacuo to yield a white viscous oil. The oil was extracted into CH_2Cl_2 and filtered through Celite to remove traces of NaBr. Upon removal of solvent, 2.40 g (90% yield) was obtained. ^1H NMR ($CDCl_3$): δ 7–8 (m, C_6H_5, 20 H), 2.6 (m, $CH_2SCH_2CH_2P$, 8 H), 2.3 (m, SCH_2CH_2P, 4 H), 1.8 (q, $SCH_2CH_2CH_2S$, 2 H).

$(Ph_2PCH_2CH_2S)_2Ni^{II}$ (4). Previously synthesized using $Ni(NO_3)_2\cdot6H_2O$ as source of nickel,[6] method A below is preferable. The more expensive method B gives yields equally high.

Method A. The $Ph_2PCH_2CH_2SH$ ligand (4.92 g, 20 mmol) was added to a solution of $Ni(acac)_2$ (2.57 g, 10 mmol) in toluene (40 mL) with immediate precipitation of a green crystalline solid. The isolated solid was washed with 50 mL of toluene and 50 mL of diethyl ether and dried in vacuo. Recrystallization from CH_2Cl_2/hexane or CH_2Cl_2/Et_2O gave 4.90 g (90% yield). Anal. Calcd (found) for $Ni(P_2S_2C_{28}H_{28})$: C, 61.2 (60.2); H, 5.13 (5.10). ^1H NMR ($CDCl_3$): δ 7.59, 7.21 (m, C_6H_5, 20 H), 2.51 (m, SCH_2, 4 H), 2.15 (m, PCH_2, 4 H).

Method B. The $Ph_2PCH_2CH_2SH$ ligand (0.98 g, 4 mmol) was added to a 30-mL toluene solution of $Ni(COD)_2$ (0.53 g, 2 mmol) cooled to 0 °C. The color of the solution changed from yellow to red-brown and finally gave green needles on standing. The crystalline solid was washed with 30 mL of toluene/diethyl ether and dried in vacuo to give 0.97 g (88% yield) of **4**.

$[(Ph_2PCH_2CH_2SCH_2CH_2CH_2SCH_2CH_2PPh_2)Ni^{II}][BF_4]_2$ or $[Ni(PSSP)][BF_4]_2$ (6). The PSSP ligand (1.68 g, 3.2 mmol) was dissolved in 10 mL of CH_2Cl_2 and added to an 80-mL solution of $Ni(BF_4)_2\cdot6H_2O$ (1.07 g, 3 mmol) in 2-propanol, previously brought to reflux. The color of the solution changed from green to purple, and a yellow precipitate formed as the mixture was refluxed for 30 min. After cooling to room temperature, the precipitate was isolated, washed with 20 mL of 2-propanol followed by 20 mL of Et_2O, and dried in vacuo. The solid was then washed with 3 × 10 mL of dry acetone and dried in vacuo to yield 2.06 g (75%). This method of preparation of the tetradentate nickel complex is superior to that resulting from the reaction of **4** with $BrCH_2CH_2CH_2Br$ described below. ^1H NMR (CD_3CN): δ 7.59, 7.40 (m, C_6H_5, 20 H), 3.41 (m, $SCH_2CH_2CH_2S$, 4 H), 3.10 (br, PCH_2CH_2S, 4 H), 2.81 (br, PCH_2CH_2S, 4 H), 2.53 (br, $SCH_2CH_2CH_2S$, 2 H).

Reactions of 4 with Organic Halides. The procedure described in detail for CH_3CH_2I was modified only slightly for $BrCH_2CH_2CH_2Br$.

CH_3CH_2I. An excess of iodoethane (0.25 mL, 4 mmol) was added to 50 mL of a CH_2Cl_2 solution containing 0.55 g (1 mmol) of **4**. The solution gradually changed color from green to purple on stirring for 5 h. The solvent was removed in vacuo, and the purple solid was washed with hexane. Recrystallization from acetone/Et_2O gave 0.65 g (75% yield) of **5** with mp (with dec) = 125 °C. Anal. Calcd (found) for $NiP_2S_2C_{32}H_{38}I_2$: C, 44.6 (44.6); H, 4.45 (4.40).

$BrCH_2CH_2CH_2Br$. Reaction of 0.55 g (1 mmol) of **4** with 0.30 mL (3 mmol) of $BrCH_2CH_2CH_2Br$ utilizing the above procedure allowed isolation of 0.11 g of a red-brown powder (15% yield). Mp: 290 °C dec. Anal. Calcd (found) for $NiP_2S_2C_{31}H_{34}Br_2$: C, 49.6 (48.9); H, 4.56 (4.23).

Reduction of 5 and 6 as BF_4^- Salts. Under argon, a Na/Hg amalgam (0.043 g Na, 2 mmol, in 2 mL of Hg) was transferred into a suspension of $[Ni(PSSP)][BF_4]_2$ (0.77 g, 1 mmol) in 50 mL of benzene and stirred vigorously until the nickel complex was taken up (approximately 1 h), resulting in a color change from

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yellow to red. The solution, designated 6^R, was filtered through thoroughly degassed Celite to remove $NaBF_4$, a green impurity, and the amalgam; it was used immediately. The $[Ni(Ph_2PCH_2CH_2SEt)_2][BF_4]_2$ salt, compound **5**, was similarly reduced, yielding a deep red solution, designated 5^R. The reduction can likewise be performed in CH_3CN for both **5** and **6**. ^1H NMR spectra (supplementary material) were obtained following reduction of the complexes in either benzene-d_6 or CD_3CN immediately before insertion of the sample into the spectrometer.

Reactions of Reduced Nickel Species. 5^R + CH_3I. At 0 °C, 30 mL of a diethyl ether solution containing 1.2 equiv (0.074 mL) of methyl iodide was added dropwise to the freshly prepared 5^R (0.78 g, 1 mmol) in benzene. The color of the solution changed to orange-red. After stirring for 30 min, an ethanol solution containing 0.34 g (1 mmol) of $NaBPh_4$ was added, immediately forming an orange-red precipitate. This solid was filtered, washed with 10 mL of ethanol and 30 mL of diethyl ether, and dried. Recrystallization from dry acetone and ether gave 0.66 g (70% yield) of orange-red crystalline $[(CH_3)Ni(Ph_2PCH_2CH_2SEt)_2][BPh_4]$ (**7**). Anal. Calcd (found) for $NiP_2S_2C_{57}H_{61}B$: C, 72.7 (71.6); H, 6.53 (6.33). Mp: 87 °C dec. ^1H NMR (acetone-d_6): δ 7.8, 6.7 (m, C_6H_5, 20 H), 2.95 (s, br, PCH_2CH_2S, 8 H), 2.16 (q, SCH_2CH_3, 4 H), 0.95 (t, CH_3, 6 H), −0.3 (s, br, Ni-CH_3, 3 H).

6^R + CH_3I. At 0 °C, 30 mL of a diethyl ether solution of iodomethane (1.2 mmol, 0.074 mL) was added dropwise to the freshly prepared red benzene solution of 6^R (0.76 g, 1 mmol). Orange-red crystals were immediately formed as the supernatant changed to colorless. The product was filtered off, washed with diethyl ether, and dried in vacuo. The orange-red solid was dissolved in ethanol and treated with $NaBPh_4$ (0.34 g, 1 mmol). After 30 min of stirring, the solvent was removed in vacuo and the solid was washed with 2 mL of ethanol and triturated with 30 mL of diethyl ether. Upon drying, an orange-red solid, $[(CH_3)Ni(PSSP)][BPh_4]$ (**8**), was obtained in 70% yield, mp 93 °C dec. Anal. Calcd (found) for $NiP_2S_2C_{56}H_{57}B$: C, 72.7 (72.8); H, 6.21 (6.40). ^1H NMR (acetone-d_6): δ 7.4, 6.8 (m, C_6H_5, 20 H), 2.75 (s, PCH_2CH_2S, 8 H), 2.44 (m, SCH_2, 4 H), 1.8 (m, $SCH_2CH_2CH_2S$, 2 H), −0.41 (t, Ni-CH_3, 3 H).

6^R + $HBF_4 \cdot Et_2O$. The procedure was the same as the reaction described above, substituting 1 equiv of $HBF_4 \cdot Et_2O$ acid in 40 mL of a diethyl ether solution for the iodomethane. Recrystallization from acetone/ether yielded 0.43 g (63%) of an orange-red powder, **9**. Anal. Calcd (found) for $Ni(P_2S_2C_{31}H_{35})BF_4$: C, 54.8 (54.4); H, 5.19 (5.37). Mp: 190 °C. IR (Nujol): ν_{Ni-H} = 1929 cm^{-1}. ^1H NMR (acetone-d_6): δ 8.5, 7.5 (m, C_6H_5, 20 H), 3.6 (m, PCH_2, 4 H), 3.1, 3.12 (m, CH_2SCH_2, 8 H), 2.1 (m, $SCH_2CH_2CH_2S$, 2 H), −17.6 (t, Ni-*H*, J_{P-H} = 48 Hz).

Preparation of $[CH_3C(O)Ni(Ph_2PCH_2CH_2SEt)_2][BPh_4]$ (10) and $[CH_3C(O)Ni(PSSP)][BPh_4]$ (11). Method A. In a typical preparation, 10 mL of the red solutions of 5^R or 6^R obtained from the reduction of 1 mmol of the nickel complexes in THF were treated with 1.5 equiv (0.11 mL) of acetyl chloride at −30 °C. The color of the solution changed to orange-red. After stirring for 30 min, 5 mL of an ethanol solution of $NaBPh_4$ (0.34 g, 1 mmol) was added and the mixture was further stirred for 20 min. Addition of 50 mL of diethyl ether gave a precipitate which was isolated cold and washed with diethyl ether. Attempts to recrystallize the products led to decomposition. IR (KBr, cm^{-1}): ν(CO) 1652 (**10**), 1665 (**11**).

Method B. These two complexes were also prepared by bubbling carbon monoxide through THF or dry acetone solutions of complexes **7** and **8** at −60 °C. The color of the solution changed from red to orange. After 50 min of CO sparging, 30 mL of diethyl ether was added to precipitate an orange-red powder which was filtered at low temperatures. A KBr pellet was made of the cold solid. If the reaction with CO was carried out at temperatures >−30 °C, ν(CO) bands at 1900 and 1836 cm^{-1} (THF) indicated the production of a nickel dicarbonyl species analogous to the known $P_2Ni(CO)_2$ complexes.[14]

Table I. Experimental Data for the X-ray Crystal Structures of $Ni(Ph_2PCH_2CH_2S)_2$ (4) and $[Ni(Ph_2PCH_2CH_2SEt)_2][BF_4]_2$ (5)

complex	4	5
chem formula	$C_{28}H_{28}P_2S_2Ni$	$C_{32}H_{38}B_2F_8P_2S_2Ni$
fw	549.3	781
space group	orthorhombic *Pbca*	monoclinic $P2_1/n$
a (Å)	9.204(2)	10.267(2)
b (Å)	15.766(3)	13.102(2)
c (Å)	17.177(3)	13.263(2)
β (deg)		93.750(10)
V (Å^3)	2492.6(8)	1780.3(5)
Z	4	2
ρ (calc, g/cm^3)	1.464	1.457
temp (°C)	23	23
radiation	Mo Kα (λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)
abs coeff (mm^{-1})	1.084	0.811
min/max trans coeff	0.8700/1.0000	0.9253/0.9703
R (%)[a]	5.04	7.6
R_w (%)[a]	5.01	7.2

[a] Residuals: $R = \sum|F_o - F_c|/\sum F_o$; $wR = \{[\sum w(F_o-F_c)^2]/[\sum w(F_o)^2]\}^{1/2}$.

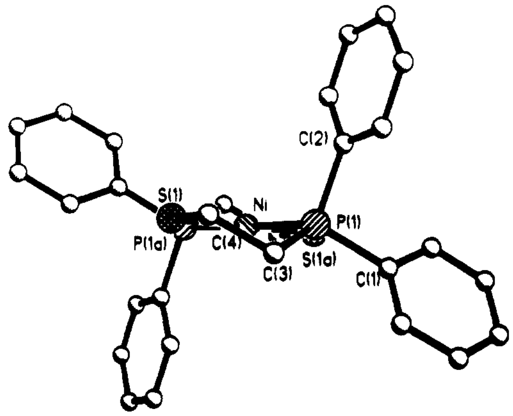

Figure 1. Molecular structure of $Ni(Ph_2PCH_2CH_2S)_2$ (4).

X-ray Structure Determinations of $Ni(Ph_2PCH_2CH_2S)_2$ (4) and $[Ni(Ph_2PCH_2CH_2SEt)_2][BF_4]_2$ (5). Crystals of **4** and **5** were grown at ambient temperature; **4** was crystallized from CH_2Cl_2/Et_2O, and **5**, from acetone/Et_2O. Preliminary examination and data collection for **4** were performed on a Rigaku RFC% rotating anode X-ray diffractometer with an oriented graphite monochromator; for **5**, a Nicolet R3m/V X-ray diffractometer equipped with an oriented graphite monochromator was used. Both instruments used Mo Kα radiation (λ = 0.710 73 Å). The structures were solved by direct methods and refined using a full-matrix least-squares anisotropic refinement for all non-hydrogen atoms. The hydrogen atoms were placed in idealized positions. Summaries of the X-ray crystallographic experimental data are given in Table I.

In both **4** and **5**, the nickel was found to partially fill its site in the asymmetric units of the crystallographic unit cells. For both compounds the site occupation for Ni was fixed on the special position to 50%. This model, corrected for variable site occupation, was used to refine the structures to convergence. In **5**, the fluorines in the BF_4^- anion were refined to 54% occupation for one counterion and 46% in the other.

Results and Discussion

Structures of $Ni(Ph_2PCH_2CH_2S)_2$ (4) and $[Ni(Ph_2PCH_2CH_2SEt)_2][BF_4]_2$ (5). Drawings of the molecular structures of **4** and the cation of **5** are given in Figures 1 and 2, respectively. Selected bond distances and angles for **4** and **5** are compared in Table II. In both structures, the nickel is found in strict square-planar geometry with the two phosphorus and two sulfur donor atoms trans to each other, as was expected by Marty et al.[6] The ∠S–Ni–P of **4** within the chelate is 87.6(1)°, slightly smaller than the ∠S–Ni–P between ligands of 92.4(1)°. The Ni–S

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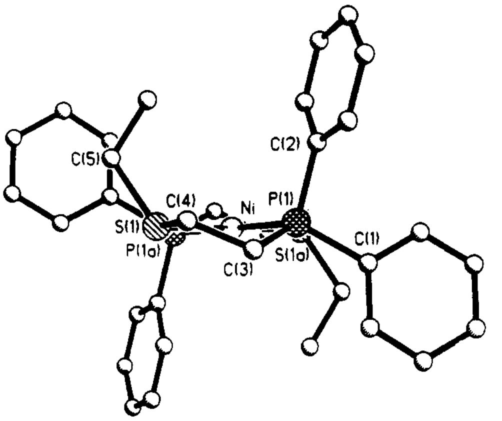

Figure 2. Molecular structure of the dication $[Ni(Ph_2P(CH_2)_2SEt)_2][BF_4]_2$ (5).

Table II. Selected Bond Distances (Å) and Angles (deg) for $Ni(Ph_2PCH_2CH_2S)_2$ (4) and $[Ni(Ph_2PCH_2CH_2SEt)_2][BF_4]_2$ (5)

	4	5
	Bond Lengths	
Ni-S(1)	2.174(1)	2.208(2)
Ni-P(1)	2.186(1)	2.234(2)
P(1)-C(1)	1.817(4)	1.809(8)
P(1)-C(2)	1.809(4)	1.807(9)
P(1)-C(3)	1.823(4)	1.827(9)
S(1)-C(4)	1.831(4)	1.824(9)
S(1)-C(5)		1.81(1)
	Bond Angles	
S(1)-Ni-P(1)	87.6(1)	86.8(1)
S(1)-Ni-P(1a)	92.4(1)	93.2(1)
P(1)-Ni-P(1a)	180.0(1)	180.0(1)
S(1)-Ni-S(1a)	180.0(1)	180.0(1)

distance is 2.174(1) Å in complex 4 but increases to 2.208(2) Å in the analogous thioether 5; the Ni-P distances also increase by approximately 0.04 Å. There are no other significant metric or structural differences between the coordination spheres of Ni in 4 and 5. The Ni-S distances reported[8] for complex 6 in the form of $[Ni(PSSP)I][BPh_4]$ are the same as in 5; however the average Ni-P distance in 6 is 2.216(6) Å, i.e., increased by only 0.03 Å relative to 4. The Ni-S distances in 4 and 5 are statistically the same as those in 1 and 2, respectively; however the increase in Ni-P distance observed as the thiolate 4 is converted to the thioether 5 is not mirrored in an increase in Ni-N distance for the analogous 1 to 2 transformation.[3] Nickel-nitrogen distances remain constant.

The ethyl groups in 5 are on either side of the NiP_2S_2 square plane, and in both 4 and 5 the phenyl rings attached to phosphorus are similarly arranged so that an ortho C-H group is directly over the Ni with a Ni···H distance of 2.907 Å in 4 and 2.821 Å in 5. The ethylene arms connecting P to S are eclipsed across the NiP_2S_2 plane in both 4 and 5.

Synthesis and Reactivity. In compound 1 the thiolate sulfur donors are constrained to a cis orientation, while in compound 4 they select a trans geometry. Both the N_2S_2 1 and P_2S_2 4 react with organic electrophiles, RX, at sulfur to yield thioether derivatives, retaining their geometries; i.e., thioether complex 2 is cis, and thioether complex 5 is trans. Nevertheless, like 1, complex 4 reacts with bifunctional electrophiles to yield products in which the sulfurs are cis to each other. That is, the reaction of the trans thiolate 4 with dibromopropane gives a low-yield product identical to that formed in good yields on reaction of Ni^{II} salts with the preformed tetradentate ligand 1,9-bis(diphenylphosphino)-3,7-dithianonane.[13] In addition, 4 reacts with $(norbornadiene)Mo(CO)_4$ to give high yields of the heterobimetallic 12 (Scheme I).[15] Hence the trans geometry observed for 4 and 5 is a result of the electronic preference of the metal; the cis geometry is not precluded by steric effects. The syntheses of the phosphino thioether complex 5 was also best accomplished by the direct reaction of the ligand, $Ph_2PCH_2CH_2SEt$, with Ni^{II} rather than by alkylation of 4; however, both routes yield products in trans configurations.

Scheme I

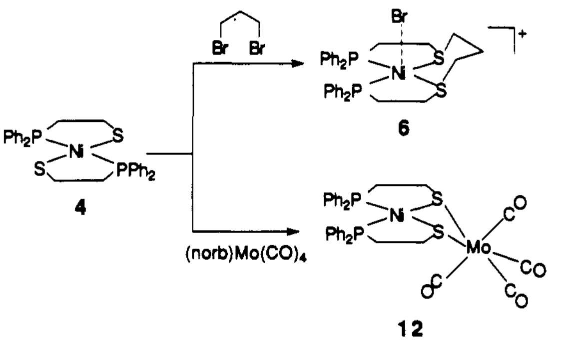

Table III. Cyclic Voltammographic Data for $Ni(Ph_2PCH_2CH_2S)_2$ (4), $[Ni(Ph_2PCH_2CH_2SEt)_2)[BF_4]_2$ (5), and $[Ni(Ph_2P(CH_2)_2S(CH_2)_3S(CH_2)_2PPh_2)][BF_4]_2$ (6)[a]

		$E_{1/2}$, mV (ΔE, mV)	
	E_{pa}(irrev), mV	Ni^{II}/Ni^I	Ni^I/Ni^0
4[b]	+262		
5[c]	+870	−558 (100)	−1139 (82)
6[c]		−614 (80)	−1166 (64)

[a] With Pt vs $Ag/AgNO_3$ electrodes and 0.1 M $[n\text{-}Bu_4N][PF_6]$ as supporting electrolyte; scan rate 200 mV/s. [b] CH_2Cl_2. [c] CH_3CN.

Electrochemistry. The voltammogram of the thiolate 4 in CH_2Cl_2 solution shows an irreversible peak at +0.26 V referenced to $Ag/AgNO_3$ presumed to be due to oxidation of thiolate S to the thiyl radical.[16] A similar irreversible oxidation of the N_2S_2 complex 1 in CH_3CN is seen at −0.03 V referenced to $Ag/AgNO_3$, and is also presumed to be sulfur-based,[16] although argument has been made for $Ni^{II/III}$ character in such oxidations.[17] Also similar to 1, complex 4 shows no reduction within the CH_2Cl_2 solvent window (to −1.75 V); however the cationic thioether complexes 2 and 3 have reversible Ni^{II}/Ni^I couples at −0.81 and −0.97 V, respectively, referenced to $Ag/AgNO_3$ in CH_3CN. (No further reduction is noted out to −1.50 V. EPR studies of bulk chemical, one-electron reductions of 2 and 3 exhibited axial Ni^I signals, and the reduction waves in the CV were therefore assigned to $Ni^{II/I}$ couples.[3,4]) In contrast, the thioether complexes 5 and 6 demonstrate two redox couples assigned to Ni^{II}/Ni^I and Ni^I/Ni^0 (Table III). The Ni^{II}/Ni^I couple of 5 is 56 mV more positive than that of 6, and the Ni^I/Ni^0 couple is 27 mV more positive for 5 as compared to 6.

The cyclic voltammograms of 3 and 6 are overlaid in Figure 3. Both the thioether functionality as well as the

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(15) Characterization of the Ni/Mo bimetallic was based on its infrared spectrum [ν(CO, cm^{-1}): 2006 (s), 1883 (s), 1844 (s) (THF); 1990 (s), 1883 (s), 1844 (s), 1830 (s) (Nujol)] as well as an X-ray crystal structure to be fully reported elsewhere. The complex crystallized in the monoclinic space group $C2/c$ (No. 15) with a = 34.88(5) Å, b = 9.586(10) Å, c = 21.30(7) Å, V = 6896(25) $Å^3$, Z = 8, and final R = 0.068 (R_w = 0.071) for 2212 unique reflections.

(16) Kruger, H. J.; Holm, R. H. *Inorg. Chem.* **1989**, *28*, 1148. Kumar, M.; Day, R. O.; Colpas, G. J.; Maroney, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 5974. Springs, J. J.; Janzen, C. P.; Darensbourg, M. Y.; Calabrese, J. C.; Krusic, P. J.; Verpeaux, J.-N.; Amatore, C. *J. Am. Chem. Soc.* **1990**, *112*, 5789.

(17) Martin, E. M.; Bereman, R. D.; Dorfman, J. *Inorg. Chim. Acta* **1990**, *176*, 247.

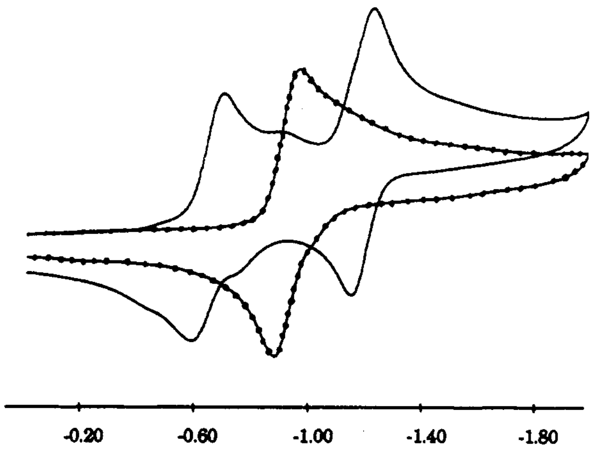
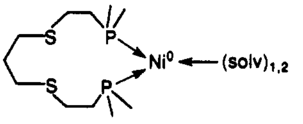


Figure 3. Cyclic voltammograms of 2–5 mM solutions of [Ni(bicycle)][BF_4]$_2$ (**3**) (···) and [Ni(PSSP)][BF_4]$_2$ (**6**) (—), in 0.1 M [(*n*-Bu)$_4$N][PF_6]/CH_3CN with a glassy carbon working electrode at 200 mV/s (scale referenced to Ag/$AgNO_3$; scan toward negative potential).

phosphine donor are needed to produce the Ni^I and Ni^0 species in **6**.

Preparation and Characterization of 5^R and 6^R. Both **5** and **6** were chemically reduced to a Ni^0 complex with Na/Hg amalgam in either benzene-d_6 or CD_3CN. Solutions of 5^R and 6^R are red and air-sensitive. Reaction with CO yielded, in the case of 6^R, a two-band infrared spectrum indicative of a $P_2Ni(CO)_2$ formulation.[14] (Ni(P-$Ph_2CH_2CH_2SEt)_2(CO)_2$ has previously been reported.[7])

The ^{31}P NMR spectrum of 6^R showed one signal at 31.8 ppm whereas that of the free ligand is at −17.1 ppm and that of the Ni^{II} complex **6** is at 58.7 ppm. The ^1H NMR spectrum of 6^R is very similar to that of the free ligand. In particular, the resonance assigned to the central methylene hydrogens ($SCH_2CH_2CH_2S$) is essentially identical in position and splitting to that of the free ligand as well as that of (PSSP)Ni(CO)$_2$. The complicated methylene region ascribed to those CH_2 groups immediately attached to P and S is better resolved in the spectrum of the free ligand as compared to the bound ligand either in 6^R or in (PSSP)Ni(CO)$_2$ (spectra available in supplementary material). Since the latter complex involves unbound thioether sulfurs, we conclude that 6^R has a similar solution structure as indicated below.



Spectral features of CH_3CN or benzene solutions of 5^R are more complicated, and a tentative assignment suggests at least one (perhaps both) PSEt ligand acts as a unidentate ligand.

Oxidative Addition Reactions to Ni^0 Species. The protonation of 5^R and spectral characterization (^1H chemical shift = −17.4 ppm (J_{P-H} = 49 Hz)) of the quite unstable [HNi($Ph_2PCH_2CH_2SEt)_2$]$^+$ species has been reported elsewhere.[7] Addition of the acid $HBF_4{\cdot}Et_2O$ to 6^R similarly results in the formation of a five-coordinate Ni^{II}–H complex, **9**.[18] The ^1H NMR spectrum of [HNi(PSSP)]$^+$ exhibits a triplet at −17.6 ppm (J_{P-H} = 48 Hz) attributable to a metal hydride coupled to phosphorus. Infrared spectroscopy of the solid shows a Ni–H stretch at 1929 cm^{-1}. The cyclic voltammogram of [HNi(PSSP)]$^+$ shows no reversible waves as observed for **5** and **6**; rather an irreversible reduction is seen at −2.11 V (glassy carbon electrode referenced to Ag/$AgNO_3$ in CH_3CN; scan rate = 200 mV/s). Whereas the hydride complex, [HNi($Ph_2PCH_2CH_2SEt)_2$]$^+$, is stable in acetone for only 6 h,[7] solutions of the tetradentate complex hydride, **9**, exist unchanged for over 6 days.

Oxidative addition of methyl iodide to 5^R and 6^R at 0 °C followed by ion exchange with BPh_4^- yielded the methyl derivatives [Ni(CH_3)($Ph_2PCH_2CH_2SEt)_2$][BPh_4] (**7**) and [Ni(CH_3)(PSSP)][BPh_4] (**8**). The Ni–CH_3 formulation was verified by elemental and ^1H NMR analyses. For **7**, the methyl group bound to the nickel is a broad (possibly due to distortion of the structure or paramagnetism of the complex) peak at −0.3 ppm. For **8** in acetone-d_6, a resonance at −0.4 ppm, a triplet with J_{P-H} = 10.5 Hz, is assigned to Ni–CH_3. Similar to the ^1H NMR data found for [Ni(H)($Ph_2PCH_2CH_2SEt)_2$]$^+$ and [Ni(CN)($Ph_2PCH_2CH_2SEt)_2$]$^+$,[7,12] the ^1H NMR shows two methylene peaks for the ethylene arm of **7**, indicating that both ligands act as chelates and the nickel is five-coordinate.[19] As was seen for [HNi(PSSP)]$^+$, [CH_3Ni(PSSP)]$^+$ is not susceptible to Ni^{II}/Ni^I reduction. An irreversible wave is seen at −1.90 V (Pt^0 electrode referenced to Ag/$AgNO_3$ in CH_3CN; scan rate = 200 mV/s).

Both of the nickel methyl complexes **7** and **8** are sensitive to acid, releasing CH_4; they also react with the nickel hydrides, [NiH($Ph_2PCH_2CH_2SEt)_2$]$^+$ and **9**, to produce CH_4. The complexes decompose slowly in solution (hours for **7**; days for **8**); however the decomposition product(s) has (have) not been characterized.

Insertion/Deinsertion of CO into Ni–CH_3 Bonds. Oxidative addition of acetyl chloride to both Ni^0 species, 5^R and 6^R, in benzene at −30 °C gives rise to a thermally unstable Ni–acetyl species and a Ni–dicarbonyl complex (Scheme II). The solid-state IR of isolated cold samples showed bands characteristic of nickel–acetyls[2,20] at 1652 and 1667 cm^{-1}, for the cations of **10**, [Ni(C(O)CH_3)($Ph_2PCH_2CH_2SEt)_2$]$^+$, and **11**, [Ni(C(O)CH_3)(PSSP)]$^+$, respectively. Qualitatively, as in the hydride and in the methyl derivatives, the tetradentate derivative **11** appears to be more stable in solution over time than **10**; however, both release CO on warming to temperatures higher than −30 °C. Gas chromatographic analysis of the head gas from the acetyl chloride reaction with 6^R shows trace amounts of H_2 and CH_4, presumed to develop in the reaction due to adventitious acid in the $CH_3C(O)Cl$ reagent. The methane can be produced by direct protonation of the nickel–methyl moiety as mentioned above.

As indicated in Scheme II, the loss of CO from **10** and **11** is reversible; on bubbling CO through THF solutions of the metal–alkyl species at −60 °C, the acetyls are regenerated. The carbon monoxide uptake is extremely

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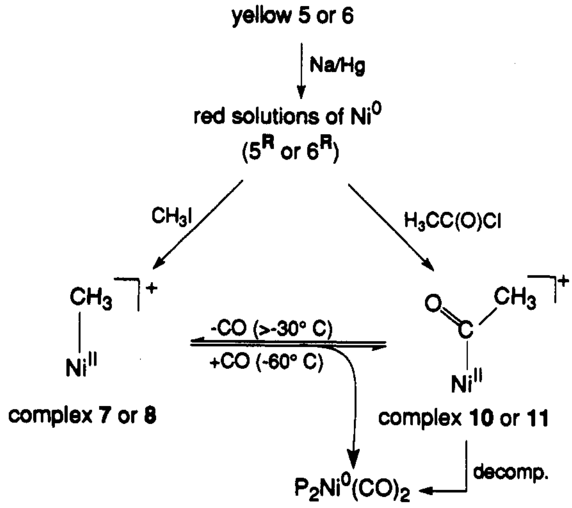
(18) The X-ray structure of [HNi(PSSP)][PF_6] has been determined and the hydride atom located (Ni–H = 1.40(5) Å) in an axial position in the pseudo-trigonal-bipyramidal geometry. The complex crystallized in the monoclinic space group $P2_1/n$ (No. 14) with a = 9.732(3) Å, b = 24.454(5) Å, c = 14.124(4) Å, V = 3253(15) Å^3, Z = 4, and final R = 0.042 (R_w = 0.038) for 4107 unique reflections. The complete structure will be reported elsewhere.

(19) We appreciate a reviewer's suggestion that an alternate interpretation is that the CH_2CH_2 groups are undergoing rapid conformational inversion and the protons are differentiated due to apical binding of a fifth ligand in a roughly square-pyramidal (or distorted-trigonal-bipyramidal) complex.

(20) Stoppioni, P.; Dapporto, P.; Sacconi, L. *Inorg. Chem.* **1978**, *17*, 718.

Scheme II



rapid (time of mixing), even at −60 °C, such that there is no difference in the reaction rates of the two complexes within the limits of our (conventional) measurements. A nickel–benzyl complex was synthesized by addition of $C_6H_5CH_2Br$ to **6**^{R} in the hope that it would take up carbon monoxide less readily and therefore permit kinetic studies; however, it also reacted with CO on time of mixing at −60 °C.[21] The methyl complexes react with CO, 1 atm at 22 °C, ultimately to produce nickel carbonyl products, $P_2Ni(CO)_2$. Gas chromatographic analyses of the head gases produced on reaction of CO with **7** and **8** indicate the *absence* of CH_4, CH_3CH_3, and $CH_2{=}CH_2$ as decomposition products. Neither was $CH_3C(O)CH_3$ detected by NMR in samples following CO addition to **8**. Finally, it is noteworthy that the Ni^{II} complexes **5** and **6** are unreactive with CO.

Comments. Despite the usefulness of nickel species in organometallic chemistry-based catalysis and the probable involvement of organonickel species in certain enzymic pathways, the rates of classical organometallic reactions involving nickel, and mechanistic details, remain largely unknown. Unfortunately, the rates of the CO migratory insertion/deinsertion reactions described above for P_2S_2Ni derivatives are too rapid for study in our laboratories. Furthermore, side reactions of the Ni—CH_3^+ and Ni—C(=O)CH_3^+ complexes with CO yield nickel carbonyl products, eliminating the alkyl or acetyl groups in forms as yet unknown and producing a system most likely too complicated for an in depth kinetic study. A facile dissociation of the thioether binding site, both in the bidentate P—SEt ligand as well as in the tetradentate PSSP ligand, most reasonably accommodates the coordination of CO and the resultant fast reactions. Such dissociation also appropriately accounts for the NMR spectra of the reduced Ni^0 species. We do not find CO to displace a thioether site and bind to Ni^{II} in the absence of a Ni—R or Ni—C(O)R functionality.

Our results and interpretation compare favorably with those of Sacconi et al.[20] for reaction of CO with a pentacoordinate, trigonal-bipyramidal, complex of nickel, $[NP_3Ni{-}CH_3]^+$; the authors also assumed that coordinate unsaturation, achieved by dissociation of the trivalent nitrogen donor cap of the tripod ligand, tris(2-(diphenylphosphino)ethyl)amine, accounted for the rapid rates observed. It would appear however that the $[NP_3NiC({=}O)CH_3]^+$ complex, stable at room temperature under CO gas, is much less apt to decarbonylate and also less apt to be reduced by CO than is $[(PSSP)NiC({=}O)CH_3]^+$. Similarly, the nickel acetyl complexes prepared using the N—$(SR)_3$ tetradentate tripod ligand[2] are also more stable than the complexes of the P—SEt bidentate or the PSSP, open-chain, tetradentate ligands. The tripod ligands impose a trigonal-bipyramidal geometry on Ni^{II}—R and are expected to form a more rigid metal-binding cavity, i.e., with a lesser tendency to provide an open site for CO binding.

Two major differences exhibited by the thioether N_2S_2Ni complexes **2** and **3** vs the thioether P_2S_2 complexes **5** and **6** are (1) the ability of the latter to achieve Ni^0 and (2) the ability of the phosphorus/sulfur environment to support Ni–H and Ni–CH_3 functionalities. The differences are possibly related by a kinetic problem in that Ni–H$^+$ and Ni–CH_3^+ are prepared via the nucleophilicity of a Ni^0 species, an oxidation state that cannot be produced in the N_2S_2 environment, where Ni^I is the lowest oxidation state available. The N/S and P/S complexes have obvious gross structural similarities; however, a subtle difference in bond distances on modification of sulfur from thiolate to thioether reflects the "softness" of the phosphorus/sulfur cavity as compared to the DACO-based nitrogen/sulfur cavity. That is, the increased size of the N/S cavity is solely in a lengthening of the Ni–S bond (0.04 Å) in the thioethers **2** and **3** vs the thiolate **1**, whereas in thioether **5** *both* the Ni–S and the Ni–P bonds are enlarged by ca. 0.04 Å compared to **4**. This larger cavity suggests easier accommodation of the larger Ni^0. The tetrahedral preference of Ni^0 is also more readily accommodated by the ligands of greater flexibility, P–SEt and PSSP,[22] as contrasted to the related DACO-based systems.

The observation of complete loss of Ni$^{II/I}$ and Ni$^{I/0}$ redox activity in the hydride and methyl complexes **7**–**9** confirms strong covalent bonding of the carbanion or hydride to Ni^{II} and the inability to produce a 19-electron species containing Ni^I or a 20-electron Ni^0 species. It is also noteworthy that the Ni^{II}–H and Ni^{II}–CH_3 species in the P_2S_2 environment do not show cyclic voltammogram responses that signal stable Ni^{III}–H or Ni^{III}–CH_3, i.e., the species which might have been produced from reaction of H$^+$ or CH_3^+ with Ni^I. Such species in N/S coordination have been proposed as intermediates in Ni hydrogenase and CO dehydrogenase cycles[1] and remain a synthetic challenge.

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Supplementary Material Available: Tables of atom positional parameters, bond lengths and angles, and anisotropic displacement parameters, packing diagrams and alternate figures of both $Ni(Ph_2PCH_2CH_2S)_2$ (**4**) and $[Ni(Ph_2PCH_2CH_2SEt)_2][BF_4]_2$ (**5**), and ^{1}H spectra of the free PSSP ligand and complexes **6**, **6**^{R}, and $(PSSP)Ni(CO)_2$ (13 pages). Ordering information is given on any current masthead page.

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[21] Chojnacki, S. S.; Darensbourg, M. Y. Unpublished results.

[22] DuBois, T. D.; Meek, D. W. *Inorg. Chem.* **1969**, *8*, 146.