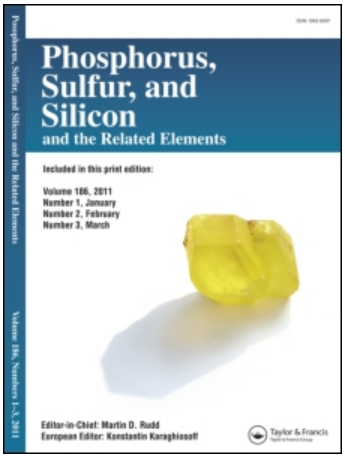

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

COMPLEXATION OF *o*-(ETHYLPHENYL-PHOSPHINO)(ETHYLTHIO)BENZENE TOWARDS NICKEL(II), PALLADIUM(II), AND PLATINUM(II) COMPLEXES

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To cite this Article Hou, Duen-Ren , Lin, Tu-Chen , Hsieh, Tung-Ying , Cheng, Ming-Chu , Peng, Shie-Ming and Liu, Shiuh-Tzung(1996) 'COMPLEXATION OF *o*-(ETHYLPHENYL-PHOSPHINO)(ETHYLTHIO)BENZENE TOWARDS NICKEL(II), PALLADIUM(II), AND PLATINUM(II) COMPLEXES', Phosphorus, Sulfur, and Silicon and the Related Elements, 108: 1, 61 — 73
To link to this Article: DOI: 10.1080/10426509608029639
URL: http://dx.doi.org/10.1080/10426509608029639

Phosphorus, Sulfur, and Silicon, 1996, Vol. 108, pp. 61–73
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COMPLEXATION OF *o*-(ETHYLPHENYL-PHOSPHINO)(ETHYLTHIO)BENZENE TOWARDS NICKEL(II), PALLADIUM(II), AND PLATINUM(II) COMPLEXES†

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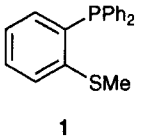
(Received May 15, 1995; in final form August 10, 1995)

Complexation of a hybrid P—S ligand *o*-(ethylphenylphosphino)(ethylthio)benzene (**2**) with $NiCl_2 \cdot$ DME (DME = $MeOCH_2CH_2OMe$), $(CH_3CN)_2PdCl_2$, and $(CH_3CN)_2PtCl_2$ provided $\{o\text{-}C_6H_4(PEtPh)(SEt)\text{-}P,S\}MCl_2$ {**3a**, M = Ni; **3b**, M = Pd, **3c**, M = Pt} respectively. Due to the stereogenic center at phosphorus atoms, complexes **3a–c** exist as a pair of geometrical isomers, which would interconvert to each other by inversion at the sulfur center. Substitution of chloride by triphenylphosphine occurs in complexes **3b–c** to provide $[\{o\text{-}C_6H_4(PEtPh)(SEt)\text{-}P,S\}M(PPh_3)Cl]Cl$ {**4b**, M = Pd; **4c**, M = Pt}, but not in **3a**. Both triphenylphosphine substituted complexes **4b** and **4c** readily undergo S-dealkylation to give $\{o\text{-}C_6H_4(PPhEt)(S)\text{-}P, S\}MCl(PPh_3)$ {**5b**, M = Pd; **5c**, M = Pt} respectively. The inversion barriers (kJ/mol) of coordinated sulfur centers were determined by NMR spectroscopy: 52 ± 2 for **3a**, 60 ± 2 for **3b**, 70 ± 2 for **3c**, 53 ± 2 for **4b** and 58 ± 3 for **4c**. During dealkylation of $[\{o\text{-}C_6H_4(PEtPh)(SEt)\text{-}P, S\}Pt(PPh_3)Cl]Cl$ (**4c**) with chloride in refluxing chloroform, side product *cis*-$[o\text{-}C_6H_4(PPhEt)(S)]_2Pt$ (**6c**) was formed. Crystal structures of **3a–c**, **5b–c**, **6c** and $[\{o\text{-}C_6H_4(PEtPh)(SEt)\text{-}P,S\}Pd(PPh_3)Cl]PF_6$ (**4b'**) were determined.

Key words: Phosphine complexes, NMR spectra, X-ray structures, geometrical isomers, P—S ligand.

Phosphine ligands with hybrid donor atoms designed to improve control over the reactivities of the metal ions receive much attention. In this area P—S hybrid ligands appeared to be a good combination because of the moderate σ-donative character of sulfide donors toward transition metal complexes. Incorporating P—S donors into a *o*-phenylene carbon frame such as **1** is well adapted for a chelating effect to increase the coordination ability of sulfide. Compound **1** thus forms stable complexes with various metals ions.[1–5] In seeking to extend this work, we synthesized a ligand *o*-(ethylphenylphosphino)(ethylthio)benzene **2**, which contains a stereochemical influence at the phosphorus center, and examined the coordination behavior of *o*-phenylene(phosphine)(sulfide) toward Ni(II), Pd(II) and Pt(II).



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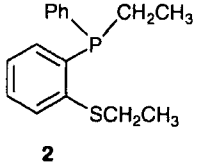

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† Studies of the Effects on Coordination of Thioether Sites Part II, please see Reference 1.

EXPERIMENTAL

^1H and ^{31}P NMR spectra were recorded on a Bruker AC-E 200 or a Bruker AM-300WB spectrometer; chemical shifts are given in parts per million relative to TMS for ^1H NMR and 85% H_3PO_4 for ^{31}P NMR spectra in $CDCl_3$, unless otherwise noted. Elemental analyses were made on a Perkin-Elmer 240C instrument. All reactions, manipulations and purification steps involving phosphines were performed under a dry nitrogen atmosphere. *o*-C_6H_4(PPhH)(SH) was prepared according to a method previously described.[6] ^{31}P NMR data and coordination chemical shifts are summarized in Table I.

o-(Ethylphenylphosphino)(ethylthio)benzene{o-C_6H_4(PEtPh)(SEt)}(**2**): To a solution of *o*-C_6H_4(PPhH)(SH) (1.9 g, 8.7 mmol) in anhydrous ether (20 mL) was added a 1.6 M hexane solution of *n*-butyllithium (10.9 mL, 17.4 mmol) at −78°C. After stirring at that temperature for 30 min, ethyl iodide (3.13 g, 20.0 mmol) was added to the solution. The reaction mixture was allowed to warm to 25°C and quenched on addition of water (6 mL). The organic layer was separated, dried and concentrated. The residue was distilled to give the desired ligand as a colorless, air-sensitive liquid (2.03 g, 85%), bp 181–186°C/0.15–0.20 mmHg (Found: C, 69.82; H, 7.14. $C_{16}H_{19}PS$ requires C, 70.05; H, 6.98%); δ_H 7.43–7.10 (9 H, m, Ar-*H*), 2.96–2.79 (2 H, m, —SC*H*$_2$—), 2.12–1.92 (2 H, m, —PC*H*$_2$—), 1.25 (3 H, t, J(HH) 7.3 Hz, —SCH$_2$C*H*$_3$), 1.10 (3 H, dt, *J*(PH) 17.2, *J*(HH) 7.6 Hz, —PCH$_2$C*H*$_3$); δ_P −21.7.

Dichloro{[o-(ethylphenylphosphino)(ethylthio)benzene] - P,S}nickel(II){o - C_6H_4(PEtPh)(SEt)-P,S}NiCl$_2$ (**3a**): A solution of **2** (66.6 mg, 0.24 mmol) in dichloromethane (6 mL) was added to a solution of $NiCl_2$(DME) [DME = 1,2-dimethoxyethane] (52.9 mg, 0.24 mmol). The resulting solution turned bright red immediately and was kept stirring for 10 h. The solvents were removed and the residue was recrystallized from dichloromethane and ether to give **3a** as a red crystalline solid (94.2 mg, 97%), mp 164–166°C (decomp) (Found: C, 47.19; H, 4.58. $C_{16}H_{19}Cl_2PSNi$ requires C, 47.57; H, 4.74%); δ_H 7.67–7.46 (9 H, m, Ar-*H*), 3.32 (2 H, br, —SC*H*$_2$—), 2.94 (1 H, br, —PC*H*—), 2.07 (1 H, br, —PC*H*—), 1.66–1.46 (6 H, m, —C*H*$_3$); δ_P 59.8 (at 25°C); 52.1, 50.2 (at −73°C).

Dichloro{[o-(ethylphenylphosphino)(ethylthio)benzene] - P,S}palladium(II){o - C_6H_4(PEtPh)(SEt)-P,S}-PdCl$_2$}(**3b**): A mixture of $PdCl_2$ (32.2 mg, 0.13 mmol) and *2* (35.6 mg, 0.13 mmol) in dichloromethane was heated to reflux for 9 h. The reaction mixture was concentrated to yield a yellow solid that was subsequently recrystallized from nitromethane. The desired complex **3b** was obtained as a light yellow crystalline solid (43.3 mg, 74%) mp 198–202°C (decomp) (Found: C, 42.34; H, 3.96. $C_{16}H_{19}Cl_2PSPd$ requires C, 42.55; H, 4.24%); δ_H 7.78–7.41 (9 H, m, Ar-*H*), 3.46 (2 H, br, —SC*H*$_2$—), 3.12 (1 H, br, —PC*H*—), 2.30 (1 H, br, —PC*H*—), 1.49–1.19 (6 H, m, —C*H*$_3$).

Dichloro{[o-(ethylphenylphosphino)(ethylthio)benzene]-P,S-}platinum(II){o-C_6H_4(PEtPh)(SEt)-P,S}PtCl$_2$

TABLE I

^{31}P NMR chemical shifts of complexes

Compound	δ_P [a]	$\Delta\delta$[b]
***syn*-3a**	50.2	71.9
***anti*-3a**	52.1	73.8
***syn*-3b**	64.2	85.9
***anti*-3b**	65.3	85.9
***syn*-3c**	39.3	61.0
***anti*-3c**	40.3	62.0
***syn*-4b**	30.7, 67.0	-
***anti*-4b**	31.2, 67.0	-
***syn*-4c**	17.1, 45.8	-
***anti*-4c**	18.1, 45.8	-
5b	58.3, 21.4	-
5c	40.1, 20.5	-
6c	40.9	-

[a] relative to 85% H_3PO_4 (in ppm). [b] Coordination chemical shift ($\Delta\delta$) = shift of complex - shift of free ligand (in ppm).

TABLE II

Crystal data of *syn*-[(2)MCl_2][a]

Compound	3a, M = Ni	3b, M = Pd	3c, M = Pt
Formula	$C_{16}H_{19}Cl_2PSNi$	$C_{16}H_{19}Cl_2PSPd$	$C_{16}H_{19}Cl_2PSPt$
M	404.11	451.81	540.51
Crystal system	monoclinic	monoclinic	monoclinic
Crystal size/mm	0.25 x 0.30 x 0.35	0.20 x 0.15 x 0.30	0.20 x 0.20 x 0.30
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	10.430(5)	10.517(5)	10.609(2)
b/Å	12.233(8)	12.060(6)	12.194(2)
c/Å	13.896(8)	14.057(7)	14.121(3)
β / °	93.24(5)	93.11(4)	93.74(2)
U/Å^3	1770.1(18)	1780.3(15)	1822.8(6)
Z	4	4	4
D_c / g cm^{-3}	1.516	1.685	1.969
μ / cm^{-1}	16.0	15.2	82.48
2θ range / °	18.58 - 23.06	18.74 - 29.24	18.74 - 31.26
F(000)	832	904	1032
T/K	298	298	298
Sacn width[b]	0.8 + 0.35 tan θ	0.70 + 0.35 tan θ	0.80 +0.35 tan θ
Transm range	0.93 - 1.00	0.95 - 1.00	0.68 - 1.00
2θ max/°	50.0	50.0	45.0
No. of unique reflns	3117	3117	2387
No. of reflns obsd [$I > 2\sigma(I)$]	1824	2538	1906
Soln method	heavy atom	heavy atom	heavy atom
No. of params.	190	191	191
R	0.039	0.023	0.039
R'	0.027	0.020	0.039
S	1.50	1.75	3.09

[a] Details in common: θ - 2θ scan mode, Mo–K α radiation (λ = 0.71069 Å); weighting scheme $w^{-1} = \sigma^2(F)$. [b] The stationary counting for background is applied.

(3c): A mixture of $(CH_3CN)_2PtCl_2$ (156 mg, 0.45 mmol) and **2** (123 mg, 0.45 mmol) was stirred at 25°C for 3 h. After concentration of the reaction mixture, the residue was chromatographed on silica gel with ethyl acetate as eluent. The eluate was concentrated and the residue was crystallized from chloroform/2,2,4-trimethylpentane to give **3c** as a colorless crystalline solid (195 mg, 73%), mp 195–197°C (decomp) (Found: C, 35.71; H, 3.15. $C_{16}H_{19}Cl_2PSPt$ requires C, 35.56; H, 3.54%); δ_H 7.3–7.8 (9 H, m, Ar-*H*), 3.79 (1 H, m, —C*H*—), 3.41 (1 H, m, —C*H*—), 3.05 (1 H, m, —C*H*—), 2.48 (1 H, m, —C*H*—), 1.33 (3 H, m, —CH_3), 1.15 (3 H, m, —CH_3).

Chloro[[o-(ethylphenylphosphino)(ethylthio)benzene]-P,S](triphenylphosphine)palladium(II) hexafluorophosphate[[o-C_6H_4*(PEtPh)(SEt)-P,S]PdCl(*PPh_3*)]*PF_6 **(4b')**: A mixture of **3b** and excess of triphenylphosphine in chloroform was stirred for 1 h. After filtration of the reaction mixture, the filtrate was treated with NH_4PF_6. After anion metathesis, the solution was filtered again and the filtrate was left to stand for 10 h. The desired complex crystallized as a colorless solid (78%) (Found: C, 49.21; H, 4.31. $C_{34}H_{34}F_6ClSP_3Pd$ requires C, 49.59; H, 4.16%).

*Chlorl[[o - (ethylphenylphosphino)(thiolato)benzene] - P,S](triphenylphosphine)platinum(II)[[o - *C_6H_4*-(PEtPh)(S)-P,S]PdCl(*PPh_3*)]* **(5b)**: A mixture of ligand **2** (67 mg, 0.24 mmol) and $(CH_3CN)_2PdCl_2$ (64

TABLE III

Crystal data of **5b**, **5c**, **4b'** and **6c**[a]

Compound	**5b**	**5c**	**4b'**	**6c**
Formula	$C_{33}H_{30}P_2SCl_4Pd$	$C_{34}H_{33}P_2SCl_3Pt$	$C_{34}H_{34}ClF_6P_3SPd \cdot 0.5\ (CHCl_3) \cdot 0.5\ (CH_3COCH_3)$	$C_{29}H_{29}Cl_2P_2S_2Pt\ (CHCl_3)$
M	769.07	837.30	912.41	805.32
Crystal system	monoclinic	triclinic	orthorhombic	monoclinic
Crystal size/mm	0.30 x 0.35 x 0.35	0.30 x 0.30 x 0.25	0.25 x 0.35 x 0.30	0.30 x 0.30 x 0.35
Space group	$P2_1/n$	P-1	Pbca	$P2_1/c$
a/Å	11.124(3)	9.888(2)	17.768(11)	10.971(5)
b/Å	18.252(4)	10.259(3)	18.635(8)	14.509(6)
c/Å	17.324(4)	17.472(4)	23.970(15)	19.708(7)
α/°	-	104.91(2)	-	-
β/°	100.98(2)	94.34(2)	-	100.29(3)
γ/°	-	94.35(2)	-	-
U/Å^3	3453.1(14)	1699.5(7)	7937(8)	3086.8(20)
Z	4	2	8	4
D_c/g cm^{-3}	1.479	1.685	1.527	1.732
μ, cm^{-1}	9.43	45.00	7.50	51.06
2θ range/°	19.02 - 24.22	18.78 - 23.24	18.72 - 22.54	18.70 - 21.20
F(000)	1552	824	3688	1576
T/K	298	298	298	298
Sacn width[b]	0.70 + 0.35 tan θ	1.0 + 0.35 tan θ	0.70 + 0.35 tan θ	0.75 + 0.35 tan θ
Transm range	0.89 - 1.00	0.73 - 1.00	0.93 - 1.00	0.88 - 1.00
2θ max/°	45.0	45	45.0	45
No. of unique reflns	4479	4425	5152	4018
No. of reflns obsd.	2871	3315	2445	2864
Soln method	heavy atom	heavy atom	heavy atom	heavy atom
No. of params.	371	370	428	335
R	0.047	0.047	0.062	0.049
R'	0.034	0.036	0.047	0.042
S	1.94	2.00	2.09	2.85

[a] [b] Same as in Table 11

mg, 0.25 mmol) in chloroform (4 mL) was stirred for 30 min at room temperature. After triphenylphosphine (72 mg, 0.27 mmol) was added, the resulting mixture was heated to reflux for 12 h. The reaction mixture was filtered and concentrated, The residue was crystallized from dichloromethane/ether to give **5b** as an orange-red crystalline solid (144 mg, 90%), mp 217.5–219.5°C (decomp) (Found: C, 58.95; H, 4.37. $C_{32}H_{29}ClSP_2Pd$ requires C, 59.18; H, 4.50%; δ_H 7.7–6.9 (24 H, m, Ar-*H*), 3.03 (1 H, m, —C*H*—), 2.22 (1 H, m, —C*H*—), 1.24 (3 H, dt, *J*(HH) 8 Hz, *J*(PH) 10 Hz, —CH_3).

Chloro{[o-(ethylphenylphosphino)(thiolato)benzene]-P,S}(triphenylphosphine)platinum(II)[{o-C_6H_4-(PEtPh)(S)-P,S}PtCl(PPh$_3$)] (**5c**): A solution of **2** (31.4 mg, 0.11 mmol) in dichloromethane (8 mL) was added to a solution of $(Ph_3P)_2PtCl_2$ (90.5 mg, 0.11 mmol) with stirring at room temperature and the mixture was stirred for 10 h. After the volume of the reaction mixture was reduced to 2 mL, ether (10 mL) was added. Upon standing 8 h, a yellow powder precipitated that was desired product **5c**. Recrystallization from a dichloroethane/ether solution gave **5c** as a light yellow crystalline solid (59.8 mg, 71%), mp 244–247°C (decomp) (Found: C, 49.02; H, 3.87. $C_{32}H_{29}ClSP_2PtClCH_2CH_2Cl$ requires C, 48.79; H, 3.97%); δ_H 7.54–6.62 (24 H, m, Ar-*H*), 2.02–1.92 (1 H, m, —C*H*—), 0.98 (3 H, dt, *J*(PH) 20.6, *J*(HH) 7.2 Hz, —CH_3), 0.70–0.59 (1 H, m, —C*H*—).

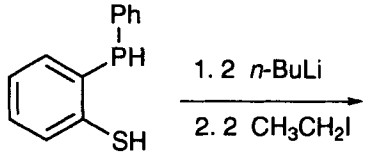
Bis{[o-(ethylphenylphosphino)(thiolato)benzene]-P,S}platinum(II)[{o-C_6H_4(PEtPh)(S)-P,S}$_2$Pd] (**6c**): A solution of $(CH_3CN)_2PtCl_2$ (133 mg, 0.5 mmol) and **2** (137.5 mg, 0.5 mmol) in chloroform (6 mL) was stirred at 25°C for 30 min. A solution of triphenylphosphine (131 mg, 0 51 mmol) was added to this solution and the resulting solution was heated to reflux for 3 h. After concentration of the mixture, the residue was chromatographed on silica gel with ethyl acetate/hexane as eluent. A yellow band was collected and concentrated. The residue was crystallized from dichloromethane/ether to give **6c** as a light yellow crystalline solid (30%), mp 203–205°C (decomp) (Found: C, 45.87; H, 3.68. $C_{28}H_{28}P_2S_2Pt \cdot 0.5\ CHCl_3$ requires C, 45.93; H, 3.85%); δ_H 8.2–6.6 (18 H, m, Ar-*H*), 2.05–1.78 (4 H, m, —CH_2—, 0.64 (6 H, dt, *J*(HH) 7 Hz, *J*(PH) 10 Hz, —CH_3).

X-ray crystallography: Single crystals suitable for X-ray analysis of complexes *syn*-**3a–c**, **4b'** (0.5 $CHCl_3$)(0.5 CH_3COCH_3), **5b**·($CHCl_3$), **5c**·($ClCH_2CH_2Cl$) and **6c**·($CHCl_3$) were obtained in each case

by slow evaporation of a solution under air. Cell parameters were determined on a CAD-4 diffractometer at 298 K with a least-squares treatment. Atomic scattering factors were taken from "International Tables for X-ray Crystallography."[8] The NRCC SDP VAX Program package was used.[9] Crystal data of *syn*-**3a–c**, **4b′**, **5b–c** and **6c** are summarized in Tables II and III. There is disorder of solvent molecules in **4b′**. Selected bond distances and angles are summarized in Tables IV and V.

RESULTS AND DISCUSSION

o-(Ethylphenylphosphino)(ethylthio)benzene (**2**) was prepared on alkylation of *o*-(phenylphosphino)thiophenol with iodoethane (Equation 1).[6] This ligand is a liquid sensitive to air and was characterized by spectral and elemental analyses. The ^{31}P NMR spectrum of **2** in $CDCl_3$ shows a singlet at −21.7 ppm, which is in a typical range of diarylalkylphosphine. The ^1H NMR spectra exhibits two sets of signals of ethyl groups; one set has splitting due to phosphorus coupling J(PH), indicating that one ethyl group is on the phosphorus atom and the other on the sulfur atom.

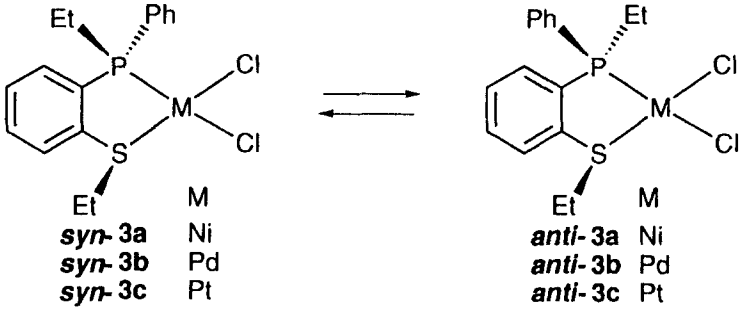


(1)

All complexes {*o*-C_6H_4(PEtPh)(SEt)-P,S}MCl_2 {**3a**, M = Ni; **3b**, M = Pd; **3c**, M = Pt] were prepared by direct ligand substitutions. Thus the nickel complex was generated on the reaction of $NiCl_2 \cdot$DME (DME = 1,2-dimethoxyethane) with **2** in 1:1 molar ratio in dichloromethane, whereas the replacement of $(CH_3CN)_2PdCl_2$ and $(CH_3CN)_2PtCl_2$ by **2** afforded the corresponding palladium and platinum complexes respectively. All complexes were obtained as crystalline solids on recrystallization.

Properties of Complexes

Coordination of sulfur in **2** to a metal center generates a new stereogenic center at the sulfur atom, which enables the complexes to form a pair of geometrical isomers. Crystallization of complexes allowed us to obtain the *syn* isomers in which ethyl groups on sulfur and phosphorus atoms are on the same side of the plane defined by the chelate ring (see crystallography). However, the *syn* isomer readily converted to the corresponding *trans* isomer (Equation 2) in solution and both species reach an equilibrium at a ratio ca. 1:1. The isomerization reflects the inversion at the sulfur center as illustrated in many complexes.[4–5]



(2)

Variable-temperature ^{31}P NMR spectra of **3a–c** were measured. A solution of complex *syn*-**3c** as typical in a mixed solvent $CDCl_3$, CD_3CN and CD_3COCD_3 (for reasons of solubility) was prepared at −78°C, which was then monitored in an NMR spectrometer. Initially only one signal corresponding to the species *syn*-**3c** in ^{31}P NMR spectrum was observed. The chemical shifts of methyl groups of *syn*-**3c** appeared were smaller than those of the *anti* isomer, which agrees with observations on the complex of $[(MeSCH_2CH_2SMe)PtCl_2]$.[5] After standing at −78°C for 1 h, another signal corresponding to *anti*-**3c** appeared; the integration ratio of both signals was about 1:1, indicating that interconversion between two diastereomers proceeded even at low temperature. As temperature elevates, these two lines broadened and finally collapsed into one signal at 268K. An observation of this kind was also found for nickel and palladium complexes **3a** and **3b**. Interconversion barriers at the sulfur centers of **3a–c** were thus estimated to be 52 ± 2 kJ/mol for **3a**, 60 ± 2 kJ/mol for **3b** and 70 ± 2 kJ/mol for **3c**. These small barriers for sulfur inversion are consistent with other reported values.[5] Due to rapid interconversion, characterizations of *anti*-**3a–c** were performed on ^1H-^1H COSY spectra, as shown in Figure 1 for *anti*-**3c**.

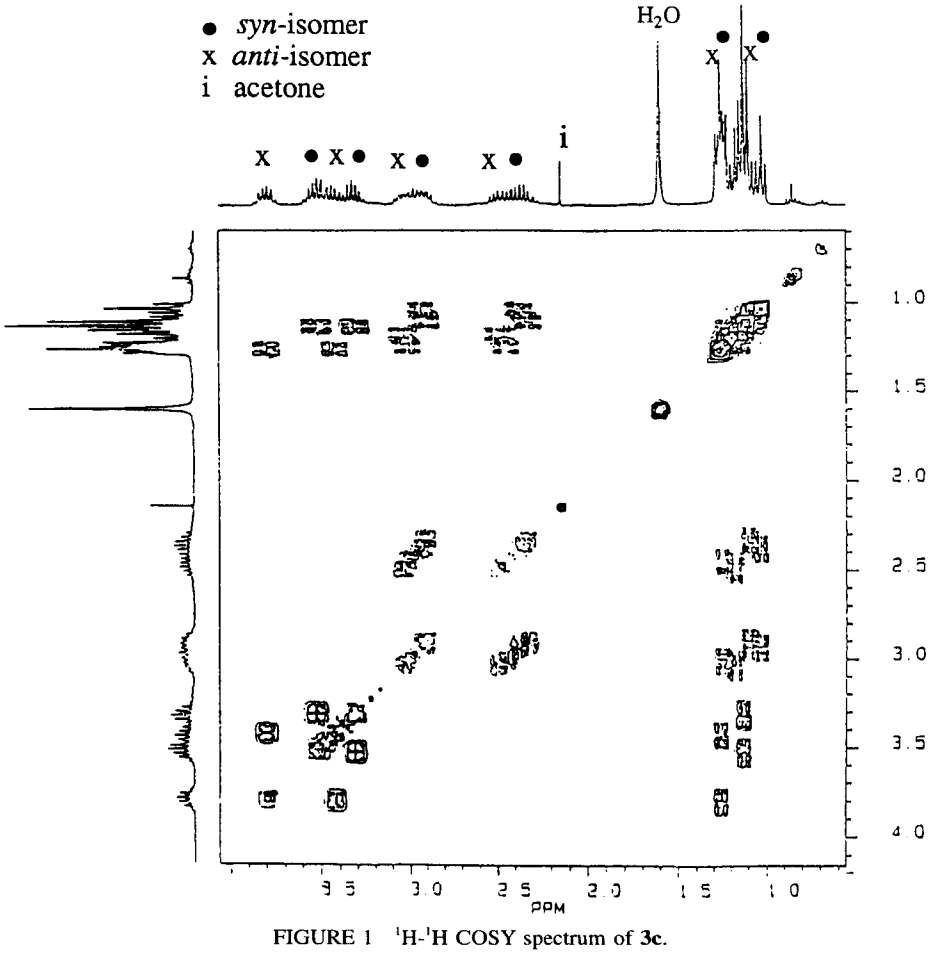


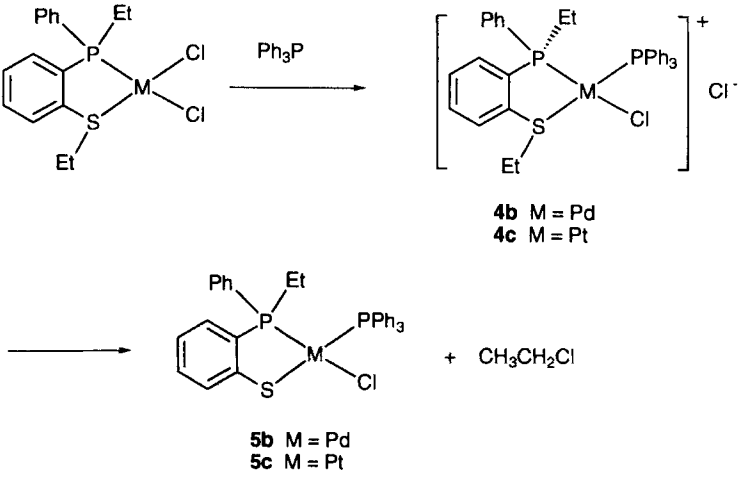
FIGURE 1 ^1H-^1H COSY spectrum of **3c**.

Ligand Substitution and S-Dealkylation

Treatment of **3b** or **3c** with triphenylphosphine yielded substitution intermediates [{*o*-C_6H_4(PEtPh)(SEt)-P,S}M(PPh_3)Cl]Cl {**4b**, M = Pd; **4c**, M = Pt}, which subsequently underwent S-dealkylation to provide [{*o*-C_6H_4(PEtPh)(S)-P,S}Pd(PPh_3)Cl] **5b** and [{*o*-C_6H_4(PEtPh)(S)-P,S}Pt(PPh_3)Cl] **5c** respectively (Scheme I), but complex **3a** resisted undergoing such a reaction. Intermediates **4b–c** were characterized by spectral methods and complex **4b** was even isolated as the salt of hexafluorophosphate, [{*o*-C_6H_4(PEtPh)(SEt)-P,S}Pd(PPh_3)Cl]PF_6 **4b′**, which was further characterized by X-ray analysis of a crystal. Substitution of **3b–c** with triphenylphosphine was complete within one hour according to ^{31}P NMR spectra. However, the substitution of the chloride ligand by PPh_3 in **3b** was reversible according to evidence of reaction of **4b′** with chloride providing **3b**, whereas formation of platinum complex **4c** was irreversible. Because of stereogenic centers remaining at both sulfur and phosphorus atoms in **4b** and **4c**, geometrical isomers seen in **3b–c** also existed. Isomerizations of the corresponding species proceeded rapidly and barriers for the interconversion are 53 ± 2 kJ/mol for **4b** and 58 ± 3 kJ/mol for **4c**, which are slightly smaller than those of **3b** and **3c**. The coordinated triphenylphosphine ligand in the complexes seems to decrease the inversion barrier at the sulfur center.

Characterization of these complexes was performed by both X-ray crystal structure and spectral analysis. Structural analysis of **4b′** (Figure 5) illustrates not only the *syn* relationship of ethyl groups but also the *cis* relationship of two phosphine donors. ^{31}P NMR spectrum of **4b** in $CDCl_3$ at 25°C shows a pair of doublets at 66.2 ppm (d, *J*(PP) 8 Hz) and 30.8 ppm (d, *J*(PP) 8 Hz), consistent with *cis* geometry of phosphines about the metal center. We confirmed the formulation of complex **4c**, like **4b**, by spectral methods.

Formation of **5b** and **5c** is the result of the free chloride undergoing nucleophilic attack at the α-carbon attached to the sulfur center. Dealkylation of **3c** in the presence of triphenylphosphine equimolar proportions in $CDCl_3$ was monitored with ^1H NMR spectroscopy. Signals of the ethyl group attached to the sulfur group disappeared slowly accompanied by the formation of chloroethane, the reaction was complete in

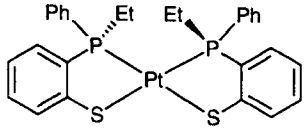


SCHEME I

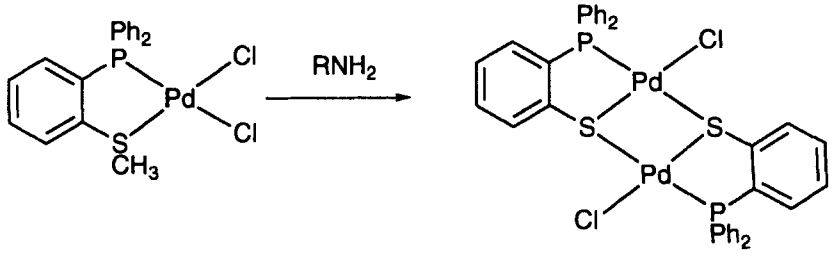
ca. 24 h, but dealkylation of **3b** required much greater duration under similar conditions.

Such dealkylation was observed by Roundhill and coworkers in the reaction of (**1**)$PdCl_2$ with iodide or thiocyanide,[3] the pathway is believed to be of an S_N2 type, i.e. iodide undergoes nucleophilic attack at the methyl group. Another relevant work of S-dealkylation in As/S systems was also reported by McAuliffe.[12] In complexes **3b** and **3c**, there are ethyl groups of two types available for dealkylation, but the ethyl group of the sulfur atom is the one attacked by free chloride. Formation of sulfido complex (**5b** or **5c**) is favored over the phosphido complex via the attack of the ethyl group at the phosphorus atom.

When **3c** and PPh_3 as a mixture in $CDCl_3$ were heated to reflux for 3 h, a mixture of products **5c** and **6c** were formed. Complex **6c** forms through disproportionation, similar to that reported by Roundhill in reaction of [*o*-$C_6H_4(PPh_2)(SMe)$]$PdCl_2$ with amines.[3c] The *cis* stereochemistry of phosphines in **6c**, determined with X-ray analysis of a single crystal, different from that of palladium complex illustrated in **7** (Equation 3).[3c] However, palladium complex **3b** or **4c** underwent no such disproportionation.



6c



(3)

7

Crystallographic Analysis

The crystal structures of complexes *syn*-**3a-c** are isomorphous in monoclinic space group $P2_1/n$; their crystal data are summarized in Table 2. Selected bond distances and angles of *syn*-**3a-c** are summarized in Table 4. An ORTEP plot of nickel complex *syn*-**3a** as typical appears in Figure 2. The metal is situated at the center of the square-planar disposition with phosphorus and sulfur donor of ligand **2** in *cis*-coordinated. Chelation of **2** is obviously favored on formation of a stable five-membered ring as observed in many *o*-phenylene systems.[10] Bond lengths M—Cl, M—S and M—P are typical and agree well with those of known complexes. P—Cl(2) bonds *trans* to phosphine donors are apparently longer than those *trans* to sulfur donors because of *trans* influences.[11]

Single crystals of complexes of {(*o*-$C_6H_4(PPh_2)(S)$-P,S}$M(PPh_3)Cl$ {**5b**, M = Pd;

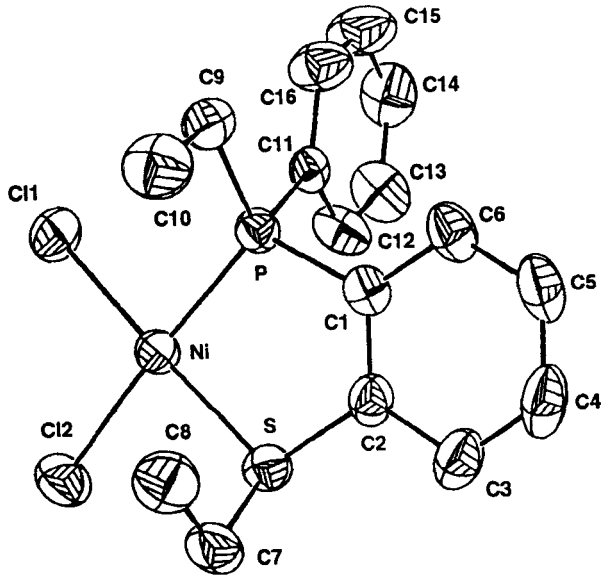


FIGURE 2 ORTEP plot of complex *syn*-**3a**.

5c, M = Pt} were well formed belonging to space groups P21/n and P-1, individually. The structures of **5b** and **5c** appears in Figures 3 and 4; crystal data are listed in Table III, and selected bond lengths and angles are found in Table V. Either complex consists of a square-planar metal center with a chelate P—S donor, a chloride and triphenylphosphine.

The structures of complexes **4b'** and **6c** were determined with X-ray diffraction of single crystals. Crystal data (Table III) and complete molecular structures appears in Figures 5 and 6. Selected bond distances and bond angles are collected in Table V. In both complexes, the coordination polyhedron about the metal centers is a square

TABLE IV
Selected bond distances (Å) and angles (°) of *syn*-(2)MCl_2

	M= Ni (*syn*-**3a**)	M = Pd (*syn*-**3b**)	M = Pt (*syn*-**3c**)
M-S	2.150(2)	2.252(1)	2.242(4)
M-P1	2.141(1)	2.206(1)	2.219(4)
M-Cl(1)	2.163(2)	2.304(1)	2.319(4)
M-Cl(2)	2.219(2)	2.370(1)	2.384(4)
S-C(2)	1.787(6)	1.781(3)	1.80(1)
P-C(1)	1.818(5)	1.816(3)	1.83(2)
S-M-P1	90.18(7)	88.93(5)	89.5(2)
S-M-Cl(1)	176.67(7)	176.64(3)	179.6(2)
S-M-Cl(2)	87.28(8)	87.47(5)	88.1(2)
P-M-Cl(1)	86.66(7)	87.75(5)	90.1(2)
P-M-Cl(2)	176.83(8)	176.04(4)	176.9(2)
Cl(1)-M-Cl(2)	95.84(8)	95.84(5)	92.3(2)

TABLE V
Selected bond distances (Å) and bond angles (°) for **4b'**, **5b–c** and **6c**

	4b' (M=Pd)	**5b (M=Pd)**	**5c (M=Pt)**	**6c (M=Pt)**
M-P1	2.238(4)	2.226(2)	2.220(4)	2.314(4)
M-P2	2.311(4)	2.324(2)	2.290(4)	2.241(4)
M-S	2.336(4)	2.300(2)	2.310(4)	2.328(4)
M-S1	-	-	-	2.314(4)
M-Cl	2.347(4)	2.352(2)	2.359(3)	-
P1-M-P2	97.6(1)	97.60(8)	98.4(1)	96.7(2)
S-Pd-P1	86.9(1)	86.4(8)	87.9(1)	87.2(1)
S-M-P2	173.1(1)	175.99(8)	173.7(1)	176.1(1)
Cl-M-P2	87.9(1)	90.30(7)	89.1(1)	-
Cl-M-P1	174.0(1)	170.63(8)	171.4(1)	-
Cl-M-S	87.8(1)	85.81(8)	84.6(1)	-
S-M-S1	-	-	-	88.2(1)
S1-M-P1	-	-	-	174.6(2)
S1-M-P2	-	-	-	88.0(2)

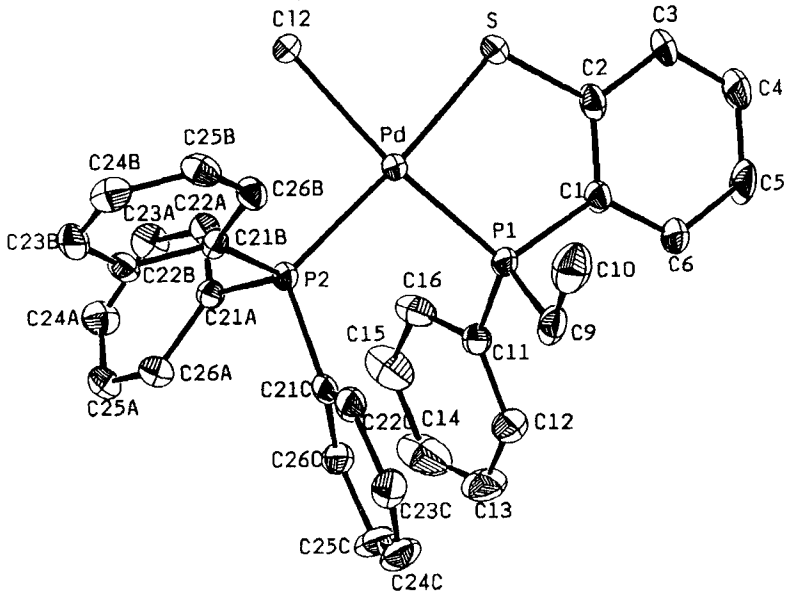


FIGURE 3 ORTEP plot of complex **5b**.

planar geometry, as expected; the crystal structure of complex **6c** confirms its formulation as a metal ion surrounded by two chelate *o*-C_6H_4(PPhEt)(S) ligands. All bond distances and bond angles (Table V) are similar to each other in the complexes tested, except M—P in **6c**. The difference 0.07 Å between M—P1 and M—P2 of **6c** is believed to be due to crystal packing, as the ^{31}P NMR spectrum shows only a singlet signal of **6c**, indicating two phosphorus atoms having at the same environment. The crystal structure of **6c** clearly shows the stereo-relationship of two ethyl

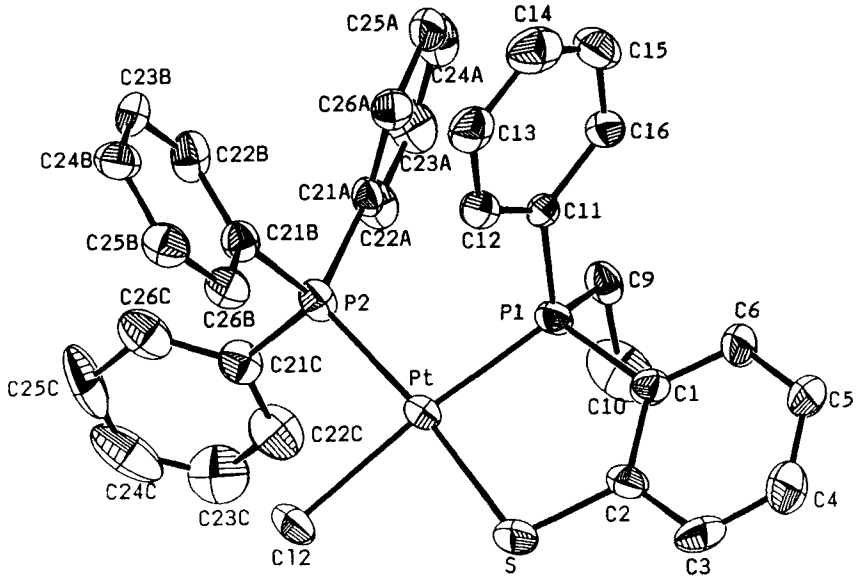


FIGURE 4 ORTEP plot of complex **5c**.

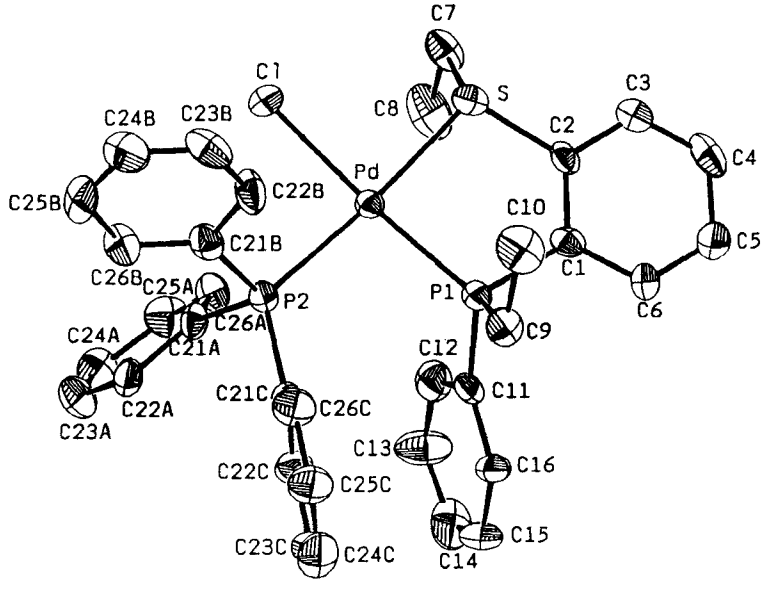


FIGURE 5 ORTEP plot of cation of $[(2)Pd(PPh_3)Cl]^+$.

groups being in a *trans* fashion with respect to the coordination plane. Distances of metal-sulfur bonds vary from coordination in sulfide or thiolato modes, indicated in Table V. The bond Pd—S in **3b** is shorter than that in **4b′** because of the *trans* influence of triphenylphosphine.

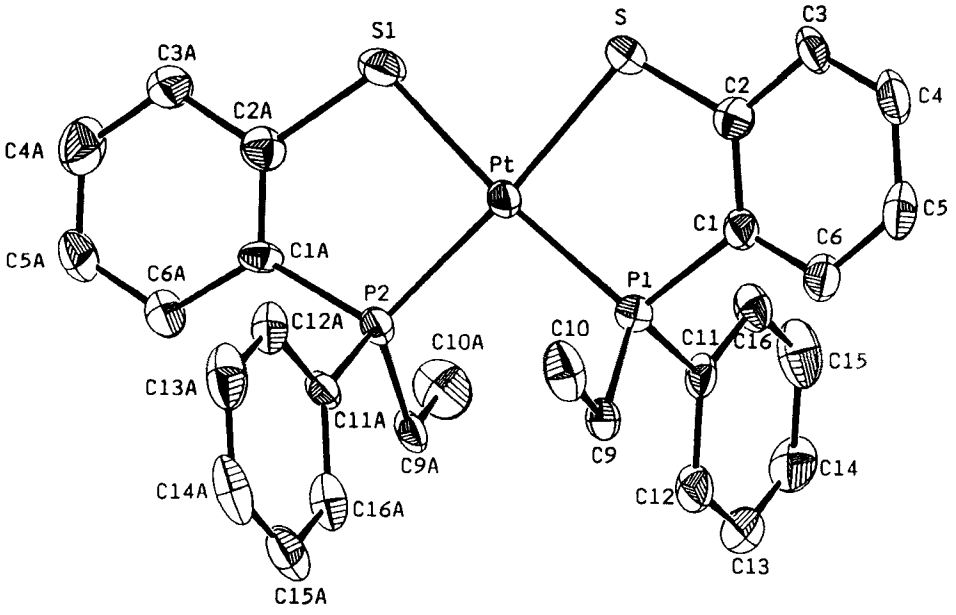


FIGURE 6 ORTEP plot of complex **6c**.

SUMMARY

Here we describe coordination study of a bidentate P—S ligand toward nickel, palladium and platinum complexes. The nickel complex **3a** was inert toward further ligand substitution by a phosphine ligand, whereas complexes **3b–c** readily underwent replacement of chloride by triphenylphosphine. The design of the stereogenic center at the phosphorus center allows us to investigate inversion at the sulfur center in this system. Dealkylation at the sulfur center is observed in the triphenylphosphine substituted palladium (II) and platinum (II) complexes.

ACKNOWLEDGEMENT

We thank the National Science Council of the Republic of China (NSC84-2113-M-002-18) for financial support. Supplementary data available: All atomic coordinates, anisotropic thermal parameters, bond distances and bond angles of *syn*-**3a**, *syn*-**3b**, *syn*-**3c**, **4b′**, **5b** and **6c** are available from authors.

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