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Synthesis, Characterization, and Reactivity of Platinum(II) Complexes of a Mesocyclic Ligand, 5-Phenyl-1-thia-5-phosphacyclooctane[†]

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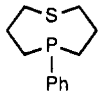
Four platinum(II) complexes of the mesocyclic ligand 5-phenyl-1-thia-5-phosphacyclooctane (8-PS) were prepared and characterized: dichloro(5-phenyl-1-thia-5-phosphacyclooctane)platinum(II) (**1**), diiodo(5-phenyl-1-thia-5-phosphacyclooctane)platinum(II), (**3**), *a*-chloro-*b*-methyl-*cd*-(5-phenyl-1-thia-5-phosphacyclooctane-*P*,*S*)platinum(II) or (*E*,*Z*)-chloromethyl(5-phenyl-1-thia-5-phosphacyclooctane)platinum(II) (**4**), and *cis*-bis(5-phenyl-1-thia-5-phosphacyclooctane)platinum(II) tetraphenylborate (**5**). The solution-phase structures of the above complexes were supported by ^{31}P NMR studies and crystal structure determinations. The crystal structure of a platinum(II) complex of the first saturated 16-membered ring phosphine–thioether, (η^4-5,13-diphenyl-1,9-dithia-5,13-diphosphacyclohexadecane)platinum(II) dichloride (**2**), is also reported. The reactions of **4** with a variety of substrates were examined by ^{31}P NMR spectroscopy: the ionic species [Pt-*a*-CH_3-*bc*(η^2-8-PS)-*d*-PPh_3]Cl or [(*Z*,*Z*)-PtCH_3-(η^2-8-PS)PPh_3]Cl and the binuclear dimer *cis*-Pt_2(η^1-8-PS-*P*)$_2$$Me_2Cl_2$($\mu$-DPP) were formed when **4** was treated with triphenylphosphine (1 equiv) and 1,3-bis(diphenylphosphino)propane (0.5 equiv), respectively. Crystal data are as follows. For $PtCl_2$(8-PS)·CH_3CN (**1**): $a = 10.839$ (8) Å, $b = 10.174$ (4) Å, $c = 15.642$ (12) Å, $\beta = 94.70$ (6)°, $Z = 4$ in the monoclinic space group $P2_1/c$. For Pt(η^4-16-*t*-PSPS)]Cl_2·CH_2Cl_2 (**2**): $a = 8.354$ (2) Å, $b = 9.429$ (2) Å, $c = 11.758$ (3) Å, $\alpha = 103.45$ (2)°, $\beta = 101.72$ (2)°, $\gamma = 107.41$ (2)°, $Z = 1$ in the triclinic space group $P\bar{1}$. For PtI_2(8-PS) (**3**): $a = 11.476$ (3) Å, $b = 17.666$ (3) Å, $c = 15.810$ (3) Å, $\beta = 93.33$ (2)°, $Z = 8$ in the monoclinic space group $C2/c$. For Pt(8-PS)MeCl·CH_2Cl_2 (**4**): $a = 10.301$ (4) Å, $b = 10.986$ (5) Å, $c = 14.976$ (7) Å, $\alpha = 98.67$ (6)°, $\beta = 92.90$ (6)°, $\gamma = 96.78$ (6)°, $Z = 4$ in the triclinic space group $P\bar{1}$. For *cis*-[Pt(8-PS)$_2$](BPh_4)$_2$ (**5**): $a = 18.966$ (5) Å, $b = 14.071$ (2) Å, $c = 23.559$ (5) Å, $\beta = 106.85$ (2)°, $Z = 4$ in the monoclinic space group $P2_1/n$.

Introduction

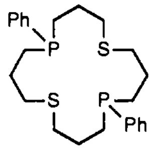
Increasing attention has recently been focused on the concept of preparing low-valent transition-metal complexes containing mixed bidentate ligands that possess one strong and one weak donor atom.[1,2] The value of such ligands with respect to homogeneous catalysis lies in the susceptibility of the weak donor to displacement by an incoming substrate molecule whereas the chelate effect provides additional stability to the catalytic precursor in the absence of the substrate. Molecules containing one phosphine and one thioether group are typical examples of mixed bidentate ligands, but fewer coordination compounds containing P,S donor ligands have been explored than those with either P,P or S,S donors.[3] Pt and Pt complexes of acyclic ambidentate ligands with dissimilar donor sites, such as $Ph_2P(CH_2)_nSPh$ (n = 1, 2) have been reported by Sanger,[1] and complexes of unsaturated 14-membered macrocyclic mixed P,S ligands with metals within the Ni(II) triad have been reported by Kyba.[4]

Mesocyclic bidentate molecules may be particularly useful ligands to facilitate some catalytic processes because they are more rigid than acyclic molecules, but they are less rigid than macrocyclic molecules and rarely bridge metal centers. Therefore, when the weak donor atom is detached in a catalytic process, it can readily recoordinate later. A few complexes of mesocyclic ligands with mixed donors are known, but little chemistry has been carried out on their complexes. Kauffman reported that the As,S mesocycle 5-phenyl-1-thia-5-arsacyclooctane is formed as a byproduct in the synthesis of the 16-membered macrocycle 5,13-diphenyl-1,9-dithia-5,13-diarsacyclohexadecane[5] but no additional chemistry of the complex was reported. A detailed spectroscopic study has been performed on Pt(II) complexes of an N,S mesocycle, 5-methyl-1-thia-5-azacyclooctane (TACO), but no reactions of this complex were done.[6]

We have recently synthesized a new mesocycle, 5-phenyl-1-thia-5-phosphacyclooctane (8-PS), containing sulfur and phosphorus atoms in the 1- and 5-positions, respectively. (Details of the synthesis, characterization, properties, and X-ray data for the 8-PS ligand will be reported elsewhere.) A number of reactions were carried out with the 8-PS ligand; the synthesis of a series of Pt(II) complexes and some reactions of the chloro complex will be the primary focus of this report.



8-PS



16-*t*-PSPS

Experimental Section

Melting points were determined by using either a Nagle hot stage or a Thomas-Hoover capillary melting point apparatus. Infrared spectra were recorded on an IBM IR-32 spectrophotometer; far-infrared measurements were obtained with either a Perkin-Elmer 1800 spectrophotometer or a Specac far-IR Michaelson interferometer. Samples for far-IR analysis (700–100 cm^{-1}) were prepared as either pressed polyethylene pellets or as Nujol mulls encased in polyethylene envelopes. All other IR samples were prepared as KBr pellets unless noted otherwise. Ultraviolet–visible spectra were obtained on a Hewlett-Packard 8450A UV-visible spectrophotometer. Solution spectra were run in either 1-mm matched quartz cells purchased from Helma Optics or in 1-cm matched quartz cells from RHO Scientific, Inc. Routine proton and carbon-13 {^{1}H} NMR spectra were run on either Nicolet NT-360 or General Electric QE-300 spectrometers. Chemical shift values are given in ppm downfield from internal tetramethylsilane. ^{31}P broad-band proton-decoupled NMR spectra were collected on a Nicolet NT-200 FT spectrometer, operating at 80.99 MHz. All chemical shift values are reported relative to an external 85% H_3PO_4 reference standard. All microanalyses were carried out by the Berkeley Microanalytical Laboratory, Berkeley, CA. All mass spectral data were collected by the Facility for Advanced Instrumentation, University of California, Davis, CA. Gravity column chromatog-

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[†] The naming of complex 4 in this paper has been done according to currently accepted IUPAC nomenclature (IUPAC. *Nomenclature of Inorganic Chemistry. Definitive Rules 1970*; Butterworths: London, 1971) where alphabetical order (the substituent with the lowest letter in the alphabet is arbitrarily assigned as *a*) is used in parallel with a possible new nomenclature for planar complexes with four different substituents. This nomenclature is an extension of the *E* and *Z* system of nomenclature that organic chemists use to name complicated cis and trans alkenes. The extension of the *E*,*Z* system to planar complexes involves prioritizing the substituents according to their atomic numbers and then noting the relationship of groups of priority 1 and 2 with respect to the metal by *E* for trans and *Z* for cis. Next, the relationship of groups 1 and 3 is determined by *E* or *Z*. The relationship of groups 1 and 4 do not have to be specified.

(1) Sanger, A. R. *Can. J. Chem.* **1983**, *61*, 2214.
(2) Anderson, G.; Kumar, R. *Inorg. Chem.* **1984**, *23*, 4064.
(3) Stelzer, O. *Transition Metal Complexes of Phosphorus Ligands*; Griffith, E. J., Grayson, M., Eds.; Wiley-Interscience: New York, 1977; p 65.
(4) Kyba, E. P.; Davis, R. E.; Fox, M. A.; Clubb, C. N.; Liu, S.-T.; Reitz, G. A.; Scheuler, V. J.; Kashyap, R. P. *Inorg. Chem.* **1987**, *26*, 1647.
(5) Kauffman, T.; Ennen, J. *Chem. Ber.* **1985**, *118*, 2703.
(6) Hirschon, A. S.; Musker, W. K.; Olmstead, M. M.; Dallas, J. L. *Inorg. Chem.* **1981**, *20*, 1702.

0020-1669/90/1329-0691$02.50/0

Table I. Summary of Crystal Data, Data Collection, and Structure Refinement Parameters for Compounds **1**–**5**[a,b]

	1	**2**	**3**	**4**	**5**
formula	$PtC_{12}H_{17}PSCl_2 \cdot CH_3CN$	$PtC_{24}H_{34}P_2S_2Cl_2 \cdot CH_2Cl_2$	$PtC_{12}H_{17}PSI_2$	$PtC_{13}H_{20}PSC \cdot CH_2Cl_2$	$PtC_{72}H7_4P_2S_2B_2$
fw	530.9	799.53	673.17	554.35	1282.17
crystal system	monoclinic	triclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/c$, No. 14	$P\bar{1}$, No. 2	$C2/c$, No. 15	$P\bar{1}$, No. 2	$P2_1/n$, No. 14
a, a	10.839 (8)	8.354 (2)	11.476 (3)	10.301 (4)	18.966 (5)
b, Å	10.174 (4)	9.429 (2)	17.666 (3)	10.986 (5)	14.071 (2)
c, Å	15.642 (12)	11.758 (3)	15.810 (3)	14.976 (7)	23.559 (5)
α, deg		103.45 (2)		98.67 (6)	
β, deg	94.70 (6)	101.72 (2)	93.3 (2)	92.90 (6)	106.85 (2)
γ, deg		107.41 (2)		96.78 (6)	
V, Å^3	1719 (2)	821.5 (3)	3200 (2)	1660 (1)	6017 (2)
Z	4	1	8	4	4
cryst dimens, mm	0.4 × 0.37 × 0.2	0.13 × 0.09 × 0.08	0.45 × 0.32 × 0.15	0.20 × 0.25 × 0.10	0.07 × 0.15 × 0.15
ρ_{calcd}, g cm^{-3}	2.05	1.62	2.79	2.22	1.42
μ (Mo Kα), cm^{-1}	91.09	50.38	132.43	94.11	26.1
range of transmissn factors	0.05–0.53	0.59–0.71	0.03–0.2	0.18–0.29	0.70–0.86
R[c]	0.040	0.038	0.084	0.033	0.072
R_w[c]	0.021	0.041	0.081	0.037	0.064

[a] a $P2_1$ difrractometer (T = 130 K) was used for collection of all data (Mo Kα, λ = 0.71069 Å). [b] $F > 4\sigma(F)$ for **1**, **3**, **4**, and **5** and $F \geq 6\sigma(F)$ for **2**. [c] $R = \sum||F_o| - |F_c||/|F_o|$ and $R_w = \sum||F_o| - |F_c||w^{1/2}|$,where $w = 1/\sigma^2(F_o)$ for **1**, **3**, and **4**, and **5**, and the weight scheme $w = 1/[\sigma^2(F_o) + gF_o^2]$ was used for **2** to put the weight an approximately absolute scale. g was refined by fitting $(F_o - F_c)^2$ to $[\sum(F) + (\mathrm{abs}(g))F^2)/K]^2$, where K is a scale factor. For **2**, g = 0.002 and K = 1.209.

raphy was performed with silica gel purchased from J. T. Baker Chemical Co. as the solid support, 60–200 mesh. Flash column chromatography was performed with silica gel 60 purchased from E. M. Science, 230–400 mesh ASTM, 0.040–0.063 mm. Thin-layer chromatography was carried out with precoated silica gel 60 F_{254} plastic sheets, 0.2-mm layer thickness, purchased from Merck.

Dichloro(1,5-cyclooctadiene)platinum(II) and diiodo(1,5-cyclooctadiene)platinum(II) were prepared by modifications of the method of Clark and Manzer.[7] Dimethyl sulfoxide (Mallinckrodt, Inc.) was distilled from BaO under reduced pressure and stored over Kodak 3-Å sieves. 1,3-Bis(diphenylphosphino)propane (98%), and tetramethyltin (99+%) were purchased from Aldrich Chemical Co., Inc. Triphenylphosphine (Aldrich Chemical Co., Inc.) was recrystallized from cyclohexane to yield white prisms. Solvents for all complexation reactions were deoxygenated by purging with either Ar or N_2 for a minimum of 15 min prior to use.

Dichloro(5-phenyl-1-thia-5-phosphacyclooctane)platinum(II), $PtCl_2(PhPC_6H_{12}S)$ (1). $Pt(COD)Cl_2$ (0.293 g, 0.790 mmol) was dissolved in 7.0 mL of CH_2Cl_2 to which a solution of 8-PS (0.176 g, 0.785 mmol, 0.14 M in CH_2Cl_2) was added dropwise. Upon mixing, the two colorless solutions became yellow. The mixture was refluxed for 18 h, during which time a white solid precipitated out of solution. The solid was filtered, washed with diethyl ether, and dried in vacuo (0.351 g, 92%). The solid, which exhibits very limited solubility, was recrystallized from hot DMSO–C_2H_5OH; however, attempts to produce single crystals by this method proved unsuccessful. ^{31}P NMR ($CDCl_3$–CH_2Cl_2): δ 1.6, ^1J(Pt,P) = 3424 Hz. Far-IR: 280, 322.4 cm^{-1} (Pt–Cl). Mp: >300 °C. Anal. Calcd for $C_{12}H_{17}Cl_2PSPt$: C, 29.39; H, 3.47. Found: C, 29.06; H, 3.49.

(η^4-5,13-Diphenyl-1,9-dithia-5,13-diphosphacyclohexadecane)platinum(II) Dichloride, $[PtC_{24}H_{34}P_2S_2]Cl_2$ (2). A second compound was also isolated from the above-mentioned CH_2Cl_2 filtrate solution from **1**; X-ray analysis revealed the platinum to be bound to the homologous 16-membered ring tetradentate ligand to form (η^4-5,13-diphenyl-1,9-dithia-5,13-diphosphacyclohexadecane)platinum(II) dichloride. A mass spectrum of a sample of the 8-PS ligand included a peak with twice the mass of the eight-membered-ring mesocycle, indicating that the 16-membered-ring macrocycle, 16-*t*-PSPS, was formed during the cyclization reaction as well. TLC, flash column chromatography, and HPLC were unsuccessful in the detection and/or isolation of the 16-membered ring macrocycle, which we suspect was formed in very small yield.

Diiodo(5-phenyl-1-thia-5-phosphacyclooctane)platinum(II), $PtI_2(PhPC_6H_{12}S)$ (3). A solution of 8-PS (0.0945 g, 0.421 mmol, 0.14 M in CH_2Cl_2) was added dropwise to a solution of $Pt(COD)I_2$ (0.166 g, 0.298 mmol) in 5 mL of CH_2Cl_2 under a dry nitrogen atmosphere. The mixture was refluxed for 24 h, cooled to room temperature, and stirred for an additional 8 h. The solid yellow precipitate was filtered, rinsed with diethyl ether, and dried in vacuo (0.149 g, 74%). ^{31}P NMR ($CDCl_3$): δ −5.6, ^1J(Pt,P) = 3436 Hz. Far-IR: 138, 182 cm^{-1} (Pt–I). UV–vis ($CHCl_3$): λ_{max} = 370 nm, ϵ = 2.6 × 10^3 M^{-1} cm^{-1}. Mp: >260 °C dec.

***a*-Chloro-*b*-methyl-*cd*-(5-phenyl-1-thia-5-phosphacyclooctane-*P*,*S*)-platinum(II) or (*E*,*Z*)-Chloromethyl(5-phenyl-1-thia-5-phosphacyclooctane)platinum(II), $PtClCH_3(PhPC_6H_{12}S)$ (4).** $PtCl_2$(8-PS) (0.343 g, 0.701 mmol) and 7.5 mL of dimethyl sulfoxide were added to a three-neck flask fitted with a septum, reflux condenser, and vacuum adapter. The mixture was vacuum degassed, and the remainder of the reaction was performed under a dry nitrogen atmosphere. Tetramethyltin (0.970 mL, 7.01 mmol) was added and the mixture stirred for 2 h at room temperature. The temperature was raised to 75 °C, additional $SnMe_4$ (0.700 mL) was added, and the reaction mixture was stirred for an additional 16 h. The dimethyl sulfoxide and volatile Sn-containing products were removed by vacuum distillation. The remaining residue was dissolved in a minimum amount of chloroform, any undissolved were removed by filtration, and the filtered solution was chromatographed on Baker silica gel by using 10% C_2H_5OH in $CHCl_3$. The main product was a white solid (0.254 g, 77%) with R_f = 0.43 (EM Merck silica gel plates, 10% C_2H_5OH in $CHCl_3$). ^1H NMR ($CDCl_3$): δ 0.435 (–CH_3), ^2J(Pt,H) = 76.2 Hz, ^3J(P,H) = 3.6 Hz. ^{31}P NMR ($CDCl_3$): δ −2.1, ^1J(Pt,P) = 4219 Hz. Far-IR: 253, 278, 281, 288 cm^{-1}. Mp: >245 °C dec. ^{13}C NMR ($CDCl_3$): δ 130.5 (para), ^4J(P,C) = 2.2 Hz; δ 130.1 (meta), ^3J(P,C) = 8.8 Hz; δ 128.6 (ortho), ^2J(P,C) = 10.5 Hz; ipso C not detected; δ 30.4, ^2J(P,C) = 4.6 Hz; δ 24.9, ^3J(P,C) = 0 Hz, ^2J(Pt,C) = 48 Hz; δ 22.3, ^1J(P,C) = 38 Hz, ^1J(Pt,C) = 23 Hz; δ −0.94, $^2J(P_{cis},C)$ = 4.0 Hz; S/N too low to detect ^{195}Pt satellites.

***cis*-Bis(5-phenyl-1-thia-5-phosphacyclooctane)platinum(II) Tetraphenylborate, *cis*-$[Pt(PhPC_6H_{12}S)_2](B(C_6H_5)_4)_2$ (5).** The ligand, 8-PS (0.129 g, 0.575 mmol), and an excess of $NaBPh_4$ (0.398 g, 1.16 mmol) were dissolved in 16.0 mL of dry, absolute ethanol. A 0.16 M aqueous solution of K_2PtCl_4 (0.119 g, 0.286 mmol) was added dropwise. Upon addition of the K_2PtCl_4, a white solid precipitated from the reaction mixture. The mixture was stirred for 2.5 h at room temperature and then filtered. The white solid was washed with successive portions of acetonitrile (20, 10, and 10 mL). The pale yellow acetonitrile washes were combined and filtered through a pad of Celite to remove any traces of undissolved material. The resultant solution was concentrated to yield a white solid, which was washed with small portions of water, ethanol, and diethyl ether and then air-dried (0.3517 g, 96%). ^{31}P NMR (CD_3CN): δ 11.1, ^1J(Pt,P) = 3076 Hz. Anal. Calcd for $C_{72}H_{74}B_2P_2S_2Pt$: C, 67.5; H, 5.8. Found: C, 66.8; H, 5.9.

X-ray Structure and Determination. Crystals of **1** were grown by slow liquid diffusion of diethyl ether into a dilute solution of the complex in acetonitrile. (Complex **1** is fairly insoluble in most common solvents.) Single crystals of **2** were isolated from the filtrate from the reaction of $Pt(COD)Cl_2$ with 5-phenyl-1-thia-5-phosphacyclooctane after the bulk of the major product, **1**, had been removed by filtration. Crystals of **3** were grown by slow liquid diffusion of absolute ethanol into a concentrated solution of the complex in DMSO. Crystals of **4** were grown by slow liquid diffusion of diethyl ether into a concentrated solution of the complex in methylene chloride. Crystals of **5** were grown by slow liquid diffusion of diethyl ether into a concentrated solution of the complex in acetonitrile. Crystals of **1**, **2**, **4**, and **5** were colorless parallelepipeds; crystals of **3** were yellow parallelepipeds.

The main details of the crystal data, data collection methods, and refinement procedures for complexes **1**–**5** are given in Table I. A more

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(7) Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *59*, 411.

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^3) for Pt(8-PS)Cl_2·CH_3CN (**1**)

	x	*y*	*z*	U^a
Pt	3823 (1)	7244 (1)	5133 (1)	11 (1)
Cl(1)	5406 (2)	7901 (2)	6131 (2)	19 (1)
Cl(2)	2427 (2)	7087 (3)	6213 (2)	21 (1)
S	2209 (2)	6640 (3)	4212 (1)	15 (1)
P	4943 (2)	7315 (3)	4017 (2)	13 (1)
C(1)	1978 (9)	7885 (10)	3361 (6)	18 (3)
C(2)	2958 ()	8959 (10)	3377 (6)	17 (3)
C(3)	4280 (8)	8525 (10)	3230 (6)	16 (3)
C(4)	4934 (9)	5755 (10)	3444 (6)	16 (3)
C(5)	3663 (8)	5359 (9)	5039 (6)	18 (3)
C(6)	2648 (9)	5209 (9)	3634 (6)	16 (3)
C(7)	6561 (9)	7696 (10)	4211 (6)	17 (3)
C(8)	7451 (9)	6692 (12)	4274 (6)	23 (3)
C(9)	8693 (10)	6989 (14)	4449 (8)	36 (4)
C(10)	932 (9)	1681 (15)	5445 (7)	35 (4)
C(11)	8195 (10)	9301 (12)	4496 (7)	29 (4)
C(12)	6960 (10)	8990 (12)	4336 (7)	27 (4)
N	58 (10)	9816 (11)	7319 (9)	53 (4)
C(13)	−472 (11)	8899 (11)	7128 (8)	33 (4)
C(14)	−1167 (15)	7683 (11)	6911 (11)	48 (5)

[a] Equialent isotropic *U* defined as one-third of the trace of the orthongalized U_{ij} tensor.

complete table as well as full listings of bond lengths and angles, hydrogen atom coordinates, and calculated and observed structure factors for the above complexes are provided in the supplementary material, Tables S1–S24.

The crystals of the title complexes were mounted in the cold stream of a Syntex $P2_1$ graphite-monochromated diffractometer (Mo Kα, λ = 0.710 69 Å) equipped with a locally modified Syntex LT-1 low-temperature device (T = 130 K). All crystallographic computing was carried out by using SHELXTL, Version 5, installed on a Data General MV/10000 Eclipse Series computer. Neutral-atom scattering factors and corrections for anomalous dispersion were from common sources.[8]

Data was collected by using the ω-scan technique up to a $2\phi_{max}$ of 50° for compounds **1**, **3**, **4**, and **5** and $2\phi_{max}$ of 55° for compound **2**. In all cases, no decay in the intensities of two standard reflections was observed during the course of data collection. The structures of complexes **1**–**5** were solved by Patterson methods. An absorption correction was applied;[9] solution and refinement of structures **1**–**5** proceeded smoothly in all cases. Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms for **1**–**4**. Final refinement for **5** was carried out with anisotropic thermal parameters for Pt, P, and S atoms. Hydrogen atoms were included by using a riding model, with a C–H distance of 0.96 Å and $U_H = 1.2U_C$.

The space group of **1** was determined to be $P2_1/c$ (No. 14). The largest feature on a final difference map was 2.5 e Å^{-3} in height and 1.25 Å from Pt, and the largest shift/esd in the final cycle of refinement was 0.029 for *x* of C(3). Complex **2** crystallized in the triclinic crystal system. The centrosymmetric space group $P\bar{1}$ (No. 2) was assumed and confirmed by the successful solution and refinement of the structure. The largest feature on the final difference map was 2.37 e Å^{-3} in height and 0.87 Å from Pt. The largest shift/esd in the final cycle of refinement was 0.149 for *x* of S. The structure contains a molecule of dichloromethane, which is disordered in two positions with relative weights 3:1. The two positions have a common site for the carbon atom C(13). The space group for **3** was determined to be $C2/c$ (No. 15). The largest feature on the final difference map was 8.8 e Å^{-3} in height and 1.00 Å from Pt; the largest shift/esd in the final cycle of refinement was 0.281 for *x* of C(1). Compound **4** crystallized in the triclinic crystal system. The space group was determined to be $P\bar{1}$ (No. 2). The largest feature on the final difference map was 1.3 e Å^{-3} in height and 1.01 Å from Pt; the largest shift/esd in the final cycle of refinement was 0.010 for *x* of C(6). The structure of **5** was solved by using the space group $P2_1/n$ (No. 14). The largest feature on a final difference map was 1.84 e Å^{-3} in height and 0.94 Å from Pt, and the largest shift/esd in the final cycle of refinement was 0.013 for *x* of C(62). There are no short intermolecular contacts. Within the cation of **5**, P(1)···P(2) = 3.570 (9) Å and S(1)···S(2) = 3.234 (9) Å.

Table III. Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^3) for [Pt(16-*t*-PSPS)]Cl_2·CH_2Cl_2 (**2**)

	x	*y*	*z*	U^a
Pt	0	0	0	20 (1)*
S	2604 (2)	465 (1)	−506 (1)	25 (1)*
P	1130 (2)	2687 (1)	919 (1)	24 (1)*
C(1)	−2837 (7)	1204 (6)	1490 (5)	32 (2)*
C(2)	−1172 (7)	2557 (7)	2333 (5)	34 (2)*
C(3)	−247 (7)	3531 (6)	1629 (5)	31 (2)*
C(4)	1577 (7)	3711 (6)	−180 (5)	29 (2)*
C(5)	2897 (7)	3334 (6)	−812 (5)	31 (2)*
C(6)	2428 (7)	1633 (6)	−1539 (5)	30 (2)*
C(7)	3166 (7)	3364 (6)	2137 (4)	26 (2)*
C(8)	3678 (7)	2302 (6)	2642 (5)	30 (2)*
C(9)	5202 (8)	2846 (7)	3624 (5)	36 (2)*
C(10)	6222 (8)	4434 (8)	4090 (5)	39 (2)*
C(11)	5715 (8)	5482 (7)	3584 (5)	37 (2)*
C(12)	4197 (7)	4959 (6)	2620 (5)	30 (2)*
Cl(1)	3200 (2)	8115 (2)	1496 (1)	34 (1)*
Cl(2)	458 (6)	−2879 (5)	4088 (4)	70 (2)*
Cl(3)	3310 (4)	224 (3)	5561 (2)	59 (1)*
Cl(4)	1276 (10)	309 (9)	4581 (8)	58 (2)
Cl(5)	282 (15)	−2505 (12)	4126 (11)	45 (2)
C(13)	1933 (12)	−969 (14)	4127 (7)	84 (4)*

[a] A An asterisk denotes the equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table IV. Bond Lengths (Å) and Bond Angles (deg) for [Pt(11-t-PSPS)]Cl_2·CH_2Cl_2 (**2**)

Pt–S	2.315 (1)	Pt–P	2.315 (1)
S–C(6)	1.832 (7)	S–C(1A)^a	1.811 (6)
P–C(3)	1.812 (7)	P–C(4)	1.817 (6)
P–C(7)	1.813 (5)	C(1)–C(2)	1.528 (6)
S–Pt–P	83.3 (1)	P–Pt–S(a)	96.7 (1)
Pt–S–C(6)	103.4 (2)	Pt–S–C(1A)	116.3 (2)
Pt–P–C(3)	116.6 (2)	Pt–P–C(4)	111.3 (2)
Pt–P–C(7)	113.1 (2)		

[a] A = −*x*, −*y*, −*z*.

Table V. Atomic Coordinates (t 10^4) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^3) for Pt(8-PS)I_2 (**3**)

	x	*y*	*z*	U^a
Pt	2722 (1)	8971 (1)	9749 (1)	20 (1)
I(1)	4471 (2)	8586 (1)	8869 (1	30 (1)
I(2)	1460 (2)	9238 (1)	8331 (1)	36 (1)
S	1129 (7)	9340 (4)	10442 (5)	24 (2)
C(1)	1555 (30)	10121 (15)	11176 (20)	33 (12)
C(2)	2887 (26)	10297 (16)	11251 (24)	36 (12)
C(3)	3648 (27)	9663 (17)	11665 (23)	37 (12)
C(4)	2803 (28)	8118 (16)	11617 (21)	32 (11)
C(5)	1668 (27)	8381 (19)	11912 (19)	34 (11)
C(6)	706 (26)	8585 (18)	11136 (21)	34 (11)
C(7)	5073 (27)	8436 (17)	11082 (20)	29 (10)
C(8)	6035 (29)	8918 (17)	10958 (18)	31 (10)
C(9)	7225 (26)	8645 (19)	10915 (18)	28 (10)
C(10)	7387 (25)	7888 (16)	11021 (19)	24 (10)
C(11)	6560 (33)	7400 (18)	11160 (21)	42 (13)
C(12)	5367 (30)	7679 (18)	11161 (19)	35 (11)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Results

The synthesis and physical properties of complexes **1**–**5** are given in the Experimental Section. The sequence of reactions that were carried out on the complexes are given in Scheme I. Crystallographic data are given in the Experimental Section, in Tables I–IX and in the supplementary material.

Discussion

Dichloro(5-phenyl-1-thia-5-phosphacyclooctane)platinum(II) (1). Preparation of the dichloroplatinum(II) species was attempted by treating Pt(COD)Cl_2 with 1 equiv of 8-PS in methylene chloride (Scheme I). Due to the very limited solubility of the white

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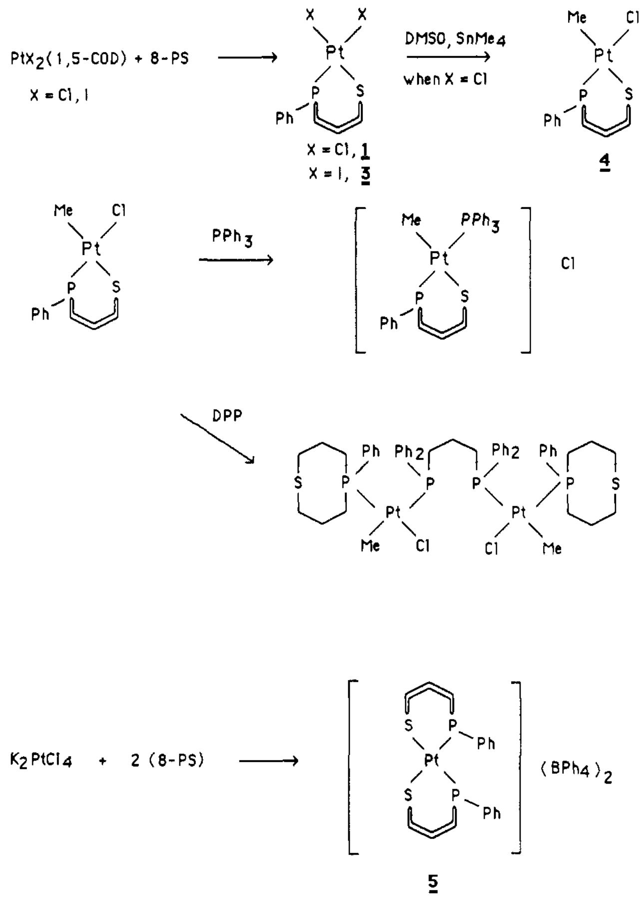
(8) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1976; Vol. IV.

(9) Program XABS: Hope, H.; Moezzi, B. University of California, Davis, CA. The program contains an absorption tensor from $F_o - F_c$ differences.

Scheme I



precipitate formed during the course of the reaction, the reaction was carried out on a smaller scale in a mixture of CH_2Cl_2 and $CDCl_3$ at room temperature, and the progress of the reaction was monitored by ^{31}P NMR spectroscopy.

Surprisingly, a phosphorus NMR spectrum of the 1:1 reaction mixture taken immediately after mixing revealed three platinum-containing species of similar intensities: δ 1.6, $^1J(\mathrm{Pt,P}) = 3424$ Hz; δ -2.3, $^1J(\mathrm{Pt,P}) = 2224$ Hz; δ -6.4 Hz, $^1J(\mathrm{Pt,P}) = 3314$ Hz. There was no indication of unreacted starting material.

The values of the one-bond coupling constants, $^1J(\mathrm{Pt,P})$, are quite diagnostic: they depend on the oxidation state of the metal, the trans influence of the remaining ligands in the complex, the chelate ring size, and the type of phosphorus ligand.[10] The peak at δ 1.6 has been tentatively assigned as belonging to the monomeric species *cis*-[Pt(8-PS)Cl_2] (**1**). Values of the one-bond platinum–phosphorus couplings in complexes of the type *cis*-$PtCl_2(PR_3)_2$ generally range from approximately 3500 to 3650 Hz;[11] the $^1J(\mathrm{Pt,P})$ value of 3424 Hz for the peak centered at 1.6 ppm falls roughly into this category. $^1J(\mathrm{Pt,P})$ values have also been reported for Pt(II) species in which the phosphorus atoms are trans to bound thioether sites; on the basis of previously reported coupling constant values in similar compounds, the value of 3314 Hz for the species centered at -6.4 ppm seems reasonable for the cis-bis(bidentate) platinum(II) dicationic species, *cis*-[Pt(η^2-8-PS)$_2$]$PtCl_4$.[6,12] The third species detected by ^{31}P NMR, centered at 2.3 ppm with a one-bond platinum–phosphorus coupling constant of 2224 Hz, has been assigned to the *trans*-(8-PS)$_2$ platinum(II) dicationic species *trans*-[Pt(η^2-8-PS)$_2$]$PtCl_4$. A large number of four-coordinate Pt(II) species containing alkyl- or aryl-substituted phosphine ligands with $^1J(\mathrm{Pt,P})$ values in this range have a trans "Pt–P–P" unit.[11]

Table VI. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^3$) for Pt(8-PS)MeCl·CH_2Cl_2 (**4**)

	x	*y*	*z*	U^a
Pt	1143 (1)	1997 (1)	4424 (1)	16 (1)
Cl(1)	-468 (2)	3228 (2)	4034 (1)	27 (1)
S	1060 (2)	1069 (2)	2881 (1)	23 (1)
P	2587 (2)	759 (2)	4689 (1)	18 (1)
C(1)	1235 (8)	2882 (8)	5763 (5)	21 (3)
C(2)	4036 (8)	1014 (8)	4020 (6)	26 (3)
C(3)	3797 (10)	1778 (8)	3262 (6)	32 (3)
C(4)	2742 (9)	1226 (8)	2517 (6)	26 (3)
C(5)	696 (8)	-608 (7)	2836 (6)	24 (3)
C(6)	1686 (10)	-1263 (8)	3315 (6)	28 (3)
C7	1938 (8)	-878 (8)	4342 (6)	23 (3)
C(8)	3248 (8)	822 (8)	5850 (5)	20 (3)
C(9)	4246 (8)	1786 (8)	6231 (6)	24 (3)
C(10)	4749 (9)	1841 (8)	7107 (6)	25 (3)
C(11)	4232 (9)	989 (9)	7640 (6)	32 (3)
C(12)	3212 (9)	80 (8)	7267 (6)	31 (3)
C(13)	2727 (8)	5 (8)	6384 (6)	25 (3)
Pt(A)	7569 (1)	3898 (1)	-14 (1)	16 (1)
Cl(1A)	7527 (2)	1995 (2)	-1009 (1)	27 (1)
S(A)	8149 (2)	2894 (2)	1211 (1)	23 (1)
P(A)	7776 (2)	5626 (2)	960 (1)	18 (1)
C(1A)	7020 (8)	4729 78)	-1111 (5)	19 (3)
C(2A)	9449 (9)	5962 (9)	1500 (7)	31 (3)
C(3A)	9791 (9)	5039 (8)	2126 (6)	28 (3)
C(4A)	9742 (9)	3693 (9)	1688 (6)	29 (3)
C(5A)	7070 (9)	3260 (8)	2127 (6)	30 (3)
C(6A)	6137 (8)	4178 (8)	1977 (5)	23 (3)
C(7A)	6714 (8)	5505 (7)	1908 (5)	20 (3)
C(8A)	7455 (9)	7038 (8)	569 (5)	23 (3)
C(9A)	8426 (10)	8030 (8)	491 (6)	32 (3)
C(10A)	8083 (10)	9054 (8)	176 (7)	35 (3)
C(11A)	6819 (10)	9187 (9)	-78 (6)	34 (3)
C(12A)	5850 (10)	8215 (8)	-31 (6)	30 (3)
C(13A)	6146 (9)	7147 (8)	275 (6)	26 (3)
Cl(2)	6186 (3)	3946 (3)	4539 (2)	50 (1)
Cl(3)	6867 (3)	4577 (3)	6480 (2)	41 (1)
C(14)	7344 (11)	4695 (10)	5393 (7)	43 (4)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Cis complexes are generally formed when the complex precursor is potassium tetrachloroplatinate(II) or (cyclooctadiene)dichloroplatinum(II); the utilization of a bidentate ligand with a relatively short backbone also favors the formation of cis complexes. The insoluble Magnus-type salts [Pt(L~L)$_2$]PtX_4 may rearrange to [Pt(L~L)X_2], depending on the nature of the ligand employed.[13]

As the reaction proceeded, the major species that remained in solution is *cis*-[Pt(8-PS)Cl_2], which exhibited a ^{31}P chemical shift at δ 1.6. This chemical shift assignment is supported by the fact that this species should be much more soluble in organic solvents ($CHCl_3$–CH_2Cl_2) than the two ionic salt species *cis*- and *trans*-[Pt(η^2-8-PS)$_2$]$PtCl_4$. On the basis of the stoichiometry employed, a 1:1 platinum:ligand ratio, an X-ray crystal structure, far-infrared data, and the high yields of Pt(8-PS)(Cl)(R) obtained from reacting the product of the above reaction with a methylating agent, it was concluded that the other two species that were observed in solution by ^{31}P NMR spectroscopy were intermediates, which, with time, equilibrated to form the thermodynamically favored product Pt(8-PS)Cl_2 (**1**). Similar observations have been reported by Anderson et al., who have studied the reactions of [$PtCl_2L_2$] (L = 1,5-COD, RCN) with bidentate ligands.[14]

The infrared data for **1** are listed in the Experimental Section. Metal–halogen stretching frequencies in compounds of the type *cis*-[PtL_2X_2] are very sensitive to ligand type and range from approximately 280 to 340 cm^{-1}.[15] A complex of cis geometry

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(10) Pregosin, P. S.; Kunz, R. W. In *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; NMR Basic Principles and Progress 16; Springer-Verlag: New York, 1979.

(11) See ref 10, p 42 and references therein.

(12) Roundhill, D. M.; Benefiel, A. *Inorg. Chem.* **1986**, *25*, 4027.

(13) Minahan, D. M. A.; Hill, W. E.; McAuliffe, C. A. *Coord. Chem. Rev.* **1984**, *55*, 31.

(14) Anderson, G.; Davies, J. A.; Schoek, D. J. *Inorg. Chim. Acta* **1983**, *76*, L 251.

(15) Hartley, F. R. *The Chemistry of Platinum and Palladium*; John Wiley: New York, 1973; p 242.

Table VII. Atomic Coordinates (× 10^4) and Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $[Pt(8\text{-}PS)_2](BPh_4)_2$ (**5**)

	x	y	z	U^a
Pt	106 (1)	3291 (1)	2568 (1)	13 (1)*
P(1)	−444 (2)	2317 (3)	1800 (2)	13 (1)*
P(2)	563 (2)	2286 (3)	3337 (2)	15 (1)*
S(1)	−53 (2)	4506 (3)	1849 (2)	22 (1)*
S(2)	372 (2)	4510 (3)	3281 (2)	26 (1)*
C(1)	87 (7)	2277 (8)	1260 (5)	15 (3)
C(2)	103 (7)	3223 (10)	961 (5)	26 (3)
C(3)	428 (7)	4078 (10)	1345 (6)	24 (3)
C(4)	−1015 (7)	4582 (10)	1414 (6)	24 (3)
C(5)	−1506 (7)	3836 (9)	1574 (5)	20 (3)
C(6)	−1353 (7)	2834 (8)	1422 (5)	15 (3)
C(7)	−662 (7)	1110 (9)	1945 (5)	13 (3)
C(8)	−380 (7)	346 (9)	1698 (5)	19 (3)
C(9)	−563 (7)	−570 (11)	1825 (6)	25 (3)
C(10)	−1035 (8)	−737 (11)	2178 (6)	29 (3)
C(11)	−1298 (8)	37 (1)	2411 (6)	28 (4)
C(12)	−1106 (7)	956 (10)	2306 (5)	22 (3)
C(13)	20 (8)	2334 (10)	3845 (6)	31 (4)
C(14)	−481 (7)	3251 (11)	3763 (6)	32 (3)
C(15)	−96 (8)	4201 (10)	3840 (6)	30 (4)
C(16)	1355 (7)	4480 (10)	3703 (6)	24 (3)
C(17)	1587 (8)	3582 (9)	4076 (6)	26 (3)
C(18)	1495 (7)	2662 (9)	3741 (6)	24 (3)
C(19)	723 (7)	1069 (10)	3162 (5)	22 (3)
C(20)	1145 (7)	888 (9)	2793 (5)	20 (3)
C(21)	1306 (7)	−6 (10)	2656 (5)	22 (3)
C(22)	1054 (7)	−768 (11)	2917 (6)	28 (3)
C(23)	620 (7)	−639 (10)	3288 (6)	23 (3)
C(24)	474 (8)	280 (10)	3431 (6)	30 (4)
C(25)	1387 (7)	6242 (9)	928 (5)	18 (3)
C(26)	2053 (7)	5729 (9)	1159 (5)	17 (3)
C(27)	2215 (8)	4896 (10)	914 (6)	27 (3)
C(28)	1713 (7)	4510 (10)	416 (5)	21 (3)
C(29)	1048 (7)	4972 (10)	184 (5)	21 (3)
C(30)	895 (7)	5824 (9)	432 (5)	17 (3)
C(31)	1272 (7)	8152 (9)	793 (5)	18 (3)
C(32)	1508 (7)	8074 (10)	268 (5)	24 (3)
C(33)	1508 (7)	8853 (10)	−92 (6)	27 (3)
C(34)	1296 (7)	9745 (10)	51 (6)	26 (3)
C(35)	1074 (9)	9835 (12)	553 (7)	42 (4)
C(36)	1061 (8)	9058 (11)	899 (6)	32 (4)
C(37)	310 (7)	7223 (9)	1191 (5)	19 (3)
C(38)	−233 (7)	7513 (9)	681 (5)	20 (3)
C(39)	−998 (8)	7505 (10)	632 (6)	25 (3)
C(40)	−1217 (8)	7251 (10)	1110 (6)	27 (3)
C(41)	−696 (7)	6983 (9)	1636 (5)	21 (3)
C(42)	49 (7)	6990 (9)	1669 (6)	23 (3)
C(43)	1744 (7)	7351 (10)	1888 (6)	23 (3)
C(44)	1824 (7)	6646 (11)	2311 (5)	27 (3)
C(45)	2287 (7)	6719 (12)	2888 (5)	29 (3)
C(46)	2712 (8)	7533 (11)	3061 (7)	34 (4)
C(47)	2662 (7)	8255 (12)	2660 (5)	32 (3)
C(48)	2192 (7)	8165 (11)	2085 (6)	29 (3)
C(49)	6516 (7)	13013 (9)	850 (5)	19 (3)
C(50)	6283 (8)	13930 (10)	964 (6)	27 (3)
C(51)	6443 (8)	14747 (11)	706 (6)	34 (4)
C(52)	6856 (8)	14669 (11)	292 (6)	28 (3)
C(53)	7087 (8)	13805 (10)	182 (6)	27 (3)
C(54)	6934 (7)	12983 (9)	444 (5)	23 (3)
C(55)	6488 (7)	11101 (9)	882 (5)	15 (3)
C(56)	7187 (8)	10689 (10)	1064 (6)	25 (3)
C(57)	7375 (7)	9834 (9)	821 (5)	22 (3)
C(58)	6863 (7)	9398 (9)	382 (5)	19 (3)
C(59)	6159 (7)	9763 (10)	163 (5)	21 (3)
C(60)	6005 (7)	10609 (9)	418 (5)	15 (3)
C(61)	6771 (7)	12057 (9)	1901 (5)	19 (3)
C(62)	6833 (7)	11253 (10)	2251 (6)	26 (3)
C(63)	7242 (7)	11199 (10)	2833 (6)	26 (3)
C(64)	7616 (8)	12009 (10)	3111 (6)	34 (4)
C(65)	7576 (8)	12832 (10)	2787 (6)	29 (3)
C(66)	7162 (7)	12838 (10)	2192 (5)	22 (3)
C(67)	5409 (7)	12145 (9)	1103 (5)	17 (3)
C(68)	5078 (7)	11860 (10)	1525 (5)	22 (3)
C(69)	4340 (7)	11915 (9)	1453 (5)	19 (3)
C(70)	3850 (8)	12251 (10)	928 (5)	25 (3)
C(71)	4152 (8)	12542 (10)	495 (6)	28 (3)
C(72)	4915 (7)	12481 (10)	577 (6)	25 (3)
B(1)	1194 (8)	7221 (11)	1211 (6)	15 (3)
B(2)	6311 (9)	12080 (11)	1190 (7)	22 (4)

[a] An asterisk denotes the equivalent isotropic U defined as one-third of the trace of the orthongalized U_{ij} tensor.

Table VIII. Selected Bond Distances (Å) and Angles (deg) for $Pt(8\text{-}PS)Cl_2$ (**1**) $Pt(8\text{-}PS)I_2$ (**3**), and $Pt(8\text{-}PS)MeCl$ (**4**)

	1 X(1), X(2) = Cl[a]	**3** X(1), X(2) = I[a]	**4** X(1) = C of Me, X(2) = Cl
Pt–X(1)	2.322 (2)	2.598 (3)	2.084 (7)
Pt–X(2)	2.363 (3)	2.639 (2)	2.365 (2)
Pt–P	2.207 (3)	2.242 (8)	2.191 (2)
Pt–S	2.258 (2)	2.280 (8)	2.374 (2)
X(1)–Pt–X(2)	91.1 (1)	89.7 (1)	89.9 (2)
X(1)–Pt–S	176.9 (1)	176.3 (2)	177.7 (2)
X(2)–Pt–S	86.0 (1)	86.6 (2)	88.9 (1)
X(1)–Pt–P	95.6 (1)	96.7 (2)	94.3 (3)
X(2)–Pt–P	173.2 (1)	173.6 (2)	175.6 (1)
S–Pt–P	87.2 (1)	86.9 (3)	87.0 (1)

[a] Atom X(1) is cis to the phosphorus atom of the 8-PS ligand.

Table IX. Selected Bond Angles (deg) and Bond Lengths (Å) for $[Pt(8\text{-}PS)_2](BPh_4)_2$ (**5**)

Pt–P(1)	2.267 (3)	Pt–S(1)	2.365 (4)
Pt–P(2)	2.263 (3)	Pt–S(4)	2.351 (4)
P(1)–Pt–P(2)	104.0 (1)	P(1)–Pt–S(1)	86.1 (1)
P(2)–Pt–S(1)	164.8 (1)	P(1)–Pt–S(2)	164.7 (1)
P(2)–Pt–S(2)	86.0 (1)	S(1)–Pt–S(2)	86.6 (1)

should display two infrared active platinum–halogen stretching frequencies. Unfortunately, Pt(II)-bound phosphine ligands often possess strong bands from 280 to 300 cm^{-1}, which have been related to asymmetric C–P–C deformations;[16] this often makes it difficult to assign M–X stretching frequencies with certainty.

A crystal structure verified the formation of *cis*-dichloro(5-phenyl-1-thia-5-phosphacyclooctane)platinum(II) (Tables I and II). 8-PS acts as a bidentate ligand by coordinating to the platinum atom through both the phosphorus and sulfur atoms; the mesocycle adopts a slightly distorted boat–chair conformation. In a similar chelate, $Pd(TACO)Cl_2$ (TACO = 5-methyl-1-thia-5-azacyclooctane), the coordinated eight-membered mesocycle was also shown to adopt a boat–chair rather than a chair–chair configuration;[5] a boat–chair conformation was similarly reported for the bidentate dithioether-bound mesocyclic ligand in the complex *cis*-dichloro(3-methylene-1,5-dithiacyclooctane)palladium(II).[17]

The core geometry about the platinum atom in **1** is slightly distorted square planar; the calculated distances (Å) from the best least-squares plane to these five atoms are as follows: Pt, −0.0082; Cl(1), 0.0133; Cl(2), −0.0100; S, 0.0149; P, −0.0100. The phenyl substituent on phosphorus is rotated about the P–C(7) bond away from the plane defined by Pt and the four directly bonded donor atoms by 100°. Selected bond lengths and bond distances are listed in Table VIII.

The Pt–Cl(2) bond distance (2.363 (3) Å) shows a substantial lengthening relative to the Pt–Cl(1) bond distance (2.322 (2) Å) due to the large trans influence of the phosphine moiety. The Pt–P and Pt–S bond lengths fall within the expected values;[18] in fact, the Pt–S distance (2.258 (2) Å) is essentially the same as that found in a similar dichloroplatinum(II) chelate, $[Pt(\text{L-methionine H})Cl_2]$, 2.26 Å.[19]

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(16) Chatt, J.; Leigh, G. J.; Mingos, D. M. *J. Chem. Soc. A* **1969**, 2972.

(17) Love, L. J. M.S. Thesis, University of California at Davis, 1985.

(18) See ref 15, p 135.

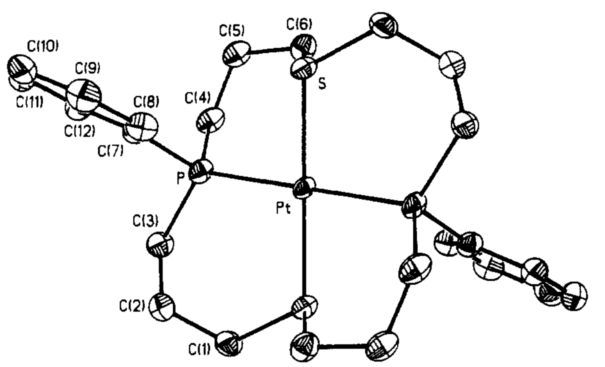

Figure 1. Molecular structure of the dication of **2**, (η^4-5,13-diphenyl-1,9-dithia-5,13-diphosphacyclohexadecane)platinum(II). The 50% probability ellipsoids are shown.

The P–Pt–Cl(1) bond angle is significantly greater than 90° (95.6 (1)°), presumably due to the repulsion between the phenyl substituent on phosphorus and the Cl(1) atom. Similarly, the N–Pd–Cl angle in dichloro(5-methyl-1-thia-5-azacyclooctane)palladium(II) is expanded to 95.5°; this has been attributed to the repulsion between the *N*-methyl group and the cis chlorine atom bound to palladium.[5] However, due to the orientation of the phenyl ring in **1**, the H(12) of the phenyl group is 3.6 Å away from Cl(1); no interaction is apparent. The rotation of the phenyl group away from the plane about platinum relieves the nonbonded repulsion between H(12) and Cl(1). Another possible explanation for the deformation of the P–Pt–Cl(1) bond angle is the nearly eclipsed conformation of the Cl(1)–Pt and P–C(7) bonds [torsion angle Cl(1)–Pt–P–C(7) = 3.9°]. In a similar chelate complex, *cis*-Pt(DPP)Cl_2 (DPP = 1,3-bis(diphenylphosphino)propane), both Cl–Pt–P bond angles deviate much less from the ideal planar value of 90°: 91.73 (3), 88.34 (3)°.[20] The nonbonded P···S distance in **1** is 3.081 Å.

(η^4-5,13-Diphenyl-1,9-dithia-5,13-diphosphacyclohexadecane)platinum(II) Dichloride (2). A second type of crystal was also isolated from the CH_2Cl_2 filtrate of the 1:1 reaction of $PtCl_2$(COD) and 8-PS after the main portion of the reaction mixture had been filtered from the solution; X-ray analysis (Figure 1) revealed the platinum to be bound to the homologous 16-membered ring tetradentate ligand to form (η^4-5,13-diphenyl-1,9-dithia-5,13-diphosphacyclohexadecane)platinum(II) dichloride (**2**) (Tables I, III, and IV). A mass spectrum of a sample of the 8-PS ligand verified that a small amount of the 16-membered macrocycle (*m/e* 448) had been formed during the cyclization reaction.

Although saturated ring systems containing exclusively sulfur donor atoms[21] or phosphorus donor atoms[22–24] are well characterized, no saturated macrocycles possessing combinations of both sulfur and phosphorus donors have been reported to date. The importance of macrocyclic multidentate phosphine–thioether ligands lies in their classification as phosphorus–sulfur analogues of the crown ethers as well as in the possible catalytic activity of their complexes. The formation of Pt(η^4-16-*t*-PSPS)Cl_2 (**2**) represents a platinum(II) complex of the first saturated 16-membered-ring phosphine–thioether, 5,13-diphenyl-1,9-dithia-5,13-diphosphacyclohexadecane (16-*t*-PSPS).

The Pt atom of **2** lies at the center of inversion symmetry so that only half of the macrocycle is in the asymmetric unit. The anion (Cl^-) is 3.974 Å away from the Pt atom. The P–Pt and S–Pt bond distances (2.315 (1) Å) are identical to within experimental error, and the central platinum atom and all four ligating sites lie within the same plane. The S–Pt–P angles vary significantly from the idealized square planar value of 90°; two P–Pt–S angles are 83.3 (1)° while the other two are 96.7 (1)°. In a similar but unsaturated macrocyclic tetradentate Pt(II) complex reported by Kyba,[4] *cis*-6,17-diphenyl-6,17-diphospha-2,13-dithiatricyclo[16.4.0.0]docosa-7(12),8,10,1(18),19,21-hexaene-$\kappa^2 S,\kappa^2 P$)platinum(II) diperchlorate, (*c*-PSPS-Pt)$(ClO_4)_2$, the analogous bond angles deviate from 90° by approximately ±3°: P(1)–Pt–S(1), 91.9°; P(1)–Pt–S(2), 87.5°; S(1)–Pt–P(2), 87.3°; P(2)–Pt–S(2), 93.3°. The P,S donor atoms in Kyba's 14-membered macrocycle are separated by alternating trimethylene bridges and 1,2-disubstituted phenyl rings as compared to the saturated 16-*t*-PSPS ligand, in which the alternating P,S atoms are each separated by a trimethylene unit. The phenyl substituents on the phosphorus atoms are trans; the plane of the phenyl ring is oriented at 112.9° to the square plane defined by Pt, P(1), and S(1). All of the η^4 six-membered rings are in chair conformations.

Diiodo(5-phenyl-1-thia-5-phosphacyclooctane)platinum(II) (3). The platinum(II) diiodo complex Pt(8-PS)I_2 (**3**) was prepared in a manner similar to **1** that used for by reacting Pt(COD)I_2 with 1 equiv of the 8-PS ligand. The product is a yellow solid that is fairly soluble in DMSO and somewhat soluble in chloroform. The product was dissolved in chloroform-*d* by Soxhlet extraction to form a solution sufficiently concentrated to examine by ^{31}P NMR spectroscopy (1 mM). The phosphorus NMR spectrum revealed one major product, δ −5.6, ^1J(Pt,P) = 3436 Hz, which was assigned to the 1:1 bidentate complex, **3**. The one-bond coupling constant value, ^1J(Pt,P), is almost identical with that of the platinum(II) dichloride species **1** (3424 Hz), in which the phosphino moiety is trans to a chloride ligand. This is somewhat surprising, since due to the larger trans influence of iodide relative to chloride, the ^1J(Pt,P) value should be smaller for the platinum diiodide complex than for the dichloride species.[25] This expected trend was observed, however, for the dichloro- and diiodoplatinum(II) species of 2-(methylthio)(diphenylphosphino)ethane, in which $PtI_2(\eta^2\text{-}Ph_2PCH_2CH_2SMe)$ exhibited a smaller ^1J(Pt,P) value, 3400 Hz, than that of the corresponding chloride complex, 3680 Hz.[12] Since a number of factors affect the values of one-bond metal–phosphorus coupling constants, the apparent contradiction between the ligand trans to P and the ^1J(Pt,P) values for the complexes Pt(8-PS)X_2, (X = Cl^-, I^-) is not easily accounted for. For example, a correlation was not observed between bond lengths and ^1J(Pt,P) values for the complexes *trans*-$PtI_2(PMe_3)_2$ and *trans*-$PtI_2(PCy_3)_2$. The Pt–P distances differ significantly for the two complexes; however, the ^1J(Pt,P) values were found to be similar and opposite from what one would expect on the basis of the Pt–P bond lengths: ^1J(Pt,PMe_3) = 2230 Hz, Pt–P = 2.315 Å; ^1J(Pt,PCy_3) = 2288 Hz, Pt–P = 2.371 Å.[26]

A minor product was also observed in the ^{31}P NMR spectrum of **3**, which, on the basis of relative integration values, was formed in approximately 4% yield. The minor component, δ −9.57, ^1J(Pt,P) = 2189 Hz, can be attributed to either the *trans*-bis(5-phenyl-1-thia-5-phosphacyclooctane)platinum(II) species, *trans*-[Pt(η^2-8-PS)$_2$]PtI_4, or the macrocyclic platinum(II) complex (η^4-5,13-diphenyl-1,9-dithia-5,13-diphosphacyclohexadecane)platinum(II) diiodide, which was detected by X-ray analysis as a minor product in the 1:1 reaction of Pt(COD)Cl_2 with 8-PS. On the basis of the stoichiometry of the reaction, the preferential cis chelation of phosphorus-containing ligands when Pt(COD)X_2 is used as a precursor, and the knowledge that the 16-membered macrocycle was formed during the ligand cyclization reaction, it seems likely that the minor product of this reaction is the macrocyclic Pt(II) complex [Pt(η^4-16-*t*-PSPS)]I_2.

When **3** is dissolved in dimethyl sulfoxide, an additional signal appears in the ^{31}P NMR spectrum, δ −5.67, ^1J(Pt,P) = 3034 Hz. This is not surprising, due to the large excess of dimethyl sulfoxide relative to platinum complex present in solution and the affinity of divalent platinum for sulfur donor ligands.[27] Assuming only

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(19) Freeman, H. C.; Golomb, M. L. *Chem. Commun.* **1970**, 1523.
(20) Robertson, G. B.; Wickramasinghe, W. *Acta Crystallogr.* **1987**, *C43*, 1694.
(21) Doi, J. T.; Musker, W. K. *J. Am. Chem. Soc.* **1978**, *100*, 3533.
(22) Horner, L.; Walach, P.; Kunz, H. *Phosphorus Sulfur* **1978**, *5*, 171.
(23) Issleib, K.; Kuhne, U.; Krech, F. *Phosphorus Sulfur* **1985**, *21*, 367.
(24) Rosen, W.; Del Donno, T. A. *J. Am. Chem. Soc.* **1977**, *99*, 8051.
(25) See ref 10, p 25.
(26) Hitchcock, P. B.; Jacobson, B.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1977**, 2038.
(27) Rochon, D. F.; Kong, P.-C.; Girard, L. *Can. J. Chem.* **1986**, *64*, 1897.

monosubstitution, one possibility for the newly formed complex is displacement of the sulfur atom of the 8-PS ligand by dimethyl sulfoxide to form Pt(η^1-8-PS)(DMSO)I_2, in which the 8-PS acts as a monodentate ligand by binding through phosphorus exclusively. Admittedly, sulfur is considered a weaker donor than phosphorus; however, the chelate effect favors the bidentate behavior of the 8-PS ligand. Additionally, the large change in the metal–phosphorus coupling constants (from 3436 Hz in **3** to 3034 Hz in the DMSO-substituted complex) and the large trans effect of phosphine ligands leads one to surmise that the dimethyl sulfoxide has displaced the iodide in the position trans to P to form the cationic species *cis*-[Pt(η^2-8-PS)(DMSO)I]I. This assignment is further supported by a recent study by Lippard in which it was shown that for *cis*- and *trans*-diamminedichloroplatinum(II), DMSO substitutes for a single chloride ligand in both cases to form *cis*-[Pt$(NH_3)_2(Me_2SO)$Cl]Cl and *trans*-[Pt$(NH_3)_2(Me_2SO)$Cl]Cl.[28]

The far-infrared data support the formation of *cis*-Pt(η^2-8-PS)I_2 with two prominent Pt–I vibrations at 138 and 182 cm^{-1}, which fall into the range established for *cis*-PtI_2 groups.[29] The structure of **3** was further verified by a single-crystal X-ray analysis (Tables I, V, and VIII). The structure is quite similar to that reported for the dichloro complex **1**; 8-PS acts as a bidentate ligand by coordinating to the platinum atom through both the phosphorus and sulfur atoms. The geometry about the central metal core is slightly distorted square planar with the calculated least-squares plane to the five central atoms as follows: Pt (–0.008), I(1) (0.007), I(2) (–0.003), S (0.008), P (–0.003). The deviation from planarity is much less for this complex than for the related Pt(TACO)I_2 molecule.[5] As was noted in the analogous dichloro compound, the Pt–I(2) bond trans to P (2.639 (2) Å) is longer than the Pt–I(1) bond trans to S (2.598 (3) Å) due to the large trans influence of the phosphino moiety. Correspondingly, both the Pt–P (2.242 (8) Å) and Pt–S (2.280 (8) Å) bonds in the iodide complex are lengthened relative to those in the chloride complex (2.207 (3) and 2.258 (2) Å, respectively) due to the larger trans effect of iodide relative to chloride. The phenyl group does not seem to exert an appreciable steric effect on the adjacent iodine since the P–Pt–I(1) angle is expanded to only 96.7 (2)°; this value is smaller than the N–Pd–I angle of the amine complex Pd(TACO)I_2, 99.8 (5)°, where there does appear to be an interaction between the N–CH_3 group and the iodine.[5] The phenyl group is rotated 81.7° from the metal–donor atom plane in **3**, which minimizes interactions. Due to the orientation of the phenyl group, the intramolecular contact between H(8) of the phenyl ring and I(1) is 3.830 Å; there is no evidence of an unfavorable nonbonding interaction between these two atoms. The nonbonded P···S distance for this chelate complex is 3.111 Å.

***a*-Chloro-*b*-methyl-*cd*-(5-phenyl-1-thia-5-phosphacyclooctane-*P*,*S*)platinum(II) or (*E*,*Z*)-Chloromethyl(5-phenyl-1-thia-5-phosphacyclooctane)platinum(II) (4).** The preparation of an alkyl-substituted Pt(II) 8-PS compound was attempted in order to form a complex that would be soluble in a variety of organic solvents and therefore permit the investigation of a number of ligand-substituted reactions. All attempts to prepare the desired Pt(COD)$(Me)_2$ precursor from Pt(COD)I_2 by reaction with methyllithium were unsuccessful.[7] An alternate procedure in which alkyl-substituted complexes such as Pt$R_2(DMSO)_2$ or PtRCl$(DMSO)_2$ are prepared by reacting Pt$Cl_2(DMSO)_2$ with tetraalkyltin reagents was also used;[30] unfortunately, yields from these reactions were consistently low, and mixtures of products were often obtained.

A novel variation of the above procedure was then explored; **1** was reacted directly with a large excess of tetramethyltin in DMSO. In all cases only the monosubstituted methyl complex was formed. Yields ranged from 65% to 80%.

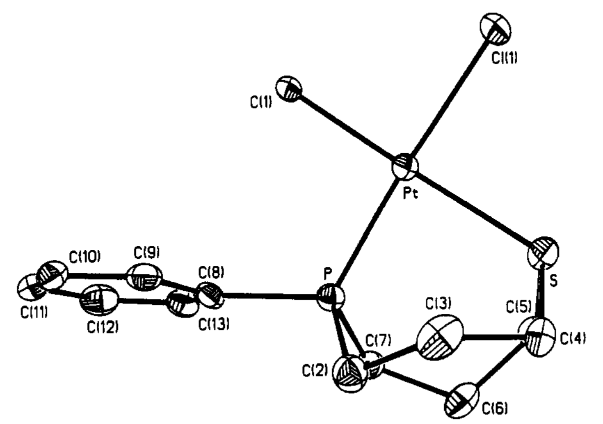

Figure 2. Computer-generated drawing of *a*-chloro-*β*-methyl-*cd*-(5-phenyl-1-thia-5-phosphacyclooctane-*P*,*S*)platinum(II) (**4**). The 50% probability ellipsoids are shown.

Spectroscopic methods, mainly ^{31}P and ^1H NMR, were quite effective in determining the structure of the product formed. The $^{31}P\{^1H\}$ NMR spectrum of Pt(8-PS)MeCl (**4**) displays one resonance at δ –2.15 with ^{195}Pt satellites, $^1J(Pt,P)$ = 4219 Hz. The large one-bond metal–phosphorus coupling constant supports the presence of the methyl substituent cis to the phosphorus atom of the 8-PS ligand.[31]

The ^1H NMR of **4** also provided valuable structural information, especially in the upfield region of the spectrum. The relative integration of aromatic protons to methyl protons (5:2.8) verified that only the monomethylated product was formed during the reaction of **1** with $SnMe_4$.

The methyl region of the spectrum displays a doublet centered at δ 0.435, which is caused by coupling with the nearby phosphorus nucleus, $^3J(P_{cis},H)$ = 3.6 Hz, and satellites due to coupling with ^{195}Pt, $^2J(Pt,H)$ = 76.2 Hz. This displacement of the chemical shift to higher fields is characteristic of protons attached to a carbon α to a platinum atom; the platinum–hydrogen coupling falls within the expected range for metal σ-bonded carbon complexes, 50–85 Hz.[32] The large value of $^2J(Pt,H)$ is characteristic of the low trans influence of the thioether group.[33]

The carbon-13 NMR spectrum of **4** is characteristic of a methyl platinum complex; the methyl carbon appears in the upfield region of the spectrum generally attributed to platinum σ-bonded carbon complexes, δ –0.94.[34] The platinum–methyl carbon-13 nucleus is weakly coupled to the phosphorus, $^2J(P,C)$ = 4.0 Hz, which reflects the cis orientation of these two groups in the complex. The small ^{195}Pt satellites were not observed. The 8-PS ligand methylene resonances were all shifted upon complexation to the platinum. The methylenes adjacent to both the sulfur and phosphorus atoms were shifted upfield upon binding to the platinum, $\Delta\delta$ –8.6 (carbons α to sulfur) and $\Delta\delta$ = –5.1 (carbons α to phosphorus), while the methylene group β to both P and S was shifted downfield, $\Delta\delta$ 3.2. The value of $^1J(P,C)$ increased from 6.0 Hz in the uncoordinated ligand to 38 Hz in the platinum(II) complex. This is not surprising as the phosphorus atom in the complex can be thought of as four coordinate, and one-bond phosphorus–carbon coupling constants in four-coordinate phosphorus molecules are often of similar magnitudes.[35]

A crystal structure of **4** is shown in Figure 2. The crystal structure verifies the cis orientation of the phosphino and the methyl groups; this was somewhat surprising at first, due to the large effect of the phosphine function. However, it has been observed in alkylation reactions of bis(triphenylphosphine)di-

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[28] Sundquist, W.; Ahmed, K. J.; Hollis, S.; Lippard, S. J. *Inorg. Chem.* **1987**, *26*, 1524.

[29] Hartley, F. R.; Murray, S. G.; Levason, W.; Soutter, H. E.; McAuliffe, C. A. *Inorg. Chim. Acta* **1979**, *35*, 265.

[30] (a) Eaborn, C.; Kundu, K.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1981**, 933. (b) Eaborn, C.; Kundu, K.; Pidcock, A. *J. Organomet. Chem.* **1979**, *170*, C18.

[31] See ref 10, p 96.

[32] See ref 15, p 334.

[33] See ref 15, p 335.

[34] Belluco, U. *Organometallic and Coordination Chemistry of Platinum*; Academic Press: London, England, 1974; p 250.

[35] Gray, G.; Cremer, S. E.; Marsi, K. L. *J. Am. Chem. Soc.* **1976**, *98*, 2109.

chloroplatinum(II) compounds with Grignard and organolithium reagents that although the cis halides are the more reactive starting materials, the preferred products are those with the two groups with the highest trans effects lying opposite one another, so that isomerization frequently occurs.[36]

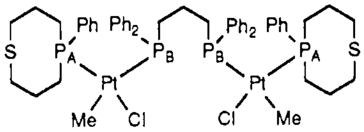
As with all of the other Pt(II) complexes of 8-PS discussed thus far, the Pt(II) is bonded to the 8-PS ligand in a bidentate fashion; the geometry about the platinum is square planar (Tables I, VI, and VIII). The best least-squares fit to the five central atoms in the square plane is as follows: Pt (−0.004), Cl (−0.031), S (0.033), P (−0.033), Cl, (0.035). The C(1)–Pt–P bond angle is 94.3 (3)°; this is somewhat smaller than the analogous bonds in **1** (Cl–Pt–P, 95.6 (1)°) and in **3** (I–Pt–P, 96.7 (2)°), presumably due to the change in substituent. The phenyl ring is rotated 81.1° from the central square plane about platinum; the orientation of the phenyl ring is approximately identical with that in **3**, 81.7°. The Pt–C(1) bond length of 2.084 (7) Å is close to that predicted from the sum of the covalent radii (2.05 Å).[37] The Pt–S bond trans to the methyl group (2.374 (2) Å) is significantly lengthened compared to the P–S bond lengths in $Pt(8\text{-}PS)Cl_2$ (2.258 (2) Å) and $Pt(8\text{-}PS)I_2$ (2.280 (8) Å) due to the high trans influence of the methyl ligand. The Pt–P bond distance is 2.191 (2) Å, only slightly shorter than that found in the corresponding dichloro compound, 2.207 (3) Å. The P···S distance is 3.146 Å.

^{31}P NMR Study of Reactions of Pt(8-PS)MeCl with a Variety of Substrates. The solubility of **4** in a wide range of organic solvents enabled us to study a number of ligand substitution reactions of this complex by ^{31}P NMR spectroscopy.

Reaction with Cyanide Anion. Due to its strong ligand field, the cyanide ion is often used to displace phosphines from Pt and Pd complexes[38] and reportedly will not displace alkyl groups.[39] However, when excess KCN was added to a chloroform solution of **4**, the resultant spectrum from this reaction revealed a complicated mixture containing three platinum-bound phosphorus species (δ 12.1, $^1J(Pt,P)$ = 2729 Hz; δ 8.2, $^1J(Pt,P)$ = 1562 Hz; δ −2.1, $^1J(Pt,P)$ = 2858 Hz) and a small amount of what appears to be an uncomplexed phosphine compound, δ −5.7, whose chemical shift value is 14 ppm downfield from that of the mesocyclic 8-PS ligand. The signal at −5.7 ppm may arise from the monodentate thioether-bound 8-PS complex $Pt(\eta^1\text{-}8\text{-}PS\text{-}S)(CN)MeCl$. No attempt was made to fully characterize the platinum species formed in this reaction; however, at this concentration, the cyanide ion was shown to be ineffective at liberating the free 5-phenyl-1-thia-5-phosphacyclooctane ligand.

Reaction with Triphenylphosphine. Addition of 1 equiv of PPh_3 to a chloroform solution of **4** results in metathetical substitution of the chloride ligand to form the cationic species $[Pt\text{-}a\text{-}Me\text{-}bc\text{-}(\eta^2\text{-}8\text{-}PS)\text{-}d\text{-}(PPh_3)]Cl$ or $[(Z,Z)\text{-}Pt\text{-}Me\text{-}(\eta^2\text{-}8\text{-}PS)\text{-}PPh_3]Cl$. Anderson et al. have similarly reported the formation of $[PtCl(PPh_3)(\widehat{PP})]$ complexes ($\widehat{PP}$ = dpm, dppe) by displacement of one chloride ligand from the corresponding $PtCl_2(\widehat{PP})$ complexes.[40] The phosphorus NMR spectrum clearly indicates the formation of the above complex, with two phosphorus signals, one centered at δ 27.8, $^1J(Pt,P)$ = 2752 Hz, and the other centered at δ 7.8, $^1J(Pt,P)$ = 2726 Hz. Each phosphorus resonance appears as a doublet due to coupling with the other inequivalent phosphorus, $^2J(P,P')$ = 394 Hz. The magnitude of the phosphorus–phosphorus coupling constant is indicative of trans phosphines.[41] Each phosphorus signal also exhibits a one-bond coupling to the directly bonded platinum; the $^1J(Pt,P)$ values further support the trans orientation of the phosphine moieties.[10] Although phosphorus is considered a stronger donor atom than sulfur, due to the chelate effect,[13] the incoming phosphine ligand does not displace the sulfur of the 8-PS chelate but instead undergoes substitution of the chloride at the position trans to the phosphorus of the 8-PS mesocycle (high trans effect) to yield the corresponding cationic platinum(II) complex *a*-methyl-*bc*-(η^2-5-phenyl-5-phospha-1-thiacyclooctane-*P*,*S*)-*d*-(triphenylphosphine)platinum(II) chloride or (*Z*,*Z*)-methyl(η^2-5-phenyl-5-phospha-1-thiacyclooctane)(triphenylphosphine)platinum(II) chloride[§].

Reaction with 1,3-Bis(diphenylphosphino)propane, DPP. Addition of 0.5 equiv of DPP to a chloroform solution of **4** results in the formation of a binuclear Pt(II) dimer, with DPP acting as a bridge between the two platinum centers. The phosphorus NMR spectrum contains only two major phosphorus resonances, and these signals are spin coupled to one another: δ 5.67, P_A; δ 3.12, P_B; $^2J(P_A,P_B)$ = 20 Hz. Therefore, there can only be two types of chemically inequivalent phosphorus centers in the product; the value of $^2J(P_A,P_B)$ indicates that they are cis to one another.[41] The one-bond platinum–phosphorus coupling constants reveal additional information about the geometry of the product: the value of $^1J(Pt,P_A)$, 4185 Hz, indicates a phosphorus cis to a methyl group,[31] which can be attributed to the 8-PS-portion of the molecule; $^1J(Pt,P_B)$, 1626 Hz, suggests a phosphorus trans to a methyl function and may be assigned to the DPP phosphorus. Considering the stoichiometry of the reaction, the number of signals present in the ^{31}P NMR and the coupling constant and chemical shift data, it appears that the product formed is *cis*-$Pt_2(\eta^1\text{-}8\text{-}PS\text{-}P)_2Me_2Cl_2(\mu\text{-}DPP)$.



The fairly labile sulfur atoms that were trans to the methyl groups (high trans effect) in the starting material have been displaced by the phosphorus atoms of the DPP; the mesocyclic 8-PS molecule acts as a monodentate ligand by binding exclusively through phosphorus.

Thus, by utilizing a bidentate phosphine substrate, we have exploited the greater lability of the thioether function of the 8-PS ligand to change its binding behavior from bidentate to monodentate. The facile displacement of the sulfur donor center by the incoming phosphine molecule suggests that the mixed-donor properties of the 8-PS ligand may be applicable to catalytic processes in which generation of a vacant site at the metal center is often an integral part of the catalytic cycle. Additionally, we have created two new sulfur donor sites within the binuclear Pt(II) product that may permit formation of heteromultinuclear complexes by coordination of the thioether functions to different metal centers.

We attempted to carry out an insertion reaction[42] into the Pt–C bond of **4** with carbon monoxide but when the gas was bubbled through a chloroform solution for 1 h at room temperature, the ^{31}P NMR spectrum only revealed unreacted starting material. Two additional synthetic approaches to a chlorohydrido(5-phenyl-1-thia-5-phosphacyclooctane)platinum(II) complex were investigated. Neither reaction of **1** with hydrazine hydrate[43] nor reaction of **1** with hot formic acid and lithium chloride[43] proved to be successful.

***cis*-Bis(5-phenyl-1-thia-5-phosphacyclooctane)platinum(II) Tetrafluoroborate (5).** The $(8\text{-}PS)_2$ complex *cis*-bis(5-phenyl-1-thia-5-phosphacyclooctane)platinum(II) tetrafluoroborate was synthesized by reacting 2 equiv of 8-PS and excess $NaBPh_4$ with aqueous K_2PtCl_4 in ethanol. The platinum-containing product was fairly soluble in acetonitrile and was further examined by ^{31}P NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum revealed one major resonance centered at δ 11.1, with a one-bond platinum–phosphorus coupling constant of 3076 Hz. While it is often misleading to draw conclusions about the geometry of a transition-metal–phosphine complex based solely on NMR data,[48] it

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(36) See ref 15, p 326.

(37) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960.

(38) Bartsch, R.; Hietkamp, S.; Morton, S.; Peters, H.; Stelzer, O. *Inorg. Chem.* **1983**, *22*, 3624.

(39) See ref 15, p 343.

(40) Anderson, G. K.; Lumetta, G. J. *Inorg. Chem.* **1987**, *26*, 1518.

(41) See ref 9, p 121 (Appendix G, Table 19).

(42) See ref 34, p 253.

(43) See ref 15, p 341.

(44) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1962**, 5075.

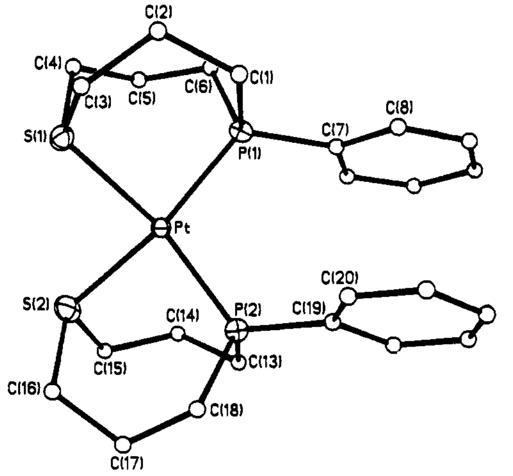

Figure 3. Molecular structure of the dication of **5**, *cis*-bis(5-phenyl-1-thia-5-phosphacyclooctane)platinum(II).

appears that the 8-PS ligands are coordinated to the platinum in a cis fashion. Sanger has attributed a peak at δ 45.9, ^1J(Pt,P) = 3041 Hz, to the 2:1 electrolyte [Pt{η^2-($Ph_2P(CH_2)_2SPh$)$_2$}-(BPh_4)$_2$],[1] and Anderson et al. have assigned the product of the reaction of PtI_2(COD) with 2 equiv of $Ph_2P(CH_2)_2SMe$ in the presence of excess $AgBF_4$ as [Pt{η^2-($Ph_2P(CH_2)_2SMe$)$_2$}(BF_4)$_2$], δ 45.5, ^1J(Pt,P) = 3100 Hz, in which the phosphino moieties occupy mutually cis positions.[6] However, neither of their structures was verified by X-ray structure determination.

It was somewhat surprising that the phosphino functions would be arranged in a cis fashion, due to the steric requirements of two phenyl-substituted phosphorus atoms; however, studies have shown that cis complexes are formed when the complex precursor is potassium tetrachloroplatinate, while the trans isomers are preferred when the starting material is Zeise's salt, K[Pt(C_2H_4)-Cl_3]·H_2O.[13] Chemical analysis supported the formation of the dicationic product [Pt(η^2-8-PS)$_2$](BPh_4)$_2$; an X-ray crystal structure verified the chelate behavior of the two 8-PS ligands and the cis orientation of the two phosphino moieties. (Figure 3; Tables I and IX).

The structure reveals a distorted planar geometry about the central Pt atom with the P(1)-Pt-P(2) angle expanded to 104.0 (1)°, presumably to accommodate the phenyl substituents on the phosphorus atoms. The distortion from ideal square-planar geometry (all central bond angles 90°) is greater in *cis*-[Pt(η^2-8-PS)$_2$](BPh_4)$_2$ (**5**) than in all of the previously mentioned Pt(II)-8-PS complexes, including the Pt(II) complex of the 16-membered-ring tetradentate homologue of 8-PS, Pt(η^4-16-*t*-PSPS)Cl_2, in which the phosphorus atoms occupy mutually trans positions. The two platinum-sulfur bonds show a characteristic lengthening due to the high trans influence of the phosphorus atoms, Pt-S(1), 2.365 (4) Å; Pt-S(2), 2.351 (4) Å. These bond lengths are comparable to the Pt-S distance in the mono-8-PS complex **4** where the Pt-S bond is similarly lengthened to 2.374 (2) Å due to the high trans influence of the methyl group. The two phosphorus phenyl substituents are oriented in a near-planar fashion, which may be indicative of a weak π-type interaction between the aromatic rings, although the product is colorless and the ^{1}H NMR does not exhibit any irregularities in the aromatic region of the spectrum. The distance between the two phenyl rings is 3.36 Å, which is approximately the sum of the van der Waals radii (3.30-3.40 Å).[49] A similar preparation of layers is found in graphite, 3.35 Å, where the layer separation is about equal to the sum of the van der Waals radii and the forces between layers are thought to be relatively slight.[50]

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Supplementary Material Available: A more detailed description of the crystallographic parameters for **1-5**, complete tables of bond lengths, bond angles, anisotropic thermal parameters, and H atom coordinates for complexes **1-5** (Tables S1-S4, S6, S7, S9-S12, S14-S17, and S19-S22), and ORTEP drawings of **1** and **2** (18 pages); tables of calculated and observed structure factors for **1-5** (Tables S5, S8, S13, S18, and S23) (118 pages). Ordering information is given on any current masthead page.

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(45) Cope, A. L.; Siekman, R. W. *J. Am. Chem. Soc.* **1965**, *87*, 3272.

(46) Kasahara, A. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1272.

(47) See ref 15, p 340.

(48) See ref 9, p 43.

(49) Huheey, James E. *Inorganic Chemistry*, 3rd ed.; Harper and Row Publishers, Inc.: New York, 1983; p 258.

(50) Cotton, F. Albert; Wilkinson, G. *Advanced Inorganic Chemistry*; John Wiley and Sons: New York, 1980; p 357.