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S-Alkyl (Triphenylstannyl)dithioformate and *N*-Alkyl(triphenylstannyl)thioformamide Derivatives of Platinum. Preparation and Phosphorus-31, Tin-119, and Platinum-195 NMR Studies. Crystal and Molecular Structure of Bis(triphenylphosphine)(*S*-methyl (triphenylstannyl)dithioformate)platinum(0)

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The reactions between $(PPh_3)_2PtC_2H_4$ and $Ph_3SnC(S)SR$ (R = Me, CH_2Ph, 2-propenyl) have been studied and the products characterized by analytical, infrared, and multinuclear magnetic resonance (^{31}P, ^{119}Sn, ^{195}Pt) techniques. All spectroscopic data are consistent with simple replacement of ethylene and coordination of the ligand via the C(S)SR portion of the molecule. Crystal data for $(PPh_3)_2Pt(Ph_3SnC(S)SMe)$ (mp 93–95 °C dec): $M_r = 1160.8$, triclinic space group $P\bar{1}$, $a = 11.9076$ (33) Å, $b = 12.4511$ (37) Å, $c = 18.4647$ (36) Å, $\alpha = 95.22$ (2)°, $\beta = 100.49$ (2)°, $\gamma = 114.92$ (2)°, $Z = 2$, $\rho_{\text{measd}} = 1.59$ g cm^{-3}, Mo Kα radiation, $R = 0.065$, $R_w = 0.067$ for 3732 independent reflections. The molecular structure determination shows there is η^2 coordination of the ligand via the C═S bond with the other sulfur being noncoordinating. The formally platinum(0) center has approximately planar stereochemistry. The initial products of the reaction between $(PPh_3)_2PtC_2H_4$ and $Ph_3SnC(S)N'$ (N′ = NMeH, $\overline{NCH_2CH_2CH_2C}H_2$ (pyrrolyl)) are also η^2-CS coordinated complexes as judged by multinuclear magnetic resonance and infrared studies. However, these complexes rearrange by an internal oxidative-addition reaction to give as the final products the complexes $(PPh_3)_2Pt(Ph)(Ph_2SnC(S)N')$, which contain a direct platinum–tin bond.

Introduction

Platinum(0) complexes show two general reactions; with many molecules they undergo oxidative addition to give platinum(II) complexes, a typical example[1] being

$$(PPh_3)_2PtC_2H_4 + SnR_4 \rightarrow (PPh_3)_2Pt(R)(SnR_3) + C_2H_4$$

which we have recently studied by platinum-195 and tin-119 NMR methods.[2] The second general reaction is simple replacement of ligands with neutral molecules. In particular, the platinum(0) complexes $(PPh_3)_2PtC_2H_4$ and $(PPh_3)_4Pt$ have been shown to react with a wide range of small molecules containing the C═S fragment. Baird and Wilkinson[3] prepared $(PPh_3)_2PtCS_2$, and a crystal structure determination[4] revealed η^2-CS coordination. Similar linkages have been observed with small molecules such as COS and CSSe to platinum and other metals.[5-9]

In this paper we report the reactions of *S*-alkyl (triphenylstannyl)dithioformates, $Ph_3SnC(S)SR$ (R = Me, CH_2Ph, 2-propenyl (allyl)), and *N*-alkyl(triphenylstannyl)thioformamides, $Ph_3SnC(S)N'$ (N′ = NMeH, $\overline{NCH_2CH_2CH_2C}H_2$ (pyrrolyl = pyrr)), with $(PPh_3)_2PtC_2H_4$, which show both types of behavior. In each case the initial product is a formally Pt(0) η^2-CS bonded complex, but for the formamide complexes further slow rearrangement occurs through an internal oxidative addition to give a platinum(II) compound with a direct platinum–tin bond.

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 temperature controller calibrated with a platinum resistance thermometer. The ^1H spectra were recorded in $CDCl_3$ at 99.60 MHz and measured against an internal reference of Me_4Si. The remaining NMR spectra were recorded in CH_2Cl_2 with an external ^7Li lock as follows: ^{31}P at 40.32 MHz (85% H_3PO_4); ^{119}Sn at 37.19 MHz (neat Me_4Sn); ^{195}Pt at 21.56 MHz (1 M H_2PtCl_6 in concentrated HCl). High-frequency positive convention is used.

Preparations. All preparations were carried out under a nitrogen atmosphere in dry degassed solvents at room temperature. The compounds $(PPh_3)_4Pt$[10] and $(PPh_3)_2PtC_2H_4$[11] were prepared by published methods and $Ph_3SnC(S)SR$ (R = Me, allyl, CH_2Ph) by a slight modification of the published method.[12] After addition of the MeI (or C_3H_5Br or $PhCH_2Cl$) to the Ph_3SnCS_2Li salt in THF, the solution was evaporated to dryness and then extracted with petroleum ether (bp 40–60 °C). The volume was reduced by evaporation, and the crystals were washed with copious volumes of hexane to yield the pure compounds ($Ph_3SnC(S)SMe$, mp 126–127 °C, lit.[12] mp 128–129 °C; $Ph_3SnC(S)SC_3H_5$, mp 71–72 °C, lit.[12] mp 57–58 °C; $Ph_3SnC(S)SCH_2Ph$, mp 65 °C). $Ph_3SnC(S)N'$ (N′ = NMeH, pyrrolyl) were prepared by adding the corresponding secondary amine in ether or methanol to a rapidly stirred solution of $Ph_3SnC(S)SMe$ in ether. Within about 10 min the solution changed from red-violet to colorless. The solvent and excess amine were removed under vacuum, and the product was recrystallized from petroleum ether (bp 40–60 °C) several times to yield colorless crystals ($Ph_3SnC(S)NMeH$, mp 146–147 °C; $Ph_3SnC(S)pyrr$, mp 143 °C).

$(PPh_3)_2Pt(Ph_3SnC(S)SR)$. A solution of $Ph_3SnC(S)SR$ in benzene (0.23 mmol in 5 cm^3) was added with stirring to a solution of $(PPh_3)_2PtC_2H_4$ (0.23 mmol in 5 cm^3) in benzene. Evolution of C_2H_4 was observed, and the red-violet color of the ligand disappeared. The pale yellow product was precipitated with hexane and recrystallized by dissolving in benzene followed by precipitation with hexane. Yields were almost quantitative.

$(PPh_3)_2Pt(Ph)(Ph_2SnC(S)N')$. A solution of $Ph_3SnC(S)NMeH$ or $Ph_3SnC(S)pyrr$ (0.24 mmol in 5 cm^3 benzene) was added to $(PPh_3)_2PtC_2H_4$ in benzene (0.23 mmol in 5 cm^3) and stirred for 24 h. The product was isolated and recrystallized as described above. Yields were approximately 50%.

Microanalyses were by AMDEL, Melbourne, and data for new compounds are given in Table I.

Crystal Structure Determination of $(PPh_3)_2Pt(Ph_3SnC(S)SMe)$. Crystallographic Data. In general, the crystals of $(PPh_3)_2Pt(Ph_3SnC(S)SMe)$ were relatively small and were of an irregular platelike shape. A preliminary X-ray study of the crystals was un-

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[1] Butler, G.; Eaborn, C.; Pidcock, A. *J. Organomet. Chem.* **1979**, *181*, 47.
[2] Carr, S. W.; Colton, R.; Dakternieks, D. *J. Organomet. Chem.* **1983**, *249*, 327.
[3] Baird, M. C.; Wilkinson, G. *Chem. Commun.* **1966**, 514.
[4] Mason, R.; Rae, A. I. M. *J. Chem. Soc. A* **1970**, 1767.
[5] Gaffney, T. R.; Ibers, J. A. *Inorg. Chem.* **1982**, *21*, 2860.
[6] Thewissen, D. H. M. W. *J. Organomet. Chem.* **1980**, *188*, 211.
[7] Robert, P.; Le Bozec, H.; Dixneuf, P. H.; Hartstock, F.; Taylor, N. J.; Carty, A. J. *Organometallics* **1982**, *1*, 1148.
[8] Werner, H. *Coord. Chem. Rev.* **1982**, *43*, 165.
[9] Boniface, S. M.; Clark, G. R. *J. Organomet. Chem.* **1980**, *184*, 125.
[10] Malatesta, L.; Cariello, C. *J. Chem. Soc.* **1958**, 2323.
[11] Cook, C. D.; Jauhal, G. S. *J. Am. Chem. Soc.* **1968**, *90*, 1464.
[12] Kunze, U.; Bolz, P.-R.; Winter, W. *Chem. Ber.* **1981**, *114*, 2744.

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Table I. Analytical Data for New Compounds

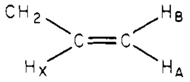
compd	% calcd		% found		mp, °C
	C	H	C	H	
$Ph_3SnC(S)SCH_2Ph$	60.37	4.29	59.61	4.37	65
$Ph_3SnC(S)NMeH$	56.64	4.52	57.02	4.59	146–147
$Ph_3SnC(S)pyrr$	59.51	4.99	59.22	4.19	143
$(PPh_3)_2Pt(Ph_3SnC(S)SMe)$	57.94	4.17	57.99	4.18	93–95 dec
$(PPh_3)_2Pt(Ph_3SnC(S)SCH_2Ph)$	60.20	4.24	60.54	4.27	110–112 dec
$(PPh_3)_2Pt(Ph_3SnC(S)SC_3H_5)$	58.69	4.25	58.58	4.30	126–127 dec
$(PPh_3)_2Pt(Ph)(Ph_2SnC(S)NMeH)$	58.80	4.32	59.49	4.35	115–116 dec
$(PPh_3)_2Pt(Ph)(Ph_2SnC(S)pyrr)$	59.86	4.51	58.19	4.44	121–122 dec

Table II. Crystal Data for $(PPh_3)_2Pt(Ph_3SnC(S)SMe)$[a]

formula	$C_{56}H_{48}PtSnS_2P_2$
M_r	1160.78
cryst system	triclinic
space group	$P\bar{1}$
a, Å	11.9076 (33)
b, Å	12.4511 (37)
c, Å	18.4647 (36)
α, deg	95.22 (2)
β, deg	100.49 (2)
γ, deg	114.49 (2)
vol, Å^3	2406.9
Z	2
ρ(calcd), g/cm^3	1.60
ρ(measd), g/cm^3	1.59
no. of unique reflcns	3732
radiation	Mo Kα (graphite monochromator) = 0.710687 Å
cryst dimens (distance in mm from centroid)	$(\bar{1}2\bar{2})$ 0.0125 $(1\bar{2}2)$ 0.0125 $(\underline{2}10)$ 0.0425 $(\bar{1}0\underline{1})$ 0.05 $(10\underline{1})$ 0.05 $(1\bar{3}4)$ 0.1625
abs coeff, cm^{-1}	39
transmission factors	max 0.8853, min 0.6882
R	6.5%
R_w	6.7%

[a] Standard deviation in parentheses.

Table III. Spectroscopic Data for the Free Ligands



ligand	NMR		IR[a] CS_2 or NCS str	
	$\delta(^1H)$	$\delta(^{119}Sn)$	ν_{asym}	ν_{sym}
$Ph_3SnC(S)SMe$	2.74 (Me)	−192	1048 s	808 w
$Ph_3SnC(S)SCH_2Ph$	4.66 (CH_2)	−191	1050 s	811 w
$Ph_3SnC(S)SC_3H_5$	4.10 (CH_2) 5.14 (H_A) 5.24 (H_B) 5.85 (H_X)	−192	1040 s	808 w
$Ph_3SnC(S)NMeH$	2.16 (Me)	−49	1579 m	1318 w
$Ph_3SnC(S)pyrr$		−55	1573 m	1320 w

[a] s = strong; w = weak.

dertaken by using oscillation and Weissenberg photographic methods. Intensity data were obtained at 298 K with Enraf-Nonius CAD-4F automatic counter diffractometer controlled by a PDP-8a computer. Crystal data are given in Table II. Accurate values of the unit cell parameters and crystal orientation matrix were determined from a least-squares treatment of the angular settings of 24 carefully centered reflections.

Data Collection and Reduction. Intensity data for $5.0° \leq 2\theta \leq 45°$ were collected in the $\omega/2\theta$ mode with use of Mo Kα (graphite monochromator) radiation. Three strong reflections were used as orientation controls (every 100 reflections) and intensity monitors (every 1800 s of X-ray exposure time). There was no indication of decay during data collection and no need to redetermine the orientation matrix. A total of 7587 reflections were measured, which yielded 4860 unique reflections ($R_{amal} = 0.041$[13]) of which 3732 ($I \geq 2\theta(I)$) were judged significant and were used in the refinement of the structure. This reflected the relatively weak scattering nature of the crystals, which was indicated by the preliminary photographic study. Corrections for Lorentz, polarization, and absorption effects were applied,[14] but no correction for extinction was made.

Structure Determination. The positions of the platinum and tin atoms were determined from a three-dimensional Patterson map. Subsequent difference maps located the remaining atoms, which were refined by using a full-matrix least-squares technique.[15] The carbon atoms were refined isotropically and the heavier atoms refined anisotropically. Hydrogen atoms (35 of a total of 48) were located but not included in the model. Refinement converged at a final $R = 0.065$ ($R_w = 0.067$) with $w^{-1} = \sigma^2(F) - 0.004F^2$ for the 3732 observed reflections. In the final difference map the only features worth noting were two peaks situated approximately 1 Å from the tin with electron densities of 1.4 and 1.6 e Å^{-3}.

Calculations were carried out with SHELX,[14] ORTEP,[16] and DISTAN[17] on a Cyber 175 computer of the University Computer Centre. Scattering curves for C, S, Sn, and P were those collected by Sheldrick,[15] and that for platinum was taken from ref 18.

Results and Discussion

Reaction of $(PPh_3)_2PtC_2H_4$ with $Ph_3SnC(S)SR$. When equimolar proportions of $(PPh_3)_2PtC_2H_4$ and $Ph_3SnC(S)SR$ (R = Me, allyl, CH_2Ph) were mixed in dry benzene under a nitrogen atmosphere, the deep red color of the tin compound was almost immediately discharged and ethylene was evolved. Addition of hexane precipitated a yellow solid that could be recrystallized from benzene solution on addition of hexane.

The crystal structure of the free ligand, $Ph_3SnC(S)SMe$, shows two very similar C–S distances[12] that were discussed in terms of two canonical forms involving significant double-bond character in both CS bonds. The infrared spectrum of this ligand shows two vibrational bands at 1048 and 808 cm^{-1}, which were assigned[12] to the symmetric and asymmetric CS stretches, and similar absorptions were found for the other ligands with varying R groups. In all cases, the isolated platinum complexes did not exhibit these absorptions, indicating that some modification of the CS bond had occurred on complexation. All spectroscopic data for the free ligands are given in Table III.

The NMR spectra of all the complexes are similar, so only those of the allyl derivative will be discussed, but data for all

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(13) $R_{amal} = [\sum(N\sum(w(F_{mean} - F)^2))/\sum((N - 1)\sum(wF^2))]^{1/2}$ where the inner summations are over N equivalent reflections averaged to give F_{mean}, the outer summations are over all unique reflections, and the weight, w, is taken as $(\sigma(F))^{1/2}$.

(14) Sheldrick, G. M. "SHELX-76, Program for Crystal Structure Determination", University of Cambridge, Cambridge, U.K., 1976.

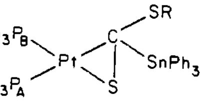
(15) The function minimized was $\sum w(|F_o| - |F_c|)^2$. The unweighted and weighted residuals were defined as $R = (\sum|F_o| - |F_c|)/\sum|F_o|$ and $R_w = \sum w^{1/2}(|F_o| - |F_c|)/\sum w^{1/2}|F_o|$.

(16) Johnson, C. K. "ORTEP", Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

(17) Kelly, B. P.; O'Day, B. P.; Pannan, C. D., unpublished program, University of Melbourne, 1974.

(18) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, p 101.

Table IV. NMR Data for Compounds $(PPh_3)_2Pt(Ph_3SnC(S)SR)$ (25 °C; in CH_2Cl_2 or $CDCl_3$ at ~0.13 M)[a]



compd	$\delta(^1H)$	$\delta(^{31}P)$	$\delta(^{119}Sn)$	$\delta(^{195}Pt)$	coupling const, Hz
$(PPh_3)_2Pt(Ph_3SnC(S)SMe)$	2.24 (Me)	P_A 22.7 P_B 19.6	−185	−4976	$^1J_{Pt,P_A} = 4458$ $^1J_{Pt,P_B} = 3040$ $^2J_{P_A,P_B} = 4$ $^2J_{Pt,Sn} = 245$ $^3J_{Sn,P_A} = 21$ $^3J_{Sn,P_B} = 13$
$(PPh_3)_2Pt(Ph_3SnC(S)SC_3H_5)$	5.78 m, 4.87 m, 3.60 m (CH_2)	P_A 22.0 P_B 18.8	−184	−4964	$^1J_{Pt,P_A} = 4452$ $^1J_{Pt,P_B} = 3042$ $^2J_{P_A,P_B} = 4$ $^2J_{Pt,Sn} = 237$ $^3J_{Sn,P_A} = 22$ $^3J_{Sn,P_B} = 12$
$(PPh_3)_2Pt(Ph_3SnC(S)SCH_2Ph)$	AB qrt (CH_2), 4.47, 3.77	P_A 22.9 P_B 19.6	−182	−4961	$^1J_{Pt,P_A} = 4445$ $^1J_{Pt,P_B} = 3034$ $^2J_{P_A,P_B} = 5$ $^2J_{Pt,Sn} = 250$ $^3J_{Sn,P_A} = 21$ $^3J_{Sn,P_B} = 13$ $^2J_{H,H} = 10.2$

[a] qrt = quartet; m = multiplet. Estimated errors in δ: ^1H, 0.01; ^{31}P, 0.1; ^{119}Sn, 2; ^{195}Pt, 2. Estimated errors in coupling constants: $^2J_{H,H}$, 0.1 Hz; $^2J_{P,P}$, $^2J_{Pt,Sn}$, and $^3J_{Sn,P}$, 1 Hz; $^1J_{Pt,P}$ and $^1J_{Pt,Sn}$, 5 Hz.

compounds are given in Table IV. The $^{31}P\{^1H\}$ NMR spectrum of $(PPh_3)_2Pt(Ph_3SnC(S)SC_3H_5)$ consisted of two doublets of equal intensity arising from two nonequivalent phosphines ($^2J_{P,P} = 4$ Hz) each of which had a pair of evenly spaced platinum-195 satellites ($^1J_{Pt,P} = 4452$, 3042 Hz) with the larger coupling constant being associated with the resonance at higher frequency. No tin satellites were observed for either resonance with use of the large spectral window necessary to observe the widely separated platinum-195 satellites, but with a smaller spectral window and higher digital resolution tin satellites did become apparent ($^3J_{Pt,Sn} = 22$ and 12 Hz) with the greater coupling constant being associated with the phosphine resonance at higher frequency.

Strictly speaking, the two phosphorus atoms show an AB pattern, and differences in the intensities of the outermost and innermost pairs of lines are discernible. However, the ratio $J/\Delta\nu_0$ is very small (0.033), and the system approximates to an AX phosphorus system.

The $^{195}Pt\{^1H\}$ NMR spectrum (Figure 1A) consists of a doublet of doublets due to coupling to the phosphorus atoms, with coupling constants equal to those derived from the phosphorus spectrum. In addition, each resonance is flanked by tin satellites ($J_{Pt,Sn} = 237$ Hz) of approximately 8% intensity each, but because of the relatively small coupling constant separate satellites for tin-117 and tin-119 were not resolved. The small platinum–tin coupling constant suggests the tin is at least two bonds distant from the platinum, as one-bond platinum–tin couplings usually exceed 7000 Hz.[2]

The $^{119}Sn\{^1H\}$ NMR spectrum (Figure 1B) is a closely spaced doublet of doublets due to coupling with two nonequivalent phosphines, together with platinum-195 satellites, with the same coupling constants as derived from the phosphorus and platinum spectra, respectively. The position of the tin-119 resonance is shifted only 8 ppm to lower frequency from the resonance of the free ligand, suggesting that little change of electron density in the tin environment had occurred on complexation.

The ^1H NMR spectrum shows three multiplets in the allyl region. The multinuclear magnetic resonance spectra of the other complexes (R = Me, CH_2Ph) are essentially the same, the only additional feature of interest being that the methylene proton resonance in the benzyl complex appears as an AB quartet.

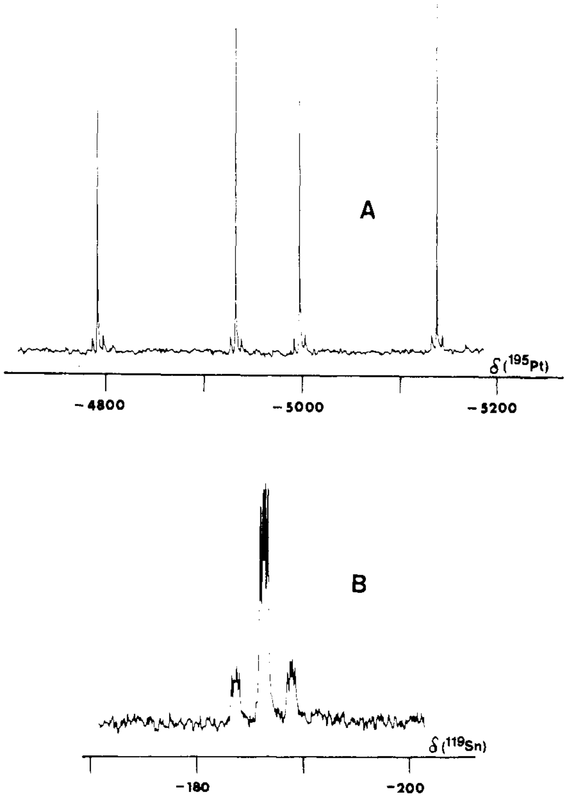


Figure 1. NMR spectra of $(PPh_3)_2Pt(Ph_3SnC(S)SC_3H_5)$ at 25 °C in CH_2Cl_2 solution: (A) $^{195}Pt\{^1H\}$; (B) $^{119}Sn\{^1H\}$.

All the NMR and infrared data reported here for the $(PPh_3)_2Pt(Ph_3SnC(S)SR)$ complexes show that the ligand is coordinated through the C(S)SR portion of the molecule, but

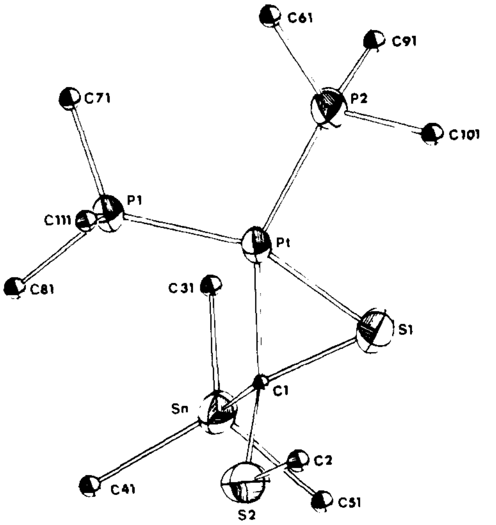
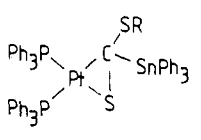
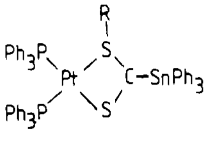


Figure 2. Molecular geometry of $(PPh_3)_2Pt(Ph_3SnC(S)SMe)$ but with only C1 of each phenyl ring included. The atoms are represented by 50% probability ellipsoids, except the carbon atoms that have been assigned artificially low thermal parameters for the purpose of clarity.

the spectroscopic data do not distinguish between the possible structures I and II. However, a single-crystal structure de-



I



II

termination of $(PPh_3)_2Pt(Ph_3SnC(S)SMe)$ confirmed structure I (see below), which means that the complex has a structure similar to that of $(PPh_3)_2PtCS_2$.[4]

Gaffney and Ibers[5] have reported the $^{31}P\{^1H\}$ NMR spectrum of $(PPh_3)_2PtCS_2$, which was superficially very similar to those reported here for $(PPh_3)_2Pt(Ph_3SnC(S)SR)$. However, these workers assigned the phosphine resonance at higher frequency to the phosphine trans to sulfur on the basis of the platinum–phosphorus coupling constants. In contrast, the opposite assignment is made for $(PPh_3)_2Pt(Ph_3SnC(S)SR)$ on the basis of long-range couplings between phosphorus and tin. Similar, but even more unambiguous, assignments can be made for the thioformamide complexes described later in this paper. In order to investigate this apparent discrepancy further, we prepared $(PPh_3)_2PtCS_2$ using enriched CS_2 (approximately 50% ^{13}C) and recorded the $^{31}P\{^1H\}$ NMR spectrum. The carbon-13 satellites in the spectrum were clearly observed ($^2J_{P,C}$ = 80 and 4 Hz)[19] with the larger coupling constant associated with the phosphine at lower frequency. Thus, the original assignment of the phosphorus spectrum[5] is correct, and the relative positions of the phosphine resonances in $(PPh_3)_2PtCS_2$ and $(PPh_3)_2Pt(Ph_3SnC(S)SR)$ are reversed. Considerable care therefore is required in the assignment of the phosphorus spectra of platinum η^2-CS bonded complexes.

The observation of two different ^{31}P resonances and two tin-phosphorus couplings shows that the η^2-CS linkage is rigid on the NMR time scale. Addition of excess ligand, CS_2, or the strong base PBu_3 caused no change in the ^{31}P NMR spectrum of $(PPh_3)_2Pt(Ph_3SnC(S)SMe)$. However, addition of MeI caused immediate reaction, and the color of the solution changed to light red. Both the ^{31}P and ^{119}Sn NMR spectra indicated that a large number of products, but not including free $Ph_3SnC(S)SMe$, were formed. This system was not investigated further.

Table V. Positional Parameters for $(PPh_3)_2Pt(Ph_3SnC(S)SMe)$[a]

	x/a	y/b	z/c	U_{iso}, Å^2
Pt	−0.13336 (7)	0.15747 (6)	0.23029 (4)	
Sn	−0.3612 (1)	−0.1236 (1)	0.2782 (1)	
P1	−0.0731 (4)	0.2863 (4)	0.3396 (2)	
P2	−0.1047 (5)	0.2895 (4)	0.1462 (3)	
S1	−0.2098 (5)	−0.0256 (4)	0.1532 (3)	
S2	−0.0668 (5)	−0.0606 (4)	0.2987 (3)	
C1	−0.1807 (16)	−0.0169 (15)	0.2545 (10)	0.042 (4)
C2	0.0693 (23)	0.0104 (23)	0.2655 (15)	0.082 (7)
C31	−0.3600 (16)	−0.1481 (15)	0.3916 (10)	0.040 (4)
C32	−0.2813 (19)	−0.1953 (18)	0.4287 (12)	0.056 (5)
C33	−0.2803 (20)	−0.2168 (19)	0.5028 (12)	0.061 (5)
C34	−0.3639 (22)	−0.1958 (22)	0.5372 (14)	0.075 (7)
C35	−0.4429 (23)	−0.1535 (22)	0.5060 (15)	0.079 (7)
C36	−0.4457 (19)	−0.1282 (19)	0.4268 (12)	0.061 (6)
C41	−0.4244 (17)	−0.2983 (16)	0.2143 (10)	0.044 (5)
C42	−0.5370 (20)	−0.3922 (19)	0.2184 (13)	0.063 (6)
C43	−0.5914 (22)	−0.5090 (21)	0.1716 (14)	0.073 (6)
C44	−0.5191 (22)	−0.5311 (21)	0.1267 (14)	0.072 (6)
C45	−0.4003 (18)	−0.4396 (17)	0.1228 (11)	0.053 (5)
C46	−0.3600 (17)	−0.3261 (17)	0.1651 (11)	0.051 (5)
C51	−0.4966 (17)	−0.0538 (16)	0.2425 (11)	0.048 (5)
C52	−0.5772 (21)	−0.1048 (21)	0.1718 (14)	0.071 (6)
C53	−0.6712 (28)	−0.0628 (27)	0.1456 (18)	0.102 (9)
C54	−0.6760 (27)	0.0295 (26)	0.1897 (17)	0.096 (8)
C55	−0.5914 (26)	0.0798 (25)	0.2592 (17)	0.093 (8)
C56	−0.4957 (21)	0.0388 (20)	0.2892 (13)	0.068 (6)
C61	−0.2539 (17)	0.2647 (16)	0.0847 (11)	0.045 (4)
C62	−0.3631 (18)	0.1716 (18)	0.0867 (12)	0.054 (5)
C63	−0.4785 (20)	0.1543 (19)	0.0412 (13)	0.065 (6)
C64	−0.4883 (21)	0.2299 (20)	−0.0065 (14)	0.069 (6)
C65	−0.3783 (22)	0.3260 (21)	−0.0065 (14)	0.074 (7)
C66	−0.2596 (21)	0.3496 (20)	0.0397 (13)	0.067 (6)
C71	−0.1482 (16)	0.3881 (16)	0.3358 (10)	0.043 (4)
C72	−0.2748 (17)	0.3360 (17)	0.2944 (11)	0.048 (5)
C73	−0.3425 (19)	0.4045 (19)	0.2911 (12)	0.061 (6)
C74	−0.2805 (23)	0.5260 (22)	0.3260 (15)	0.079 (7)
C75	−0.1569 (20)	0.5778 (19)	0.3657 (12)	0.063 (6)
C76	−0.0895 (18)	0.5098 (18)	0.3693 (12)	0.054 (5)
C81	0.0957 (17)	0.3749 (16)	0.3728 (10)	0.044 (4)
C82	0.1763 (18)	0.3661 (17)	0.3272 (11)	0.051 (5)
C83	0.3096 (22)	0.4283 (21)	0.3503 (14)	0.074 (6)
C84	0.3647 (21)	0.5050 (20)	0.4208 (13)	0.068 (6)
C85	0.2852 (20)	0.5111 (19)	0.4655 (13)	0.062 (6)
C86	0.1578 (19)	0.4509 (18)	0.4454 (12)	0.056 (5)
C91	−0.0157 (19)	0.2633 (18)	0.0820 (12)	0.058 (5)
C92	0.0432 (26)	0.1945 (25)	0.0953 (16)	0.092 (8)
C93	0.1179 (32)	0.1706 (32)	0.0443 (21)	0.108 (9)
C94	0.1264 (29)	0.2274 (29)	−0.0164 (19)	0.125 (11)
C95	0.0666 (38)	0.2948 (37)	−0.0313 (25)	0.147 (14)
C96	0.0029 (41)	0.3262 (41)	0.0216 (27)	0.162 (15)
C101	−0.0260 (17)	0.4532 (16)	0.1774 (11)	0.046 (5)
C102	−0.0944 (20)	0.5164 (19)	0.1900 (12)	0.062 (5)
C103	−0.0281 (21)	0.6428 (21)	0.2163 (13)	0.068 (6)
C104	0.0940 (25)	0.6978 (25)	0.2249 (16)	0.089 (8)
C105	0.1669 (31)	0.6398 (31)	0.2135 (20)	0.116 (10)
C106	0.1039 (25)	0.5150 (24)	0.1898 (16)	0.085 (7)
C111	−0.1119 (15)	0.2256 (14)	0.4242 (10)	0.035 (4)
C112	−0.1884 (18)	0.2559 (18)	0.4640 (12)	0.054 (5)
C113	−0.2138 (19)	0.2074 (19)	0.5280 (13)	0.061 (5)
C114	−0.1572 (20)	0.1366 (19)	0.5544 (13)	0.062 (5)
C115	−0.0828 (20)	0.1040 (19)	0.5140 (12)	0.061 (6)
C116	−0.0601 (18)	0.1507 (17)	0.4482 (12)	0.054 (5)

[a] Standard deviation in parentheses.

Description of the Structure of $(PPh_3)_2Pt(Ph_3SnC(S)SMe)$. The crystal structure of $(PPh_3)_2Pt(Ph_3SnC(S)SMe)$ consists of discrete molecules, two per unit cell related by a center of symmetry. There are no intermolecular contacts at distances less than the sum of the respective van der Waals radii.

Figure 2 shows the molecular geometry of $(PPh_3)_2Pt(Ph_3SnC(S)SMe)$, but with only the first carbon atom of each phenyl ring included to clarify the stereochemistry about the

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(19) These values agree with those previously observed from the ^{13}C NMR spectrum of $(PPh_3)_2PtCS_2$: Vergamini, P. J.; Eller, P. G. *Inorg. Chim. Acta* **1979**, *34*, L291.

Table VI. Bond Lengths (Å) and Bond Angles (deg) (Excluding Phenyl Rings) for $(PPh_3)_2Pt(Ph_3SnC(S)SMe)$[a]

Pt-P1	2.261 (4)	P1-Pt-P2	100.3 (2)
Pt-P2	2.329 (5)	S1-Pt-P2	103.0 (2)
Pt-S1	2.302 (5)	P1-Pt-C1	108.2 (5)
Pt-S2	3.407 (5)	C1-Pt-S1	48.5 (5)
Pt-C1	2.122 (17)	S2-C1-Sn	109.1 (8)
Sn-C1	2.17 (2)	Pt-C1-S1	70.9 (6)
S2-C1	1.75 (2)	Pt-C1-Sn	122.2 (8)
S1-C1	1.82 (2)	S1-C1-Sn	106.7 (8)
S2-C2	1.75 (3)	S1-C1-S2	118.5 (9)
Sn-C31	2.14 (2)	S2-C1-Pt	122.7 (9)
Sn-C41	2.14 (2)	Pt-S1-C1	60.6 (5)
Sn-C51	2.16 (2)	C1-S2-C2	107.0 (1)
P1-C71	1.82 (2)	C1-Sn-C31	117.1 (6)
P1-C81	1.81 (2)	C1-Sn-C41	105.3 (7)
P1-C111	1.85 (2)	C1-Sn-C51	110.9 (7)
P2-C61	1.82 (2)	Pt-P1-C71	112.7 (6)
P2-C91	1.82 (2)	Pt-P1-C81	114.4 (6)
P2-C101	1.84 (2)	Pt-P1-C111	118.7 (5)
		Pt-P2-C61	111.9 (6)
		Pt-P2-C91	110.8 (7)
		Pt-P2-C101	122.4 (6)

[a] Standard deviation in parentheses.

platinum center. The phenyl carbon atoms attached to the heteroatoms are designated C31, C41, ..., C111, and the carbons in each ring are numbered 1 to 6 such that C31–C36 specifies phenyl ring 3. Positional parameters, bond distances, and bond angles are listed in Tables V and VI. Bond lengths, bond angles, and least-squares planes of the phenyl rings are included in the supplementary data.

The molecular geometry clearly indicates that the $Ph_3SnC(S)SMe$ ligand is coordinated to platinum in a η^2 mode, very similar to that observed in $(PPh_3)_2PtCS_2$[4] and $(PPh_3)_2Pt(C_{12}H_8CSO)$.[20] There appears to be little interaction between the platinum and S2 (the methylated sulfur), as the distance between them is 3.407 (5) Å and the sum of their van der Waals radii is 3.5 Å.[21] These features establish that the CS_2 group does not coordinate through both sulfur atoms (structure II) nor as a heteroallyl system.

The coordination about platinum is observed to be approximately planar. The dihedral angle between the two planes defined by Pt, C1, S1 and Pt, P1, P2 is only 3.5°, and the η^2 pair of atoms (C1, S1) are displaced relative to the second plane by −0.06 (2) and 0.054 (6) Å, respectively. However, these distortions are smaller than those observed in similar formally platinum(0) η^2 systems.[4,20] The platinum–phosphorus bond distances are 2.261 (4) and 2.329 (5) Å, and it is interesting to note that the shorter bond length is trans to C1 as in $(PPh_3)_2PtCS_2$.[4] The angle C1–Pt–S1 is 48.5 (5)° and the angle P1–Pt–P2 is 100.3 (2)°, which are slightly larger and smaller, respectively, than those observed in closely related compounds as shown in Table VII. Similarly, both Pt–C1 and Pt–S1 bond distances are also comparable to those of related compounds.

There are substantial changes in the geometry of the ligand $Ph_3SnC(S)SMe$ on coordination, as can be seen from Table VIII. The free ligand[12] has essentially trigonal geometry about C1 with approximately equal CS bond distances (1.64 (2), 1.66 (2) Å), whereas in the complex C1 is nonplanar and the angle Sn–C1–S1 is reduced to 109.1 (8)°. Also, on coordination, both carbon–sulfur distances lengthen—C1–S1 = 1.82 (2) Å and C1–S2 = 1.75 (2) Å. By comparison with the distance of 1.75 (2) Å found for the C2(methyl)–S2 bond, it can be seen that both C1–S1 and C1–S2 are of single-bond character, suggesting that resonance within the CS_2 unit has been lost.

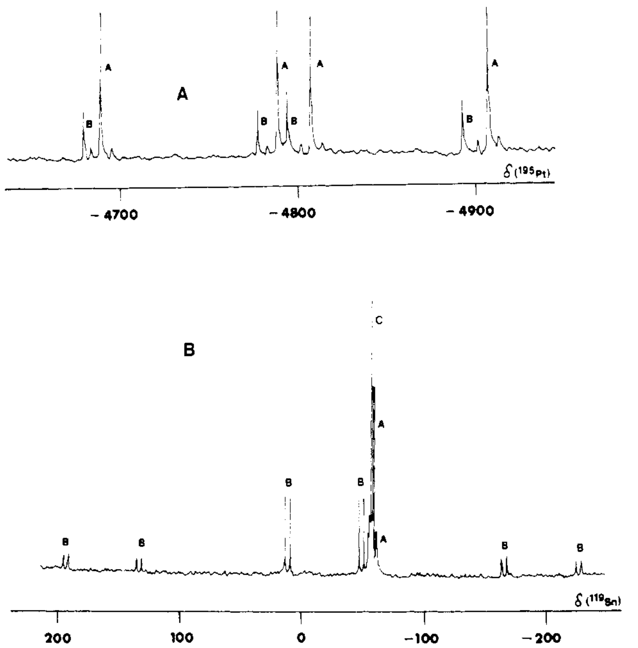

Figure 3. NMR spectra of the mixture of $(PPh_3)_2PtC_2H_4$ and $Ph_3SnC(S)pyrr$ at 25 °C in CH_2Cl_2: (A) $^{195}Pt\{^1H\}$ spectrum accumulated 2.5–5.5 h after mixing; (B) $^{119}Sn\{^1H\}$ spectrum accumulated 5.5–8.5 h after mixing. Compound A is identified as $(PPh_3)_2Pt(Ph_3SnC(S)Spyrr)$, compound B as $(PPh_3)_2Pt(Ph)(Ph_2SnC(S)Spyrr)$, and compound C as free $Ph_3SnC(S)Spyrr$.

Other, more subtle changes about C1 are also observed. Both the SMe and $SnPh_3$ groups are displaced away from the platinum center, and as a result the environment about C1 can be described as "quasi-tetrahedral", which is a feature also characteristic of η^2-coordinated olefins.[22] The Sn, C1, S2 plane makes an angle of 19° to the plane passing through the C1–S1 line perpendicular to the Pt, C1, S1 plane. This and other observed differences between the free and coordinated ligand are similar to those found in a wide range of η^2-type ligands.[4,20,22,23] No unusual features were observed in the molecular dimensions of either the PPh_3 or Ph_3Sn moieties.

Reaction of $(PPh_3)_2PtC_2H_4$ with $Ph_3SnC(S)N'$. Reactions of $(PPh_3)_2PtC_2H_4$ with a slight excess of $Ph_3SnC(S)N'$ (N′ = NMeH or pyrrolyl) were carried out in situ in an NMR tube. Similar NMR spectra were observed in both cases so only the results for the pyrrolyl system will be described in detail, but the data for the other ligand are also included in Table IX.

Thirty minutes after mixing, the $^{31}P\{^1H\}$ NMR spectrum showed resonances due to $(PPh_3)_2PtC_2H_4$ and two new doublets of equal intensity (δ 26.1, 23.1; $^2J_{P,P}$ = 14 Hz), each flanked by platinum-195 satellites ($J_{Pt,P}$ = 2512, 2118 Hz). This species, which will be designated compound A, has NMR parameters for all nuclei (see below) that are comparable to those described for the $(PPh_3)_2Pt(Ph_3SnC(S)SR)$ compounds, and it is identified as the corresponding η^2-bonded derivative (see Scheme I).

Two hours after mixing the reactants the $^{31}P\{^1H\}$ NMR spectrum showed that all the $(PPh_3)_2PtC_2H_4$ had reacted but that in addition to compound A there was now another species (compound B) present in the solution. The spectrum of compound B also consisted of two doublets of equal intensity (δ 27.1, 21.4; $^2J_{P,P}$ = 15 Hz) arising from nonequivalent phosphines. Each doublet does have platinum satellites, but in the mixture after a 2-h reaction time three of the four satellites

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(20) Gosselink, J. W.; van Koten, G.; Spek, A. L.; Duisenberg, A. J. M. *Inorg. Chem.* **1981**, *20*, 877.
(21) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.
(22) Mingos, D. M. P. *Adv. Organomet. Chem.* **1977**, *15*, 19.
(23) Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801.

Table VII. Comparison of Molecular Parameters for $(PPh_3)_2Pt(Ph_3SnC(S)SMe)$ with Those for Similar Compounds[a]

complex	Pt-P1, Å	Pt-P2, Å	Pt-C1, Å	Pt-S1, Å	P1-Pt-P2, deg	C1-Pt-S1, deg	C1-S1, Å
$(PPh_3)_2Pt(Ph_3SnC(S)SMe)$	2.261 (4)	2.329 (5)	2.122 (17)	2.302 (5)	100.3 (2)	48.5 (5)	1.82 (2)
$(PPh_3)_2PtCS_2$[b]	2.240 (15)	2.346 (10)	2.063 (46)	2.328 (16)	107.1 (5)	45.5 (24)	1.72 (5)
$(PPh_3)_2Pt(C_{12}H_8CSO)$[c]	2.302 (1)	2.295 (1)	2.122 (5)	2.313 (1)	106.42 (5)	46.6 (1)	1.762 (5)

[a] Standard deviations in parentheses. [b] Data from ref 4. [c] Data from ref 20.

Table VIII. Comparison of Molecular Parameters for $Ph_3SnC(S)SMe$ in Free and Coordinated Modes[a]

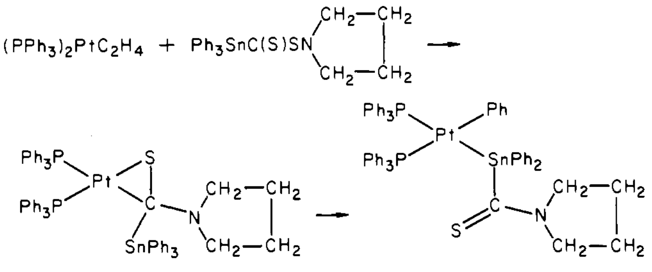
	free ligand[b]	coordinated ligand
C1-S1, Å	1.66 (2)	1.82 (2)
C1-S2, Å	1.64 (2)	1.75 (2)
C2-S2, Å	1.79 (5)	1.75 (3)
C1-Sn, Å	2.139 (9)	2.17 (2)
Sn-C1-S2, deg	118.6 (6)	109.1 (8)

[a] Standard deviations in parentheses. [b] Data from ref 12.

were obscured by the ^{195}Pt satellites of the more abundant compound A. However, they could be identified by a consideration of the relative intensities of the satellites, and the assignment was later confirmed by using an isolated sample of compound B. No tin satellites were observed in the ^{31}P spectrum for either compound.

The $^{195}Pt\{^1H\}$ NMR spectrum of the solution, accumulated over the period 2.5–5.5 h after mixing the reactants, is shown in Figure 3A. It shows two sets of doublets of doublets due to compounds A and B assigned by the platinum–phosphorus coupling constants derived from the ^{31}P spectrum. Each resonance due to compound A shows tin satellites ($^2J_{Pt,Sn}$ = 244 Hz), but the signal to noise ratio was insufficient to observe tin satellites for the resonances of the less abundant compound B.

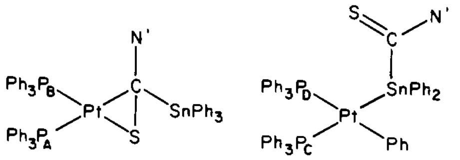
Scheme I



A B

The $^{119}Sn\{^1H\}$ NMR spectrum of the mixture, accumulated over the period 5.5–8.5 h after the initial mixing of the reactants, is shown in Figure 3B. The singlet at δ −55 (compound C) is readily assigned to excess ligand $Ph_3SnC(S)pyrr$; compound A appears as a doublet ($^3J_{Sn,P}$ = 44 Hz) with platinum-195 satellites ($^2J_{Pt,Sn}$ = 244 Hz). Coupling to the second phosphine was not well resolved due to the large spectral window required for compound B. After this reaction time compound B is almost as abundant as compound A, and its ^{119}Sn spectrum appears as a doublet of doublets due to nonequivalent phosphines together with widely spaced platinum-195 satellites ($J_{Pt,Sn}$ = 13 290 Hz). The magnitude of the platinum–tin coupling constant indicates that there is a direct platinum–tin bond.[2]

Table IX. NMR Data for Compounds $(PPh_3)_2Pt(Ph_3SnC(S)SN')$ and $(PPh_3)_2Pt(Ph)(Ph_2SnC(S)SN')$ (25 °C; in CH_2Cl_2 at ~0.13 M)



compd	$\delta(^{31}P)$	$\delta(^{119}Sn)$	$\delta(^{195}Pt)$	coupling const, Hz
$(PPh_3)_2Pt(Ph_3SnC(S)NMeH)$	P_A 25.9 P_B 22.7	−54	−4789	$^1J_{Pt,P_A} = 2530$ $^1J_{Pt,P_B} = 2136$ $^2J_{P_A,P_B} = 16$ $^2J_{Pt,Sn} = 245$ $^3J_{Sn,P_A} = 42$ $^3J_{Sn,P_B} = 6$
$(PPh_3)_2Pt(Ph_3SnC(S)pyrr)$	P_A 26.1 P_B 23.1	−56	−4797	$^1J_{Pt,P_A} = 2512$ $^1J_{Pt,P_B} = 2128$ $^2J_{P_A,P_B} = 14$ $^2J_{Pt,Sn} = 244$ $^3J_{Sn,P_A} = 44$ $^3J_{Sn,P_B} = 5$
$(PPh_3)_2Pt(Ph)(Ph_2SnC(S)NMeH)$	P_C 26.8 P_D 21.1	−31	−4785	$^1J_{Pt,P_C} = 2458$ $^1J_{Pt,P_D} = 2094$ $^2J_{P_C,P_D} = 15$ $^1J_{Pt,Sn} = 13\,870$ $^2J_{Sn,P_C} = 2202$ $^2J_{Sn,P_D} = 156$
$(PPh_3)_2Pt(Ph)(Ph_2SnC(S)pyrr)$	P_C 27.1 P_D 21.4	−17	−4785	$^1J_{Pt,P_C} = 2446$ $^1J_{Pt,P_D} = 2096$ $^2J_{P_C,P_D} = 15$ $^1J_{Pt,Sn} = 13\,290$ $^2J_{Sn,P_C} = 2210$ $^2J_{Sn,P_D} = 150$

Compound B has NMR parameters (^{31}P, ^{119}Sn, ^{195}Pt) very similar to those of compounds of the type *cis*-$(PPh_3)_2$Pt(Ph)$(SnPh_3Cl)$[2] and hence is identified as *cis*-$(PPh_3)_2$Pt(Ph)$(Ph_2SnC(S)$pyrr (Scheme I). Compound B was isolated by mixing $(PPh_3)_2PtC_2H_4$ and $Ph_3SnC(S)$Spyrr in benzene and allowing the reaction to proceed for 24 h. Its analysis confirmed the identification (Table I).

The two classes of platinum(0) complexes described above represent the first examples of η^2-CS bonded compounds where the ligand contains a large heteroatom, in this case tin. The inclusion of such a large heteroatom leads to quite different properties of the complexes compared to those of smaller η^2-CS bonded ligands.

Platinum(0) complexes containing small η^2 ligands (e.g. CS_2, COS, RNCS) react readily with excess ligand, and the η^2-CS bond to platinum is replaced by two σ-bonds during intermolecular processes involving the central carbon atom. In contrast, the compounds containing η^2-CS bonded $Ph_2SnC(S)N'$ ligands undergo intramolecular rearrangement involving bond cleavage at the tin. An even greater contrast is given by the derivatives containing η^2-CS bonded $Ph_3SnC(S)SR$, which are quite stable, and no further reactions are observed on addition of excess ligand or CS_2.

The differences between the behavior of these Ph_3Sn ligands and those of the type Ph_3SnX (X = Ph, Cl, Br), which oxidatively add to platinum(0) with immediate cleavage of the Sn–Ph bond,[1] are also noteworthy.

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

Registry No. I (R = Me), 87451-03-4; I (R = CH_2Ph), 87451-04-5; I (R = C_3H_5), 87451-02-3; $(PPh_3)_2Pt(Ph)(Ph_2SnC(S)NMeH)$, 87451-00-1; $(PPh_3)_2Pt(Ph)(Ph_2SnC(S)pyrr)$, 87451-01-2; $(PPh_3)_2Pt(Ph_3SnC(S)NMeH)$, 87451-05-6; $(PPh_3)_2Pt(Ph_3SnC(S)pyrr)$, 87451-06-7; $(PPh_3)_2PtC_2H_4$, 12120-15-9; $(PPh_3)_2PtCS_2$, 15308-68-6; Pt, 7440-06-4; Sn, 7440-31-5; $Ph_3SnC(S)SCH_2Ph$, 87451-07-8; $Ph_3SnC(S)NMeH$, 87451-08-9; $Ph_3SnC(S)pyrr$, 87451-09-0; $PhCH_2Cl$, 100-44-7; Ph_3SnCS_2Li, 84448-52-2; $Ph_3SnC(S)SMe$, 73137-42-5; pyrr, 109-97-7; dimethylamine, 124-40-3.

Supplementary Material Available: Tables S-I–S-V, listing bond lengths, bond angles, and equations of least-squares planes of the phenyl rings, anisotropic thermal parameters, and structure factors (17 pages). Ordering information is given on any current masthead page.

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tert-Butylperoxo Complexes of Platinum(II): Synthetic, Spectroscopic, and Structural Investigations. Oxygenation of 1-Octene by Trans Species

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Stable monomeric *tert*-butylperoxo complexes of Pt(II) of the type *trans*-$P_2Pt(Rx)(OO$-*t*-Bu) (P = tertiary phosphine; Rx = CF_3, Ph-*o*-CN, Ph) have been prepared by condensation reactions of the corresponding hydroxo complexes with *t*-BuOOH. These have been characterized with conventional spectroscopic techniques: IR and ^{1}H, ^{19}F, and ^{31}P NMR. The X-ray crystal structure of *trans*-$(PPh_3)_2Pt(Ph)(OO$-*t*-Bu) is also reported, which confirms the end-bonded peroxidic nature of these complexes. The crystals are triclinic, space group $P\bar{1}$ with 2 molecular units in a cell and lattice parameters a = 20.11 (1) Å, b = 10.114 (7) Å, c = 12.024 (8) Å, α = 103.4 (1)°, β = 118.5 (1)°, and γ = 98.5 (1)°. The structure was refined to an R value of 0.045 (R_w = 0.055) for 3335 independent reflections. Spectroscopic investigations with ^{31}P and ^{19}F NMR suggest a considerable covalent character for the Pt–O bond in both *tert*-butylperoxo and hydroperoxo species. All trans *tert*-butylperoxo derivatives except one (P = PBz_3) proved effective in the selective oxygenation of 1-octene to 2-octanone. The influence on the yield of the oxygenation reaction due to the ancillary phosphines and Rx ligand, along with conductivity and spectroscopic studies, constitutes the basis for a discussion of the possible oxygen-transfer pathways occurring in this system.

Introduction

Within the framework of our interest in the synthesis and reactivity of group 8 metal complexes containing "activated" oxygen, we have reported some stable hydroperoxo[2,3] and *tert*-butylperoxo[3] complexes of Pd(II) and Pt(II) of the type $P_2M(Rx)(OOR)$ (P_2 = 1,2-bis(diphenylphosphino)ethane (diphos) or -ethylene (diphoe), 2 PPh_3, 2 PPh_2Me; M = Pd, Pt; Rx = CF_3, Me, CH_2CN, CH_2CF_3; R = H, *t*-Bu). These compounds have been employed in oxygen-transfer reactions using a variety of substrates, namely PPh_3, CO, NO, benzaldehyde, and olefins. With the latter substrates oxygenation to the corresponding methyl ketones could be accomplished only with *trans*-$(PPh_2Me)_2Pt(CF_3)(OO$-*t*-Bu), which was the only *tert*-butylperoxo complex with a trans geometry available in the prepared series. It seemed desirable to determine what factors controlled the ease of olefin oxidation: first, whether a trans geometry was essential; second, some observations by Bennett[4] on the behavior of closely related trans hydroxo complexes of platinum (which dissociate strongly as bases in protic media) seemed to suggest a possible role for an ionic intermediate of the type $[(PPh_2Me)_2Pt(CF_3)]^+(t\text{-BuOO})^-$ in our observed olefin oxidation. In this paper we report the synthesis and characterization of a new series of trans-*tert*-butylperoxo complexes of platinum(II) along with their behavior in the oxygenation of 1-octene. In addition, we report the X-ray crystal structure of *trans*-$(PPh_3)_2Pt(Ph)(OO$-*t*-Bu), which represents the first structural characterization of a d^8 metal complex containing a nonbridging, end-bonded alkylperoxo moiety.

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[2] Michelin, R. A.; Ros, R.; Strukul, G. *Inorg. Chim. Acta* **1979**, *37*, L491.

[3] Strukul, G.; Ros, R.; Michelin, R. A. *Inorg. Chem.* **1982**, *21*, 495.

[4] Arnold, D. P.; Bennett, M. A. *J. Organomet. Chem.* **1980**, *199*, 119.

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