

S-Alkyl (Diorganothiophosphinoyl)dithioformate, N-Phenyl(diorganophosphino)thioformamide, and N-Phenyl(diorganothiophosphinoyl)thioformamide Complexes of Platinum. Preparation and Hydrogen-1, Phosphorus-31, and Platinum-195 NMR Studies

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The reactions between $(\text{PPh}_3)_2\text{PtC}_2\text{H}_4$ and $\text{R}_2\text{P}(\text{S})\text{C}(\text{S})\text{SR}'$ ($\text{R} = \text{Ph}$, cyclohexyl (Cy); $\text{R}' = \text{Me}$, CH_2Ph) have been studied and the products characterized by elemental analysis and by infrared and multinuclear magnetic resonance techniques. All spectroscopic data are consistent with the simple replacement of ethylene and coordination of the ligands in a η^2 mode through the CS portion of the molecule. The initial products of the reactions between $(\text{PPh}_3)_2\text{PtC}_2\text{H}_4$ and $\text{R}_2\text{PC}(\text{S})\text{NPhH}$ and $\text{R}_2\text{P}(\text{S})\text{C}(\text{S})\text{NPhH}$ ($\text{R} = \text{Ph}$, Cy) are also η^2 -CS-coordinated complexes. With the exception of the complex derived from $\text{Ph}_2\text{P}(\text{S})\text{C}(\text{S})\text{NPhH}$, which is stable in the η^2 -CS-coordinated form, these compounds rearrange to give the platinum(II) hydrides $(\text{PPh}_3)_2\text{Pt}(\text{H})(\text{R}_2\text{PC}(\text{S})\text{NPh})$ and $(\text{PPh}_3)_2\text{Pt}(\text{H})(\text{Cy}_2\text{P}(\text{S})\text{C}(\text{S})\text{NPh})$. Intermediates were observed in these internal oxidative-addition reactions, which are believed to involve P,S and S,S coordination of the ligands. The overall rates of these reactions decrease with decreasing basicity of the phosphorus portion of the ligands.

Introduction

Platinum(0) complexes with small η^2 -CS-coordinated ligands (e.g., CS_2 , COS, RNCS) react readily with excess ligand, and in each case, the η^2 -CS bonding is replaced by two σ bonds.¹ This is postulated to occur via intermolecular processes involving the central carbon atom of the η^2 ligand.¹ In contrast, the platinum(0) compounds containing η^2 -CS-bonded $\text{Ph}_3\text{SnC}(\text{S})\text{SR}$ ($\text{R} = \text{Me}$, C_3H_5 , CH_2Ph) ligands and η^2 -CS-bonded $\text{Ph}_3\text{SnC}(\text{S})\text{N}'$ ($\text{N}' = \text{NHMe}$, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$) ligands do not react with either excess ligand or excess CS_2 .² The N-alkylformamide complexes do undergo a slow rearrangement, but this involves bond cleavage at tin.²

There seem to be exacting electronic requirements on the metal-ligand-bonding interaction for the formation of stable η^2 -CS complexes of platinum(0). In order to further investigate the factors that influence the stability of η^2 -CS bonds to platinum(0), we have extended the range of ligands used in our earlier publication² to include S-alkyl (diorganothiophosphinoyl)dithioformates, $\text{R}_2\text{P}(\text{S})\text{C}(\text{S})\text{SR}'$, N-phenyl(diorganothiophosphinoyl)thioformamides, $\text{R}_2\text{P}(\text{S})\text{C}(\text{S})\text{NPhH}$, and N-phenyl(diorganophosphino)thioformamides, $\text{R}_2\text{PC}(\text{S})\text{NPhH}$.

No metal complexes with S-alkyl (diorganothiophosphinoyl)dithioformates have been reported previously, but some mercury(II) derivatives of N-alkyl(diorganophosphino)thioformamides have been prepared.³ More recently, some manganese(I) and rhenium(I) carbonyl complexes of the deprotonated N-phenyl(diorganophosphino)thioformamide were prepared and were shown to involve both phosphorus and sulfur coordination to the metal.⁴ Gal and co-workers⁵ have reported the reactions of $\text{Ph}_2\text{PC}(\text{S})\text{NPhH}$ with $(\text{PPh}_3)_3\text{RhCl}$ and $(\text{PPh}_3)_4\text{Pt}$ to give $(\text{PPh}_3)_2\text{Rh}(\text{Ph}_2\text{PC}(\text{S})\text{NPh})$ and $(\text{PPh}_3)_2\text{Pt}(\text{H})(\text{Ph}_2\text{PC}(\text{S})\text{NPh})$, respectively, with the ligand coordinating through phosphorus and sulfur. The phosphorus(V) thioformamides $\text{Ph}_2\text{P}(\text{Q})\text{C}(\text{S})\text{NPhH}$ ($\text{Q} = \text{O}$, S) have been prepared, and carbonyl derivatives of molyb-

Table I. Analytical Data

compd	% calcd		% found	
	C	H	C	H
$\text{Cy}_2\text{P}(\text{S})\text{C}(\text{S})\text{SMe}$	52.46	7.86	52.70	7.58
$\text{Cy}_2\text{P}(\text{S})\text{C}(\text{S})\text{SCH}_2\text{Ph}$	60.57	7.37	60.43	7.20
$\text{Cy}_2\text{P}(\text{S})\text{C}(\text{S})\text{NPhH}$	62.43	7.72	62.41	7.55
$(\text{PPh}_3)_2\text{Pt}(\text{Ph}_2\text{P}(\text{S})\text{C}(\text{S})\text{SMe})$	58.41	4.22	58.82	4.13
$(\text{PPh}_3)_2\text{Pt}(\text{Ph}_2\text{P}(\text{S})\text{C}(\text{S})\text{SCH}_2\text{Ph})$	60.91	4.29	61.06	4.16
$(\text{PPh}_3)_2\text{Pt}(\text{Cy}_2\text{P}(\text{S})\text{C}(\text{S})\text{SMe})$	57.73	5.33	57.78	5.69
$(\text{PPh}_3)_2\text{Pt}(\text{Cy}_2\text{P}(\text{S})\text{C}(\text{S})\text{SCH}_2\text{Ph})$	60.25	5.33	58.14	5.15
$(\text{PPh}_3)_2\text{Pt}(\text{Ph}_2\text{PC}(\text{S})\text{NPhH})$	63.45	4.45	61.83	4.48
$(\text{PPh}_3)_2\text{Pt}(\text{Ph}_2\text{PC}(\text{S})\text{NPh}(\text{SiMe}_3))^a$	62.58	4.89	62.06	4.80
$(\text{PPh}_3)_2\text{Pt}(\text{Ph}_2\text{PC}(\text{S})\text{NPh}(\text{SiMe}_3))^b$	62.58	4.89	62.97	4.97
$(\text{PPh}_3)_2\text{Pt}(\text{Cy}_2\text{PC}(\text{S})\text{NPhH})$	62.72	5.55	64.20	5.97
$(\text{PPh}_3)_2\text{Pt}(\text{H})(\text{Cy}_2\text{PC}(\text{S})\text{NPh})$	55.91	5.96	56.15	5.79
$(\text{PPh}_3)_2\text{Pt}(\text{Ph}_2\text{P}(\text{S})\text{C}(\text{S})\text{NPhH})$	61.50	4.32	61.67	4.16
$(\text{PPh}_3)_2\text{Pt}(\text{H})(\text{Ph}_2\text{P}(\text{S})\text{C}(\text{S})\text{NPhH})$	60.87	5.39	59.95	5.30
$(\text{PPh}_3)_2\text{Pt}(\text{H})(\text{Cy}_2\text{P}(\text{S})\text{C}(\text{S})\text{NPhH})$	54.00	5.27	53.07	5.55

^a η^2 -CS-bonded isomer. ^b P,S-bonded isomer.

denum(II) and tungsten(II) with the deprotonated form of the ligand ($\text{Q} = \text{O}$) contain the ligand coordinated through oxygen and sulfur.⁶

In this paper we report the reactions of $(\text{PPh}_3)_2\text{PtC}_2\text{H}_4$ with $\text{R}_2\text{P}(\text{S})\text{C}(\text{S})\text{SR}'$, $\text{R}_2\text{PC}(\text{S})\text{NPhH}$, and $\text{R}_2\text{P}(\text{S})\text{C}(\text{S})\text{NPhH}$ ($\text{R} = \text{Ph}$, cyclohexyl (Cy); $\text{R}' = \text{Me}$, CH_2Ph) to give η^2 -CS-bonded complexes of platinum(0). The complexes with $\text{R}_2\text{PC}(\text{S})\text{NPhH}$ and $\text{Cy}_2\text{P}(\text{S})\text{C}(\text{S})\text{NPhH}$ undergo rearrangement to give the platinum(II) complexes $(\text{PPh}_3)_2\text{Pt}(\text{H})(\text{R}_2\text{PC}(\text{S})\text{NPh})$ and $(\text{PPh}_3)_2\text{Pt}(\text{H})(\text{Cy}_2\text{P}(\text{S})\text{C}(\text{S})\text{NPh})$. Intermediate products between the η^2 complex and the final hydride complexes were observed, and mechanisms are proposed for the rearrangements. All of the reactions were studied by multinuclear (^1H , ^{31}P , and ^{195}Pt) magnetic resonance methods.

Experimental Section

Instrumentation. Infrared spectra were recorded on a Jasco A-302 spectrometer. NMR spectra were recorded on a JEOL FX 100 spectrometer with an NM 5471 variable-temperature controller, calibrated with a platinum resistance thermometer. The ^1H NMR spectra, recorded in CDCl_3 solution at 99.60 MHz, were referenced against internal Me_4Si . All other NMR spectra were recorded in CH_2Cl_2 solution by using an external ^7Li lock. ^{31}P NMR spectra were

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Table II. Spectroscopic Data for the Free Ligands

compd	NMR ^a		infrared ^b			
	$\delta(^1\text{H})$ (J, Hz)	$\delta(^{31}\text{P})$	ν_{CS}	ν_{PS}	$\nu_{1\text{NCS}}, \nu_{2\text{NCS}}$	ν_{NH}
Ph ₂ P(S)C(S)SMe	2.69 (Me, ⁴ J _{P,H} = 1)	49.4	1081 s, br	651 s		
Ph ₂ P(S)C(S)CH ₂ Ph	4.41 (CH ₂)	49.3	1080 s, br	652 s		
Cy ₂ P(S)C(S)SMe	2.66 (Me, ⁴ J _{P,H} = 0.7)	73.6	1070 s, 1080 s	618 s		
Cy ₂ P(S)C(S)SCH ₂ Ph	4.39 (CH ₂ , ⁴ J _{P,H} = 1)	73.2	1072 s, br	620 m		
Ph ₂ PC(S)NPhH	8.72 (NH)	19.2			1525 s, 1384 s	3300
Ph ₂ PC(S)NPh(SiMe ₃)	0.33 (Me)	19.3			1530 w, 1320 vs	
Cy ₂ PC(S)NPhH	9.34 (NH)	44.3			1500 s, 1330 s	3200
Ph ₂ P(S)C(S)NPhH	11.92 (NH)	47.5		640 s	1539 s, 1382 s	3125
Cy ₂ P(S)C(S)NPhH	11.54 (NH)	80.2		622 s	1537 s, 1372 s	3020

^a ¹H NMR spectra in CDCl₃; ³¹P NMR spectra in CH₂Cl₂. ^b KBr disks.

recorded at 40.32 MHz (external 85% H₃PO₄), and ¹⁹⁵Pt spectra at 21.56 MHz (1 M H₂PtCl₆ in concentrated HCl). High-frequency positive convention is used.

Preparations. All preparations were carried out in dry degassed solvents under a nitrogen atmosphere. Dicyclohexylphosphine was obtained commercially. The compounds Ph₂PH₂,⁷ PhNCS,⁸ Ph₂PC(S)NPhH,³ Ph₂PC(S)NPh(SiMe₃),⁹ Cy₂PC(S)NPhH,³ Ph₂P(S)C(S)SR',¹⁰ (PPh₃)₂Pt,¹¹ (PPh₃)₂PtC₂H₄,¹² and (PPh₃)Pt(H)(Ph₂PC(S)NPh)⁵ were prepared by published methods. Cy₂P(S)C(S)SR' (R' = Me, mp 215 °C; R' = CH₂Ph, mp 107 °C) were prepared analogously to Ph₂P(S)C(S)SR'. The ligands R₂P(S)C(S)NPhH (R = Ph, Cy) were prepared by refluxing R₂PC(S)NPhH with a slight excess of sulfur in benzene for 3 h. The products were recrystallized from *n*-propyl alcohol (R = Ph, mp 154 °C, lit.¹³ mp 163–164 °C; R = Cy, mp 115 °C). Analytical data for all new compounds are given in Table I.

(PPh₃)₂Pt(R₂P(S)C(S)SR') (R = Ph, Cy; R' = Me, CH₂Ph). A solution of R₂P(S)C(S)SR' in benzene (0.23 mM in 5 cm³) was added with stirring to a solution of (PPh₃)₂PtC₂H₄ in benzene (0.23 mM in 5 cm³). Evolution of ethylene was observed, and within 10 min the color of the ligand had disappeared. The resulting pale yellow product was precipitated with hexane and recrystallized by dissolution in the minimum volume of benzene followed by addition of hexane. Yields were almost quantitative.

η^2 -(PPh₃)₂Pt(Ph₂PC(S)NPhH) and (PPh₃)₂Pt(R₂P(S)C(S)NPhH). Equimolar quantities (0.23 mM) of (PPh₃)₂PtC₂H₄ and Ph₂PC(S)NPhH or R₂P(S)C(S)NPhH (R = Ph, Cy) were stirred in 5 cm³ of benzene at 0 °C for 10 min. The product was precipitated in almost quantitative yield by addition of hexane.

(PPh₃)₂Pt(Ph₂PC(S)NPh(SiMe₃)). Equimolar quantities (0.23 mM) of (PPh₃)₂PtC₂H₄ and Ph₂PC(S)NPh(SiMe₃) were stirred in benzene (5 cm³) at 0 °C for 5 min. The product η^2 -(PPh₃)₂Pt(Ph₂PC(S)NPh(SiMe₃)) (mp 78 °C dec) was precipitated in almost quantitative yield. Dissolving this compound in dichloromethane led to formation of the P,S-bonded isomer, which was isolated by evaporation of the solution (mp 130 °C dec).

(PPh₃)Pt(H)(Cy₂PC(S)NPh) and (PPh₃)Pt(H)(Cy₂P(S)C(S)NPh). A slight excess of the ligand Cy₂PC(S)NPhH or Cy₂P(S)C(S)NPhH (0.25 mM) was added to (PPh₃)₂PtC₂H₄ (or (PPh₃)₄Pt) (0.23 mM) in 10 cm³ of dichloromethane, and the mixture was stirred for 24 h. The solution was evaporated to dryness, and the pale yellow product was recrystallized by dissolution in benzene followed by addition of hexane. Yields were approximately 50%.

η^2 -(PPh₃)₂Pt(Cy₂PC(S)NPhH). Solutions of (PPh₃)₂PtC₂H₄ (0.23 mM) and Cy₂PC(S)NPhH (0.23 mM) in 2 cm³ of dichloromethane were cooled to -30 °C and then mixed with rapid stirring. The pale yellow solid that precipitated was washed with cold CH₂Cl₂ and hexane. Yield was about 40%.

Results and Discussion

Reactions with R₂P(S)C(S)SR' Ligands. Mixing equimolar quantities of (PPh₃)₂PtC₂H₄ and R₂P(S)C(S)SR' (R = Ph,

Table III. Selected Infrared Data for the Complexes

compd	ν_{PS}	ν_{NH}	ν_{CN}	ν_{PtH}
(PPh ₃) ₂ Pt(Ph ₂ P(S)C(S)SMe)	619 m			
(PPh ₃) ₂ Pt(Ph ₂ P(S)C(S)CH ₂ Ph)	645 s			
(PPh ₃) ₂ Pt(Cy ₂ P(S)C(S)SMe)	619 m			
(PPh ₃) ₂ Pt(Cy ₂ P(S)C(S)CH ₂ Ph)	620 m			
(PPh ₃) ₂ Pt(Ph ₂ PC(S)NPhH)		3054 s		
(PPh ₃) ₂ Pt(Cy ₂ PC(S)NPhH)		3050 m		
(PPh ₃)Pt(H)(Ph ₂ PC(S)NPh)			1560 s	2105 m
(PPh ₃)Pt(H)(Cy ₂ PC(S)NPh)			1560 s	2079 s
(PPh ₃) ₂ Pt(Ph ₂ P(S)C(S)NPhH)	640 s	3050 s		
(PPh ₃) ₂ Pt(Cy ₂ P(S)C(S)NPhH)	620 m	3051 m		
(PPh ₃)Pt(H)(Cy ₂ P(S)C(S)NPh)	605 m		1520 s	2152 m

Cy; R' = Me, CH₂Ph) in dry benzene under nitrogen at room temperature caused immediate evolution of ethylene and disappearance of the red or purple color of the ligand. Pale yellow solids whose analyses (Table I) agree with the formulation (PPh₃)₂Pt(R₂P(S)C(S)SR') were readily precipitated in almost quantitative yields upon addition of *n*-hexane.

Comparison of the infrared spectra of the isolated complexes with those of the free ligands shows that the absorptions assigned¹⁰ to the ν_{CS} stretch, 1050–1080 cm⁻¹ (Table II), in the ligands are not present in the spectra of the complexes. However the ν_{PS} stretch, 620–650 cm⁻¹, in the free ligands is in all cases almost unchanged in the complexes (Table III). This suggests that coordination is not via the sulfur on phosphorus but rather through the C(S)SR' portion of the ligand.

The multinuclear magnetic resonance data for all the compounds of the type (PPh₃)₂Pt(R₂P(S)C(S)SR') are given in Table IV. The ³¹P{¹H} NMR spectrum of (PPh₃)₂Pt(Ph₂P(S)C(S)SMe) in dichloromethane at 25 °C consists of three signals (δ 54.2, 21.9, 17.6) of equal intensity. Each of these resonances has a pair of equally spaced platinum-195 satellites (²J_{Pt,P} = 44, ¹J_{Pt,P} = 4443 and 3232 Hz, respectively). On the spectral window required to observe the platinum satellites, the main signals are not well resolved, but on a small spectral window (500 Hz), the signal at δ 17.6 appears as an apparent triplet with a phosphorus-phosphorus coupling of 3.8 Hz and the resonances at δ 54.2 and 21.9 appear as doublets of doublets (²J_{P,P} = 5.0 and 3.8 Hz). The apparent triplet is, in fact, an overlapping doublet of doublets, and this was confirmed with selective ³¹P{¹H}{³¹P} decoupling experiments. Irradiation of either of the two multiplets at higher frequency causes the triplet to become a doublet with the same coupling constant. The two resonances are assigned to inequivalent triphenylphosphine groups directly bound to platinum. The third resonance at highest frequency is assigned to the phosphorus of the dithioformate ligand and is close to the resonance of Ph₂P(S)C(S)SMe itself. The triphenylphosphine group at higher frequency has the larger one-bond coupling constant to platinum and also the larger coupling constant with the phosphorus of the dithioformate ligand (5.0 Hz compared to 3.8 Hz).

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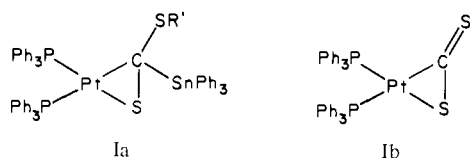
Table IV. NMR Data for the Compounds $(PPh_3)_2Pt(R_2P(S)C(S)SR')^a$

compd	$\delta(^1H)(R')$	$\delta(^{31}P)$	coupling const, Hz	$\delta(^{195}Pt)$
$(PPh_3)_2Pt(Ph_2P(S)C(S)SMe)$	2.07	P_B 21.9 P_A 17.6 P_C 54.2	$^1J_{Pt,PB} = 4443$ $^1J_{Pt,PA} = 3232$ $^2J_{Pt,PC} = 44$ $^2J_{PA,PB} = 3.8$ $^3J_{PB,PC} = 5.0$ $^3J_{PA,PC} = 3.8$ $^2J_{PB,C} = 4.4$ $^2J_{PA,C} = 67.7$ $^1J_{PC,C} = 51.4$ $^4J_{PC,H} = 0.7$	-4999
$(PPh_3)_2Pt(Ph_2P(S)C(S)SCH_2Ph)$	AB qrt 3.97, 3.86	P_B 20.9 P_A 16.4 P_C 53.1	$^1J_{Pt,PB} = 4385$ $^1J_{Pt,PA} = 3242$ $^2J_{Pt,PC} = 45$ $^2J_{PA,PB} = 3.8$ $^3J_{PA,PC} = 5.1$ $^3J_{PB,PC} = 3.8$ $^2J_{H,H} = 11.5$ $^4J_{P,H} = 0.7$	-4993
$(PPh_3)_2Pt(Cy_2P(S)C(S)SMe)$	2.11	P_B 21.1 P_A 15.2 P_C 68.4	$^1J_{Pt,PB} = 4428$ $^1J_{Pt,PA} = 3126$ $^2J_{Pt,PC} = 46$ $^3J_{PA,PC} = 4.3$ $^3J_{PB,PC} = 2.7$ $^2J_{PB,C} = 4.3$ $^2J_{PA,C} = 69.7$ $^1J_{PC,C} = 40.0$ $^4J_{PC,H} = 0.7$	-4944
$(PPh_3)_2Pt(Cy_2P(S)C(S)SCH_2Ph)$	AB qrt 4.02, 3.91	P_B 21.2 P_A 14.6 P_C 67.6	$^1J_{Pt,PB} = 4406$ $^1J_{Pt,PA} = 3114$ $^2J_{Pt,PC} = 50$ $^3J_{PA,PC} = 3.9$ $^3J_{PB,PC} = 2.6$ $^2J_{H,H} = 10.2$ $^4J_{PC,H} = 1$	-4922

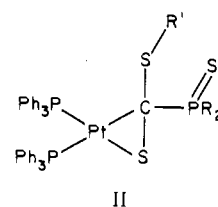
^a CH₂Cl₂ at 25 °C at approximately 0.13 M.

The $^{31}P\{^1H\}$ NMR spectrum of $(PPh_3)_2Pt(Cy_2P(S)C(S)SMe)$ is similar to that of the diphenyl derivative described above (see Table IV) although there are some differences. No coupling could be detected between the signals due to the two inequivalent triphenylphosphine groups. The triphenylphosphine resonance at higher frequency still has the larger platinum–phosphorus coupling constant as with the diphenyl derivative, but it has the smaller coupling with the phosphorus of the $Cy_2P(S)C(S)SMe$ ligand, which is the opposite of the situation for the diphenyl compound.

The $^{31}P\{^1H\}$ NMR data for these complexes are very similar to those reported for $(PPh_3)_2Pt(Ph_3SnC(S)SR)^2$ and $(PPh_3)_2PtCS_2$,¹ both of which have been shown by crystallographic methods^{2,14} to contain η^2 -CS-bonded ligands as shown in structures Ia and Ib. On the basis of the similar ^{31}P and



^{195}Pt (see below) NMR data and the evidence from the infrared spectra, it is proposed that $(PPh_3)_2Pt(R_2P(S)C(S)SR')$ also contain a η^2 -CS linkage as shown in structure II.



However, the long-range phosphorus–phosphorus coupling between the triphenylphosphine groups and the dithioformate ligand is small and similar so that they cannot provide an unambiguous assignment of the individual phosphine resonances. In order to do this, the complexes were prepared with 20% ¹³C enrichment (using enriched ¹³CS₂) at the C(S)SMe carbon. The $^{31}P\{^1H\}$ NMR spectra of both the diphenyl- and dicyclohexyl-enriched derivatives show that the triphenylphosphine resonance at lower frequency has the larger coupling to carbon ($^2J_{PC} = 67.7$ (Ph), 69.7 Hz (Cy)) while the phosphine resonance at higher frequency has a much smaller coupling to carbon ($^2J_{PC} \approx 4$ Hz) in each case. These dif-

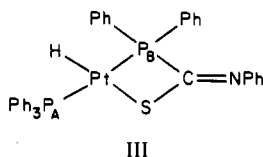
ferences are sufficiently great to enable an assignment to be made with the phosphine at lower frequency trans to carbon. Similar coupling constants were observed for enriched $(\text{PPh}_3)_2\text{PtCS}_2$.² The above data also show that the η^2 -CS-bonded ligand is not fluxional at room temperature. Similar conclusions have been reached for $(\text{PPh}_3)_2\text{PtCS}_2$ ¹⁵ and $(\text{PPh}_3)_2\text{Pt}(\text{Ph}_2\text{SnC}(\text{S})\text{SR})$.²

The $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectra of $(\text{PPh}_3)_2\text{Pt}(\text{R}_2\text{P}(\text{S})\text{C}(\text{S})\text{SMe})$ ($\text{R} = \text{Ph}, \text{Cy}$) are very similar and consist of doublets of doublets of doublets. Coupling constants agree with those derived from the phosphorus spectra and confirm the presence of two directly bound triphenylphosphine groups and a third phosphorus not directly bound to platinum.

The ^1H NMR spectra of these two compounds show a broad ill-defined multiplet centered at δ 7.4 with relative intensity 40, which is assigned to the phenyl protons, and a doublet of intensity 3, assigned to the methyl group.

All of the NMR spectra of the complexes $(\text{PPh}_3)_2\text{Pt}(\text{R}_2\text{P}(\text{S})\text{C}(\text{S})\text{CH}_2\text{Ph})$ are essentially the same as those described for the methyl derivatives. The only additional feature of interest is the methylene signal in the ^1H NMR spectrum that appears as an AB quartet.

Reactions with $\text{Ph}_2\text{PC}(\text{S})\text{NPh}$ and $\text{Ph}_2\text{PC}(\text{S})\text{NPh}(\text{SiMe}_3)$. The reaction between $(\text{PPh}_3)_4\text{Pt}$ and $\text{Ph}_2\text{PC}(\text{S})\text{NPh}$ has been reported previously⁵ and the product shown to have structure III on the basis of ^1H NMR and infrared spectral studies. The

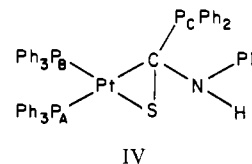


mechanism originally suggested⁵ for the formation of this hydride involved an initial oxidative addition of the N-H bond to platinum followed by the displacement of one triphenylphosphine by the sulfur atom of the ligand. We have repeated this preparation and isolated a product with properties similar to those reported. The ^1H NMR spectrum at room temperature is the same as that reported,⁵ and at 0 °C the hydride resonance appears as a broad doublet (δ -10.82, $w_{1/2} \sim 15$ Hz) with well-defined, although broad, platinum-195 satellites ($^1J_{\text{Pt,H}} = 1160$ Hz). Coupling to the two phosphorus nuclei is not resolved. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at 0 °C consists of two main resonances, one very broad signal (δ 23.0, $w_{1/2} \sim 35$ Hz) with broad platinum-195 satellites ($^1J_{\text{Pt,P}} = 3393$ Hz) and a sharper signal (δ 14.1, $w_{1/2} \sim 20$ Hz, $^1J_{\text{Pt,P}} = 1384$ Hz). The integrated intensities of the resonances are equal. Clearly some exchange process involving the triphenylphosphine group is operative at 0 °C, but studies at lower temperatures are impossible because the complex precipitates from solution.

In order to follow the course of the formation of the hydride in solution, equimolar amounts of $(\text{PPh}_3)_2\text{PtC}_2\text{H}_4$ (a more convenient starting material than $(\text{PPh}_3)_4\text{Pt}$) and $\text{Ph}_2\text{PC}(\text{S})\text{NPh}$ were mixed in an NMR tube in dichloromethane and the reaction was monitored at 30 °C by NMR methods. Ten minutes after mixing, the ^{31}P NMR spectrum showed the presence of neither the starting materials nor the final hydride product $(\text{PPh}_3)\text{Pt}(\text{H})(\text{Ph}_2\text{PC}(\text{S})\text{NPh})$. The observed $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum consists of three main multiplets (δ 33.1, 26.1, 18.1) each with a set of platinum-195 satellites. The two lower frequency resonances have coupling constants to platinum of 4618 and 3026 Hz and a small coupling to each other ($^2J_{\text{P,P}} = 7$ Hz), which suggests two triphenylphosphine groups cis to each other. The resonance at δ 33.1 shows a platinum-phosphorus coupling of 34 Hz and a small coupling of 7 Hz

to the phosphine resonance at higher frequency. The $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectrum, accumulated between $1/2$ and $2 1/2$ h after the mixing of the reactants, consists of a doublet of doublet of doublets, centered at δ -4809, with the same coupling constants as those derived from the phosphorus spectrum. No hydride resonance was detected in the ^1H NMR spectrum, but instead a broad doublet at δ 5.54 ($^3J_{\text{P,H}} = 6.4$ Hz) is observed and assigned to a proton bonded to nitrogen (Table V).

The compound was isolated in good yield, and its infrared spectrum is similar to that of free $\text{Ph}_2\text{PC}(\text{S})\text{NPhH}$ with the exception that ν_{NCS} and ν_{NCS} of the free ligand at 1525 and 1384 cm^{-1} , respectively, are absent and ν_{NH} moved from 3300 cm^{-1} to lower frequency (see Tables II and III). These data and the analytical data (Table I) are consistent with this complex being the η^2 -CS-bonded complex $(\text{PPh}_3)_2\text{Pt}(\text{Ph}_2\text{PC}(\text{S})\text{NPhH})$ as shown in structure IV.



If η^2 - $(\text{PPh}_3)_2\text{Pt}(\text{Ph}_2\text{PC}(\text{S})\text{NPhH})$ is redissolved in dichloromethane, new peaks gradually appear in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. At room temperature, these consist of two extremely broad resonances ($w_{1/2} \approx 300, 70$ Hz), but at -100 °C, the spectrum is resolved into three slightly broadened resonances of equal intensities at δ 25.3, 23.2, and 10.8. The two resonances at the higher frequencies have well-defined platinum-195 satellites ($^1J_{\text{Pt,P}} = 3360, 2640$ Hz) and are assigned to *cis*-triphenylphosphine groups although no phosphorus-phosphorus coupling can be detected because of the broadness of the lines. The resonance at lowest frequency (δ 10.8) is also quite broad ($w_{1/2} \approx 30$ Hz) with broad platinum-195 satellites that show a coupling constant of 1400 Hz. This resonance is assigned to the PPh_2 group of the ligand directly bonded to platinum. No resonance corresponding to free triphenylphosphine is observed in this spectrum. The $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectrum, centered at δ -4872, is a very broad doublet of doublets ($w_{1/2} \approx 300$ Hz) with platinum-phosphorus coupling constants the same as those derived from the phosphorus spectrum to the phosphine groups.

The new compound, which gives rise to the NMR spectra described above, is present in only relatively low concentrations in the solution, and it cannot be isolated. It is proposed that at -100 °C the compound is predominantly of structure 2A (Scheme I) with the ligand coordinated to platinum through phosphorus and sulfur. It has previously been shown^{4,5,16} that sulfur coordination is generally favored over nitrogen coordination for these ligands. At temperature above -100 °C, it is proposed that exchange occurs between different isomers of $(\text{PPh}_3)_2\text{Pt}(\text{Ph}_2\text{PPC}(\text{S})\text{NPhH})$ (structures 2A-C, Scheme I), which leads to line broadening in the NMR spectra. Exchange between P,S and P,N coordination (2A,B) involves rotation about the P-C bond of the ligand and is supported by evidence from the complex made from the silylated ligand $\text{Ph}_2\text{PC}(\text{S})\text{NPh}(\text{SiMe}_3)$ (see below) while exchange between 2A and 2C involves proton transfer similar to that observed for pyridinethiols.¹⁷

After a few more hours an NMR spectrum of the solution showed signals due to the hydride $(\text{PPh}_3)\text{Pt}(\text{H})(\text{Ph}_2\text{PC}(\text{S})\text{NPh})$ and free triphenylphosphine, and it is the formation of the hydride that limits the concentration of the species 2A-C. Presumably, the final hydride product is formed by initial

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Table V. NMR Data for the Thioformamide Complexes in CH₂Cl₂ at Approximately 0.13 M

compd, temp, °C	$\delta(^1\text{H})$	$\delta(^{31}\text{P})^a$	coupling const, Hz	$\delta(^{195}\text{Pt})$
(PPh ₃) ₂ Pt(Ph ₂ PC(S)NPh) (IV), 25	5.54	P _B 26.1 P _A 18.1 P _C 33.1	¹ J _{Pt,P_B} = 4618 ¹ J _{Pt,P_A} = 3026 ² J _{Pt,P_C} = 34 ² J _{P_A,P_B} = 7 ³ J _{P_B,P_C} = 7 ³ J _{P,H} = 6.4	-4809
(PPh ₃) ₂ Pt(Ph ₂ PC(S)NPh(SiMe ₃)) (similar to IV), 25		P _B 26.0 P _A 18.2 P _C 34.2	¹ J _{Pt,P_B} = 4604 ¹ J _{Pt,P_A} = 3032 ² J _{Pt,P_C} = 30 ² J _{P_A,P_B} = 7	
(PPh ₃) ₂ Pt(Ph ₂ PC(S)NPh) (2A), ^b -100		P _A 25.3 P _B 23.2 P _C 10.8	¹ J _{Pt,P_A} = 3360 ¹ J _{Pt,P_B} = 2640 ¹ J _{Pt,P_C} = 1400	-4872
(PPh ₃) ₂ Pt(Ph ₂ PC(S)NPh(SiMe ₃)) (similar to 2A), ^b -100	0.5 (Me)	P _A 30.3 P _B 21.5 P _C 13.1	¹ J _{Pt,P_A} = 3554 ¹ J _{Pt,P_B} = 2732 ¹ J _{Pt,P_C} = 1423	
(PPh ₃) ₂ Pt(Cy ₂ PC(S)NPhH) (similar to 2A), ^b -90		P _A 27.6 P _B 24.3 P _C 18.2 P _C 18.2	¹ J _{Pt,P_A} = 3391 ¹ J _{Pt,P_B} = 2400 ¹ J _{Pt,P_C} = 1387 ² J _{P_B,P_C} = 4	-4816
(PPh ₃)Pt(H)(Cy ₂ PC(S)NPh) (similar to III), -60	-11.34	P _A 17.2 P _B 30.0	¹ J _{Pt,P_A} = 2274 ¹ J _{Pt,P_B} = 2906 ² J _{P_A,P_B} = 370 ¹ J _{Pt,H} = 1155 ² J _{P,H} = 18.2	-4858
(PPh ₃) ₂ Pt(Ph ₂ P(S)C(S)NPh) (V), 25	6.35	P _B 24.6 P _A 17.2 P _C 53.8	¹ J _{Pt,P_B} = 4598 ¹ J _{Pt,P_A} = 2986 ² J _{Pt,P_C} = 24 ² J _{P_A,P_B} = 5.1 ³ J _{P_B,P_C} = 8.0 ³ J _{P_A,P_C} = 5.0 ³ J _{P_C,H} = 6	-4873
(PPh ₃) ₂ Pt(Cy ₂ P(S)C(S)NPh) (similar to V), 25	5.35	P _B 25.8 P _A 16.4 P _C 70.5	¹ J _{Pt,P_B} = 4680 ¹ J _{Pt,P_A} = 2848 ² J _{Pt,P_C} = 22 ² J _{P_A,P_B} = 10.3 ³ J _{P_B,P_C} = 4.1 ³ J _{P_A,P_C} = 2.2	-4815
(PPh ₃) ₂ Pt(Cy ₂ P(S)C(S)NPh) (VI), -80		P _A 28.6 P _B 17.7 P _C 68.2	¹ J _{Pt,P_A} = 3408 ¹ J _{Pt,P_B} = 2861 ² J _{Pt,P_C} = 49 ² J _{P_A,P_B} = 4	-4701
(PPh ₃)Pt(H)(Cy ₂ P(S)C(S)NPh) (VII), -100	-12.97	P _A 24.0 P _B 60.0	¹ J _{Pt,P_A} = 3528 ² J _{Pt,P_B} = 24 ¹ J _{Pt,H} = 1230 ² J _{P_A,H} = 16 ³ J _{P_B,H} = 1	-4704

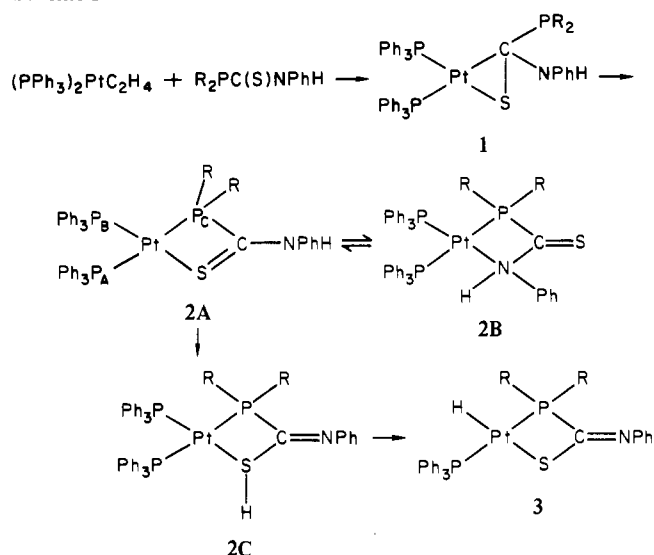
^a Phosphorus atoms identified in the appropriate structure diagrams. ^b The identities of P_A and P_B cannot be determined in 2A.

transfer of hydrogen to sulfur (structure 2C, Scheme I), but no direct spectroscopic evidence for this intermediate was obtained.

In an effort to obtain further evidence for this mechanism, the reaction between (PPh₃)₂PtC₂H₄ and the silylated ligand Ph₂PC(S)NPh(SiMe₃) was studied. The ligand has been shown⁹ to exist with the SiMe₃ group bonded to nitrogen, not sulfur. The reaction at 25 °C in dichloromethane gave a product in solution with NMR parameters (Table V) very similar to those observed for the complex η^2 -(PPh₃)₂Pt-(Ph₂PC(S)NPh) (structure 1, Scheme I). The complex was subsequently isolated, and analytical data (Table I) are consistent with its formulation as the η^2 -CS-bonded complex (PPh₃)₂Pt(Ph₂PC(S)NPh(SiMe₃)) with a structure similar to that of IV.

Subsequent dissolution of this compound in dichloromethane results in the gradual formation of a new species in solution for which the ³¹P{¹H} NMR spectrum (Table V) and its variation with temperature are very similar to that described above for complexes 2A–C (Scheme I). Significantly, no further reaction occurred, so in this case the labile compound could be isolated by simple evaporation of the solution after the reaction was complete. Analytical data confirmed that the empirical formula is still (PPh₃)₂Pt(Ph₂PC(S)NPh-(SiMe₃)) so that only a rearrangement (without loss of any ligand) had occurred during its formation. Its ¹H NMR spectrum at room temperature shows a very broad singlet (δ 0.5, $w_{1/2} \approx 30$ Hz) for the protons of the SiMe₃ group. When the mixture is cooled to -100 °C, the resonance sharpens considerably ($w_{1/2} \approx 8$ Hz) but not sufficiently to observe

Scheme I



coupling to phosphorus or silicon. This dynamic behavior is consistent with rapid exchange between P,S and P,N coordination of the ligand as shown in Scheme I, structures 2A,B (read SiMe_3 for H). It is assumed that the isolated solid was in the preferred P,S-coordinated form. It is interesting that transfer of a SiMe_3 group from nitrogen to platinum does not occur even though the NMR spectra suggest that the dynamic properties in solution of $(\text{PPh}_3)_2\text{Pt}(\text{Ph}_2\text{PC}(\text{S})\text{NPhH})$ and $(\text{PPh}_3)_2\text{Pt}(\text{Ph}_2\text{PC}(\text{S})\text{NPh}(\text{SiMe}_3))$ are very similar, which presumably means that transfer of SiMe_3 to sulfur (structure 2C) does not occur.

Reaction with $\text{Cy}_2\text{PC}(\text{S})\text{NPhH}$. Reaction of $\text{Cy}_2\text{PC}(\text{S})\text{NPhH}$ with $(\text{PPh}_3)_2\text{PtC}_2\text{H}_4$ follows essentially the same course as that described in the previous section for $\text{Ph}_2\text{PC}(\text{S})\text{NPhH}$, with the main difference being that the reaction with $\text{Cy}_2\text{PC}(\text{S})\text{NPhH}$ is much faster. Mixing of equimolar proportions of the reactants in dichloromethane at room temperature causes immediate formation of the hydride $(\text{PPh}_3)\text{Pt}(\text{H})(\text{Cy}_2\text{PC}(\text{S})\text{NPh})$ analogous to structure III.

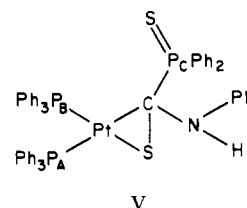
At room temperature, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $(\text{PPh}_3)\text{Pt}(\text{H})(\text{Cy}_2\text{PC}(\text{S})\text{NPh})$ is similar to that of its phenyl analogue $(\text{PPh}_3)\text{Pt}(\text{H})(\text{Ph}_2\text{PC}(\text{S})\text{NPh})$ and consists of two broad resonances ($w_{1/2} \approx 60$ Hz) with broad platinum-195 satellites. However, this compound is more soluble than its phenyl analogue, which allows cooling to -60 °C. At this temperature the phosphorus resonances are sharp and appear as an AB spectrum with ABX satellite subspectra. The ABX spectra were analyzed giving the parameters shown in Table V, which were consistent with those observed in the platinum-195 NMR spectrum. The $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectrum is a doublet of doublets, but the lines are surprisingly broad ($w_{1/2} = 100$ Hz) to temperatures as low as -100 °C. The proton-coupled ^{195}Pt NMR spectrum shows the expected additional coupling due to the hydride atom. In the ^1H NMR spectrum recorded at -60 °C in CDCl_3 , the hydride resonance ($\delta -11.34$) shows well-resolved couplings to the two phosphorus nuclei and to platinum (Table V). All these data are consistent with the proposed structure III.

In an attempt to slow the formation of the hydride $(\text{PPh}_3)\text{Pt}(\text{H})(\text{Cy}_2\text{PC}(\text{S})\text{NPh})$ in order to observe intermediate species, solutions of $(\text{PPh}_3)_2\text{PtC}_2\text{H}_4$ and $\text{Cy}_2\text{PC}(\text{S})\text{NPhH}$ in dichloromethane were mixed at -30 °C. The pale yellow solid that precipitated immediately showed an infrared spectrum very similar to that of η²-CS-bonded $(\text{PPh}_3)_2\text{Pt}(\text{Ph}_2\text{PC}(\text{S})\text{NPhH})$ (structure IV), and analytical data confirm the formulation $(\text{PPh}_3)_2\text{Pt}(\text{Cy}_2\text{PC}(\text{S})\text{NPhH})$ (Table I). When this solid is dissolved in dichloromethane at room temperature, the

$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum observed is that of $(\text{PPh}_3)\text{Pt}(\text{H})(\text{Cy}_2\text{PC}(\text{S})\text{NPh})$ (and free PPh_3), confirming that the η²-CS-bonded complex in this system is unstable.

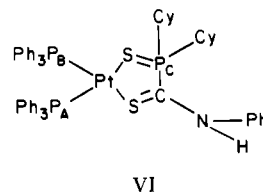
When a suspension of freshly precipitated η²-CS-bonded $(\text{PPh}_3)_2\text{Pt}(\text{Cy}_2\text{PC}(\text{S})\text{NPhH})$ in dichloromethane at -30 °C is warmed slightly, the solid dissolves, and when it is rapidly cooled to -80 °C, a $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum is observed with parameters very similar to those described for the P,S-coordinated compound $(\text{PPh}_3)_2\text{Pt}(\text{Ph}_2\text{PC}(\text{S})\text{NPhH})$ (structure 2A, Scheme I). The η²-CS-bonded $(\text{PPh}_3)_2\text{Pt}(\text{Cy}_2\text{PC}(\text{S})\text{NPhH})$ was dissolved in tetrahydrofuran and precooled to -80 °C, and once again the ^{31}P spectrum observed is that of the P,S-coordinated form of $(\text{PPh}_3)_2\text{Pt}(\text{Cy}_2\text{PC}(\text{S})\text{NPhH})$. These results indicate that the η²-CS-bonded isomer is only stable in the solid state. On dissolution, it converts rapidly to the P,S-coordinated form (observed only at low temperatures), which in turn rapidly converts to the hydride $(\text{PPh}_3)\text{Pt}(\text{H})(\text{Cy}_2\text{PC}(\text{S})\text{NPh})$. Thus, the proposed mechanism for the formation of $(\text{PPh}_3)\text{Pt}(\text{H})(\text{Cy}_2\text{PC}(\text{S})\text{NPh})$ is similar to that of the phenyl analogue (Scheme I) except that the rates of reaction are faster.

Reaction with $\text{R}_2\text{P}(\text{S})\text{C}(\text{S})\text{NPhH}$ Ligands. Reaction of equimolar quantities of $\text{R}_2\text{P}(\text{S})\text{C}(\text{S})\text{NPhH}$ ($\text{R} = \text{Ph}, \text{Cy}$) and $(\text{PPh}_3)_2\text{PtC}_2\text{H}_4$ in benzene or dichloromethane for 5 min, followed by addition of hexane, yields pale yellow solids. Their infrared spectra show well-defined ν_{NH} vibrations and ν_{PS} stretches that are essentially unchanged from those for the free ligands (Tables II and III). The ν_{INC} and ν_{NCS} vibrations of the free ligands are absent from the infrared spectra of the complexes. The ^1H , ^{31}P , and ^{195}Pt NMR spectra of the complexes in dichloromethane at room temperature are very similar to those of the η²-CS-bonded complexes described earlier (Table V). Thus, these complexes are formulated as η²-CS-bonded $(\text{PPh}_3)_2\text{Pt}(\text{R}_2\text{P}(\text{S})\text{C}(\text{S})\text{NPhH})$ (structure V), and

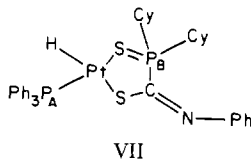


these formulations are supported by analytical data (Table I).

The compound $(\text{PPh}_3)_2\text{Pt}(\text{Ph}_2\text{P}(\text{S})\text{C}(\text{S})\text{NPhH})$ is relatively stable in solution, but after several hours decomposition is evident with deposition of platinum metal. No evidence was found for the formation of a hydride complex. In contrast, at 25 °C a solution of $(\text{PPh}_3)_2\text{Pt}(\text{Cy}_2\text{P}(\text{S})\text{C}(\text{S})\text{NPhH})$ in dichloromethane a few hours after dissolution shows some new broad and ill-defined resonances in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. However, the spectrum becomes sharp at -80 °C, and the ^1H , ^{31}P , and ^{195}Pt NMR spectra at -80 °C (Table V) allow identification of two compounds in solution. One of these is the S,S-bonded complex $(\text{PPh}_3)_2\text{Pt}(\text{Cy}_2\text{P}(\text{S})\text{C}(\text{S})\text{NPhH})$ (structure VI), which is never present in substantial concen-



trations and could not be isolated, so that its identity could only be inferred from the NMR spectra by analogy with the P,S-coordinated forms of $(\text{PPh}_3)_2\text{Pt}(\text{R}_2\text{PC}(\text{S})\text{NPhH})$. The second product is believed to be the S,S-coordinated hydride $(\text{PPh}_3)\text{Pt}(\text{H})(\text{Cy}_2\text{P}(\text{S})\text{C}(\text{S})\text{NPh})$ (structure VII). After about 10 h, only this complex and free PPh_3 were present in solution and it was readily isolated. The solid-state infrared spectrum



shows a platinum-hydrogen stretch at 2154 cm^{-1} , a strong band at 1540 cm^{-1} assigned to the CN stretch, and a P-S stretch at 602 cm^{-1} (622 cm^{-1} for the free ligand). All these data together with the NMR data (Table V) are consistent with the proposed structure VII.

Conclusions

We have compared the reactions of a range of ligands of the types $\text{R}_2\text{P}(\text{S})\text{C}(\text{S})\text{SR}'$, $\text{R}_2\text{PC}(\text{S})\text{NPhH}$, and $\text{R}_2\text{P}(\text{S})\text{C}(\text{S})\text{NPhH}$ with $(\text{PPh}_3)_2\text{PtC}_2\text{H}_4$. $\text{R}_2\text{P}(\text{S})\text{C}(\text{S})\text{SR}'$ ligands form stable η^2 -CS-bonded complexes in a manner similar to that previously reported² for $\text{Ph}_3\text{SnC}(\text{S})\text{SR}'$ ligands. None of the complexes with these types of ligands show any tendency to internally rearrange through oxidative addition. In contrast, the thioformamide ligands $\text{Ph}_3\text{SnC}(\text{S})\text{NPh}$,² $\text{R}_2\text{PC}(\text{S})\text{NPhH}$, and $\text{R}_2\text{P}(\text{S})\text{C}(\text{S})\text{NPhH}$ give η^2 -CS-bonded complexes, which

in general do undergo internal oxidative additions of various types. For the phosphorus-based ligands, the rate of reaction of the initially formed η^2 -CS compound appears to depend upon the base strength of the phosphorus portion of the ligand, reactivity decreasing in the sequence $\text{Cy}_2\text{P} \gg \text{Ph}_2\text{P} > \text{Cy}_2\text{P}(\text{S}) \gg \text{Ph}_2\text{P}(\text{S})$. In all cases, hydride transfer to platinum is the last step in the reaction.

Acknowledgment. S.W.C. thanks the Commonwealth Government for a Commonwealth Postgraduate Research Award.

Registry No. 1 (R = Ph), 88548-34-9; 1 (R = Cy), 88548-37-2; II (R = Ph, R' = Me), 88548-30-5; II (R = Ph, R' = CH_2Ph), 88548-31-6; II (R = Cy, R' = Me), 88548-32-7; II (R = Cy, R' = CH_2Ph), 88548-33-8; V, 88548-39-4; VI, 88548-40-7; VII, 88548-41-8; 3 (R = Cy), 88548-38-3; $(\text{PPh}_3)_2\text{Pt}(\text{Ph}_2\text{PC}(\text{S})\text{NPh}(\text{SiMe}_3))$ (η^2 -CS-bonded isomer), 88548-35-0; $(\text{PPh}_3)_2\text{Pt}(\text{Ph}_2\text{PC}(\text{S})\text{NPh}(\text{SiMe}_3))$ (P,S-bonded isomer), 88548-36-1; $(\text{PPh}_3)_2\text{PtC}_2\text{H}_4$, 12120-15-9; $(\text{PPh}_3)_4\text{Pt}$, 14221-02-4; $\text{Ph}_2\text{PC}(\text{S})\text{NPhH}$, 739-61-7; $\text{Cy}_2\text{PC}(\text{S})\text{NPhH}$, 899-27-4; $\text{Ph}_2\text{P}(\text{S})\text{C}(\text{S})\text{SMe}$, 28658-59-5; $\text{Cy}_2\text{P}(\text{S})\text{C}(\text{S})\text{SMe}$, 88525-71-7; $\text{Ph}_2\text{P}(\text{S})\text{C}(\text{S})\text{SCH}_2\text{Ph}$, 28658-61-9; $\text{Cy}_2\text{P}(\text{S})\text{C}(\text{S})\text{SCH}_2\text{Ph}$, 88525-72-8; $\text{Ph}_2\text{P}(\text{S})\text{C}(\text{S})\text{NPhH}$, 7067-81-4; $\text{Cy}_2\text{P}(\text{S})\text{C}(\text{S})\text{NPhH}$, 14633-83-1; $\text{Ph}_2\text{PC}(\text{S})\text{NPh}(\text{SiMe}_3)$, 18789-75-8; sulfur, 7704-34-9.

Contribution from Central Research—New England Laboratory, Dow Chemical USA, Wayland, Massachusetts 01778, and the Department of Chemistry, Indiana University, Bloomington, Indiana 47405

Reexamination of the Reactions of $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1-4$) with $\text{RuCl}_2(\text{PPh}_3)_3$

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A reinvestigation of the reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with the chelating diphosphines $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$, $n = 1-4$, reveals chemistry very dependent on the length of the methylene chain. Only for $n = 4$ is the complex $\text{RuCl}_2(\text{PPh}_3)(\text{chelate})$ isolatable. ³¹P NMR studies reveal numerous halo-bridged species in solution for the various ligands. Neither dppe nor dpmm forms coordinatively unsaturated $\text{RuCl}_2(\text{PPh}_3)(\text{chelate})$, which is explained as a function of the chelate bite angle.

Our recent studies on the dehydrogenation of alcohols¹ and amines² using Ru(II) phosphine catalysts led us to prepare several Ru(II) complexes containing the bidentate phosphine ligands $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1$, dpmm; $n = 2$, dppe; $n = 3$, dppp; $n = 4$, dppb). Others³ have noted that the addition of 2 equiv of $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1-3$) to a suspension of RuCl_2L_3 (L = PPh_3) gives yellow complexes of composition $\text{RuCl}_2[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]_2$. Such complexes were shown to have octahedral stereochemistry with trans chloride ligands. When $n = 4$, however, it has been reported⁴ that an insoluble, dimeric, light green complex analyzing as $[\text{RuCl}_2(\text{dppb})_{1.5}]_2$ results. We have conducted detailed studies on such reactions using ³¹P{¹H} NMR in hope of determining the optimum conditions for the isolation of species of the type $\text{RuCl}_2\text{PPh}_3(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)$, and herein we report these studies.

Experimental Section

Unless indicated otherwise, all operations were conducted under purified argon or nitrogen by using standard inert-atmosphere techniques. NMR spectra were recorded on JEOL FX90-Q and Varian XL-100 spectrometers. Phosphorus-31 chemical shifts were referenced to external H_3PO_4 , positive chemical shifts being downfield of this reference. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

The diphosphines $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1-4$) were obtained from Strem Chemical, Inc., and were used without further purification.

Solvents were reagent grade, dried with 3-Å molecular sieves, and deoxygenated with bubbling argon or under vacuum prior to use. Literature methods and modifications of these (see below) were used to prepare $\text{RuCl}_2(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)_2$ ($n = 1-3$)³ and $[\text{RuCl}_2(\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2)_{1.5}]_2$.⁴

$\text{RuCl}_2(\text{chelate})_2$, $\text{trans-RuCl}_2(\text{dppe})_2$ and $\text{trans-RuCl}_2(\text{dpmm})_2$ were prepared from $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and the bidentate phosphine (mole ratio 1:2.5) by reflux in ethanol.^{5,6} The absence of the cis isomer in the precipitated product was established by ³¹P NMR. The analogous reaction (2-h reflux in methanol) was carried out for dppp, but product isolation was carried out by removal of methanol under vacuum followed by dissolving the solid residue in CH_2Cl_2 . This solution was sealed under vacuum in an NMR tube. The ³¹P NMR spectrum of this solution showed (in addition to dppp and its monoxide) *cis*- and *trans*- $\text{RuCl}_2(\text{dppp})_2$ in a 2:1 mole ratio. ³¹P NMR parameters of *cis*- $\text{RuCl}_2(\text{dppp})_2$ (in CH_2Cl_2 at 303 K) are as follows: 42.0 (t), -2.7 ppm (t, $J = 31.5$ Hz).

Preparation of $\text{RuCl}_2(\text{PPh}_3)(\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2)$. $\text{RuCl}_2(\text{PPh}_3)_3$ (1.004 g, 1.047 mmol) and dppb (0.449 g, 1.053 mmol) were mixed together in a Schlenk tube under argon in 50 mL of CH_2Cl_2 . A bright green material began to precipitate immediately. The suspension was stirred an additional 0.5 h and then transferred by cannula to 150 mL of dry degassed ethanol to precipitate the remaining Ru complexes and remove PPh_3 . The precipitate was filtered, washed with 100 mL of ethanol and 100 mL of petroleum ether, and vacuum dried;⁷ yield

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