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Crystal and Solution Structure of Triphenylmethylphosphonium Pentakis(trichlorostannyl)platinate(II), $[Ph_3PCH_3]_3[Pt(SnCl_3)_5]$

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The crystal structure of triphenylmethylphosphonium pentakis(trichlorostannyl)platinate(II), $[Ph_3PCH_3]_3[Pt(SnCl_3)_5]$, has been determined from three-dimensional X-ray data collected by counter methods. The material crystallizes in space group $R\bar{3}$ with two formula units in a unit cell 15.897 (1) Å on an edge with $\alpha = 82.02$ (1)°. The structure has been refined by least-squares methods to a final R factor of 0.034, including hydrogen atoms for the 2437 reflections above background. The $[Pt(SnCl_3)_5]^{3-}$ ion is a regular trigonal bipyramid with the average axial Pt-Sn bond length 2.5530 (7) Å, which is shorter than the equatorial Pt-Sn bond length 2.5722 (10) Å, consistent with current theoretical predictions. Comparison of this structure with other structures containing coordinate trichlorostannyl allows conclusions to be drawn regarding the π-acceptor ability of $SnCl_3^-$. In acetone solution the $[Pt(SnCl_3)_5]^{3-}$ ion retains the trigonal-bipyramidal structure but is stereochemically nonrigid between 183 and 363 K as evidenced by ^{195}Pt and ^{119}Sn NMR spectroscopy. Throughout this temperature range, spin correlation is preserved, establishing that the nonrigidity is due to intramolecular exchange, probably via Berry pseudorotation. No dissociation products such as $[Pt(SnCl_3)_4]^{2-}$ or $[Pt(SnCl_3)_2Cl_2]^{2-}$ could be detected in solution.

Introduction

Pentacoordinate species have attracted considerable recent interest with regard to their stereochemistry[2] and solution dynamics[3] and because of their mechanistic importance.[4] Among the first pentacoordinate transition-metal complexes to be described,[5] the $[Pt(SnCl_3)_5]^{3-}$ species is noteworthy for several reasons. First, it is one of the few species that readily catalyzes the homogeneous hydrogenation[5b] of ethylene and acetylene under mild conditions (room temperature and atmospheric pressure) and is probably the catalyst or catalyst precursor in the catalyzed coupling of vinyl halides[6] and the hydrogenation of styrene.[7] Second, preliminary structural data[5a] have indicated that all five platinum-tin bond lengths are the same within experimental error, while current theory[8] predicts that for d^8 trigonal-bipyramidal complexes the axial bonds should be stronger and shorter than the equatorial bonds. Third, trigonal-bipyramidal species are commonly found to be stereochemically nonrigid,[3] with activation energy barriers for their permutational isomerizations that are usually large enough for the static structure to be observed at low temperatures. The activation energy barrier is sterically influenced and typically increases with an increase in ligand steric bulk. Yet, our preliminary NMR data[9] suggested that, unexpectedly, $[Pt(SnCl_3)_5]^{3-}$ is nonrigid even at 183 K, in contrast to $\{Pt[P(OCH_3)_3]_5\}$,[24] which is stereochemically rigid at similar temperatures.[3d] Fourth, it has been proposed[10] that $SnCl_3^-$ is a strong π acceptor, and current theory[8] suggests that for trigonal-bipyramidal species, equatorial π bonding is stronger than axial π bonding. A previous report of the crystal structure of the title compound failed to shed light on these points. We have redetermined this structure to high accuracy and further investigated the solution behavior by ^{119}Sn and ^{195}Pt NMR spectroscopy.

Experimental Section

Triphenylmethylphosphonium chloride was prepared by literature procedures.[11] Triphenylmethylphosphonium pentakis(trichlorostannyl)platinate(II) was prepared in the following two ways:[12]

Method A. To a solution containing 1.017 g (1.96 mmol) of $H_2PtCl_6{\cdot}6H_2O$ and 2.86 g (12.68 mmol) of $SnCl_2{\cdot}2H_2O$ in 15 mL of methanol was added a solution of 3.30 g (10.56 mmol) of $(Ph_3PCH_3)Cl$ in 10 mL of methanol. Immediately upon mixing of the two solutions a microcrystalline red-orange precipitate formed. The product was filtered, washed with methanol, and air-dried.

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Table I. Atomic Coordinates for $[CH_3PPh_3]_3[Pt(SnCl_3)_5]$[a]

atom	x	y	z	U,[b] Å^2	atom	x	y	z	U, Å^2
Pt	7281.6 (3)	7281.6	7281.6	31	C(33)	9114 (10)	4786 (11)	−388 (10)	89
Sn(1)	8101.2 (6)	8101.2	8101.2	58	C(34)	9528 (9)	4088 (13)	−709 (8)	85
Sn(2)	6460.9 (5)	6460.9	6460.9	30	C(35)	9365 (9)	3292 (12)	−367 (10)	83
Sn(3)	8699.2 (6)	6490.4 (7)	6645.1 (6)	37	C(36)	8734 (7)	3190 (9)	348 (8)	65
Cl(1)	7316 (4)	8871 (4)	9168 (4)	99	C(4)	6470 (7)	4161 (8)	1063 (7)	59
Cl(2)	6312 (3)	6944 (3)	5017 (2)	57	H(41)	6369 (155)	3915 (156)	553 (159)	82 (77)
Cl(31)	8870 (3)	6164 (4)	5215 (3)	80	H(42)	6019 (155)	4031 (157)	1479 (161)	123 (76)
Cl(32)	9188 (3)	5103 (3)	7286 (3)	65	H(43)	6454 (154)	4808 (157)	851 (157)	123 (77)
Cl(33)	10028 (3)	7038 (3)	6562 (3)	70	H(12)	6315 (153)	2532 (154)	1852 (153)	55 (77)
P	7441 (2)	3846 (2)	1527 (2)	45	H(13)	6319 (154)	1133 (155)	2463 (155)	141 (77)
C(11)	7491 (7)	2755 (7)	2032 (6)	48	H(14)	7593 (153)	476 (154)	3125 (155)	86 (77)
C(12)	6815 (7)	2284 (8)	2069 (7)	58	H(15)	8714 (154)	1275 (154)	3053 (153)	97 (79)
C(13)	6871 (9)	1444 (8)	2468 (8)	70	H(116)	8675 (153)	2721 (154)	2441 (155)	97 (78)
C(14)	7589 (10)	1092 (10)	2824 (10)	83	H(122)	8820 (153)	4274 (154)	2235 (154)	91 (77)
C(15)	8249 (10)	1567 (9)	2791 (10)	92	H(23)	8963 (155)	5008 (153)	3460 (154)	96 (77)
C(16)	8213 (8)	2395 (8)	2395 (8)	75	H(24)	7640 (154)	5805 (154)	4096 (154)	158 (77)
C(21)	7525 (7)	4542 (6)	2293 (6)	44	H(25)	6329 (153)	5788 (153)	3630 (154)	92 (77)
C(22)	8314 (7)	4554 (7)	2580 (7)	57	H(26)	6177 (153)	5020 (154)	2458 (154)	123 (77)
C(23)	8356 (8)	5035 (8)	3236 (8)	68	H(32)	8171 (153)	5304 (153)	542 (154)	107 (77)
C(24)	7645 (8)	5484 (8)	3614 (8)	68	H(33)	9220 (154)	5302 (153)	−573 (154)	139 (77)
C(25)	6870 (8)	5476 (7)	3317 (9)	68	H(34)	9957 (154)	4109 (154)	−1240 (154)	95 (77)
C(26)	6801 (7)	5012 (7)	2658 (7)	56	H(35)	9687 (154)	2713 (153)	−626 (154)	142 (77)
C(31)	8311 (6)	3916 (7)	685 (7)	48	H(36)	8557 (153)	2535 (155)	617 (155)	103 (78)
C(32)	8493 (9)	4720 (9)	322 (8)	73					

[a] Values ×10^4, with standard deviations in parentheses. [b] Average isotropic U values ×10^3 for anisotropic atoms.

Recrystallization by dissolution in acetone and filtering followed by slow addition of methanol to the filtrate afforded 4.55 g (84.6%) of red crystalline product, mp 264–266 °C (N_2-filled capillary).

Method B. To a solution containing 0.415 g (1 mmol) of K_2PtCl_4 and 1.128 g (5 mmol) of $SnCl_2{\cdot}2H_2O$ in 40 mL of 3 M HCl was added a solution of 0.938 g (3 mmol) of $(Ph_3PCH_3)Cl$ in 20 mL of 3 M HCl. Immediately upon mixing of the two solutions a microcrystalline red-orange precipitate formed. The product was filtered, washed with 3 M HCl and methanol, and air-dried. Recrystallization from acetone/methanol, as above, afforded 2.16 g (78.7%) of red crystalline product, mp 265 °C (N_2-filled capillary).

The $^{119}Sn\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectra were recorded at 37.10 and 21.29 MHz, respectively, on a JEOL FX-100 spectrometer in the FT mode, with use of saturated acetone-d_6 solutions. The spectra were recorded at a 20-kHz sweep width, 8K data points, 20-μs pulse widths, and 0.3-s (^{119}Sn) or 0.1-s (^{195}Pt) pulse delays. Coupling constants are believed accurate to ±5 Hz and chemical shifts to ±0.5 ppm. Chemical shifts are relative to external $(CH_3)_4Sn$ and H_2PtCl_6, with upfield shifts negative and downfield shifts positive.

X-ray Data Collection and Refinement. Block-shaped red crystals were obtained by crystallization from acetone/methanol. A suitable crystal (0.20 × 0.20 × 0.21 mm) was mounted on a Syntex $P2_1$ four-circle diffractometer. Maximum 2θ was 42° (with a few reflections in the 42–47° range collected before data collection was terminated as the intensities appeared to be too low to be of use), with a scan range ±0.8° (2θ) around the $K\alpha_1$–$K\alpha_2$ angles. A scan speed of 2–29° min^{-1} was utilized, depending upon the intensity of a 2-s prescan; backgrounds were measured at each end of the scan for 0.25 of the scan time. Three standard reflections were monitored every 200 reflections and showed no significant changes during data collection. Unit cell dimensions and standard deviations were obtained by least-squares fit to 15 angle reflections. In refinement, 9348 reflections, of which 6650 were considered observed ($I/\sigma(I) > 3.0$), were used and corrected for Lorentz, polarization, and absorption effects, the last with ABSCOR;[13] maximum and minimum transmission factors were 0.66 and 0.56. The data were originally collected for the $C\bar{1}$ cell of the first publication.[5a] As the original coordinates were not available, a preliminary structure was determined by direct methods, with some difficulty. With use of MULTAN 78,[14] an H-shaped atom group was found on E maps which was identified as the superposition of two Sn_3Pt groups. From assignment of one of these in space group $C1$, the entire heavy-atom group was built up and the center of symmetry correctly located. From this, refinement proceeded successfully, until the close equivalence of independent bond lengths and angles led to the suspicion that the crystal contained additional symmetry. Examination of alternative unit cells revealed the rhombohedral unit cell, and averaging of the data under the symmetry operations of $R\bar{3}$ and $R\bar{3}m$ showed R factors for internal agreement of 0.022 and 0.164. Space group $R\bar{3}$ was therefore assumed for further refinements, starting from appropriately transformed atomic positions, with molecular symmetry 3 (position 2(C) for Pt, Sn(1), and Sn(2)). The original 6650 observed reflections ($I/\sigma(I) \geq 3.0$) were reduced by averaging to 2437 reflections. Refinement proceeded smoothly with anisotropic temperature factors for all atoms except the hydrogen atoms (refined isotropically) to a final R of 0.034. A final difference Fourier synthesis showed no significant peaks. The final atomic coordinates are listed in Table I, and bond lengths and angles are listed in Table II.

Table II. Bond Lengths (Å) and Angles (Deg) for $[Ph_3PCH_3]_3[Pt(SnCl_3)_5]$, with Standard Deviations in Parentheses

Pt–Sn, Sn–Cl, and P–C Bond Lengths

Pt–Sn(1)	2.5514 (7)	Sn(3)–Cl(32)	2.372 (4)
Pt–Sn(2)	2.5545 (6)	Sn(3)–Cl(33)	2.374 (5)
Pt–Sn(3)	2.5722 (10)	P–C(11)	1.80 (1)
Sn(1)–Cl(1)	2.344 (6)	P–C(21)	1.78 (1)
Sn(2)–Cl(2)	2.351 (4)	P–C(31)	1.79 (1)
Sn(3)–Cl(31)	2.372 (5)	P–C(4)	1.78 (1)

Phenyl Group Bond Lengths

	n		
	1	2	3
C(n1)–C(n2)	1.38 (2)	1.40 (2)	1.38 (2)
C(n2)–C(n3)	1.39 (2)	1.39 (2)	1.39 (2)
C(n3)–C(n4)	1.36 (2)	1.36 (2)	1.34 (2)
C(n4)–C(n5)	1.37 (2)	1.38 (2)	1.35 (3)
C(n5)–C(n6)	1.38 (2)	1.39 (2)	1.41 (2)
C(n6)–C(n1)	1.38 (2)	1.38 (1)	1.39 (2)

Bond Angles[a]

Sn(1)–Pt–Sn(3)	90.23 (3)	Cl(31)–Sn(3)–Cl(32)	97.0 (2)
Sn(2)–Pt–Sn(3)	89.77 (3)	Cl(31)–Sn(3)–Cl(33)	96.5 (2)
Pt–Sn(1)–Cl(11)	117.7 (2)	Cl(32)–Sn(3)–Cl(33)	95.3 (2)
Cl(11)–Sn(1)–Cl(11′)	100.1 (2)	C(11)–P–C(21)	109.9 (5)
Pt–Sn(2)–Cl(21)	119.4 (1)	C(11)–P–C(31)	108.3 (5)
Cl(21)–Sn(2)–Cl(21′)	98.0 (1)	C(11)–P–C(4)	111.0 (6)
Pt–Sn(3)–Cl(31)	120.3 (1)	C(21)–P–C(31)	109.8 (5)
Pt–Sn(3)–Cl(32)	119.5 (1)	C(21)–P–C(4)	109.9 (5)
Pt–Sn(3)–Cl(33)	122.3 (1)	C(31)–P–C(4)	107.8 (5)

[a] All angles involving phenyl ring carbon atoms are in the range 119–121° (individual esd's 1°).

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Table III. Metal–Ligand Bond Distances in Trigonal-Bipyramidal Pentacoordinate Complexes

complex	d(M–L)$_{ax}$, Å	d(M–L)$_{eq}$, Å	diff, Å	n (for d^n)	ref
$Fe(N_3)_5{}^{2-}$	2.04 (2)	2.00 (2)	0.04	5	22
$Co(2\text{-}CH_3C_5H_4NO)_5{}^{2+}$	2.100 (4)	1.975 (8)	0.125	7	23
$Ni[P(OCH{=}CH_2)_3]_5{}^{2+}$	2.14 (1)	2.19 (1)	0.05	8	24
$Fe(CO)_5$	1.806 (5)	1.833 (4)	0.027	8	25
$Co(CNCH_3)_5{}^{+}$	1.84 (2)	1.88 (2)	0.04	8	26
$CuCl_5{}^{3-}$	2.296 (2)	2.391 (2)	0.095	9	27
$CuBr_5{}^{3-}$	2.450 (2)	2.519 (2)	0.069	9	28
$Ni(CN)_5{}^{3-}$	1.839 (14)	1.907 (13)	0.068	8	29
$Pt(GeCl_3)_5{}^{3-}$	2.4005 (3)	2.434 (3)	0.0335	8	17
$Pt(SnCl_3)_5{}^{3-}$	2.5530 (7)	2.5722 (10)	0.192	8	this work

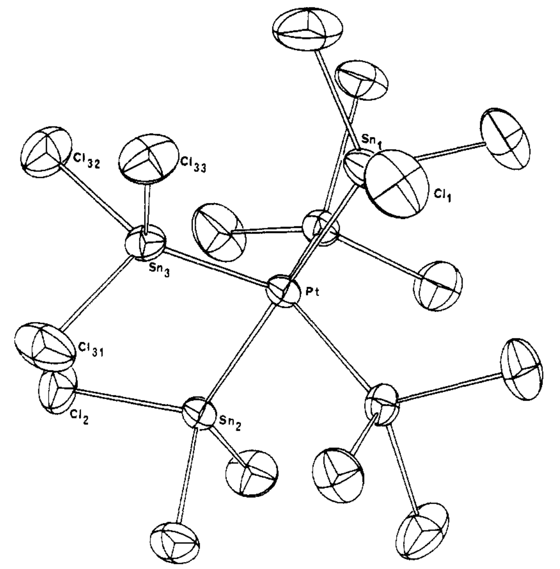

Figure 1. $[Pt(SnCl_3)_5]^{3-}$ ion with 50% probability ellipsoids and atom numbering scheme.

Computing was done with the XRAY 76 and XRAY 72 systems[15,16] running on Burroughs B6700 and CDC 7600 computers, respectively [crystal data: trigonal, space group $R\bar{3}$, $a = 15.897$ (1) Å, $\alpha = 82.02$ (1)°, $V = 3910.4$ (9) Å^3 ($C\bar{1}$ cell constants: $a = 23.997$ (4) Å, $b = 20.862$ (3) Å, $c = 15.892$ (1) Å, $\alpha = 90.01$ (1)°, $\beta = 100.59$ (1)°, $\gamma = 89.99$ (1)°, $V = 7820.8$ (1.8) Å^3), Mo Kα = 0.71069 Å, μ(Mo Kα) = 39.9 cm^{-1}, $Z = 3$, $\rho_c = 1.83$ g/cm^3, $\rho_m = 1.84$ g/cm^3].

Discussion

The trigonal-bipyramidal anion $[Pt(SnCl_3)_5]^{3-}$ (Figure 1) has crystallographic 3-fold symmetry, but the heavy atoms are extremely close to 3/*mm* symmetry with ∠Sn(ax.)–Pt–Sn(eq) 90.2° (Table II). The Sn(ax.)–Pt–Sn(ax.) moiety is essentially linear, with the platinum only 0.0007 Å from the line. The platinum and three equatorial tin atoms are coplanar, with the platinum atom deviating from the plane by only 0.0082 Å. A packing diagram (Figure 2) shows the interesting result that the two $[Pt(SnCl_3)_5]^{3-}$ ions pack in the unit cell with the two platinum and four axial tin atoms collinear, lying along the body diagonal of the rhombohedron. This packing, however, does not impose any unusual platinum–tin bond distances or tin–tin intermolecular contacts (Tabl II).

Comparison of the structures of $[Pt(GeCl_3)_5]^{3-}$ (see Table III) and $[Pt(SnCl_3)_5]^{3-}$ reveals some very interesting differences. $[Pt(GeCl_3)_5]^{3-}$[17] is highly distorted, whereas $[Pt(SnCl_3)_5]^{3-}$ is a very regular trigonal bipyramid. This difference is not anticipated on the basis of electronic arguments since the Lewis base strengths[18,19] and Lewis acid strengths[20] of $GeCl_3^-$ and $SnCl_3^-$ are thought to be identical. It is also believed that the distortions in $[Pt(GeCl_3)_5]^{3-}$ are not steric in origin as there are no abnormal intramolecular contacts despite unusually short Pt–Ge bonds.[17] Further, there is no a priori symmetry-based reason for the distortion of the $[Pt(GeCl_3)_5]^{3-}$ complex. It is possible that crystal packing forces caused by smaller and therefore more strongly polarizing $N(CH_3)_4{}^+$ cations in $[(CH_3)_4N]_3[Pt(GeCl_3)_5$ compared to $[PPh_3PCH_3]^+$ in $[PPhPCH_3]_3[Pt(PtCl_3)_5]$ are responsible for the distortions of the former. In light of the observations by Raymond[21] et al. that crystal packing can determine the overall geometry in the $Ni(CN)_5{}^{3-}$ system, this appears to be the most logical explanation for the distortion of the $[Pt(GeCl_3)_5]^{3-}$ ion away from D_{3h} symmetry.

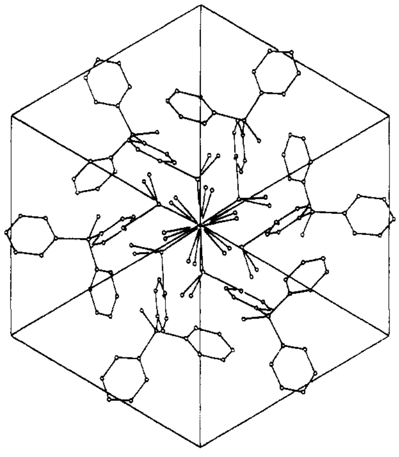

Figure 2. Packing diagram viewed down the 3-fold axis. Three phosphonium cations are packed around each of the anions, one of which is at the top of the cell and one at the bottom.

For trigonal-bipyramidal d^8 transition-metal complexes, current theory[8] predicts that the axial metal–ligand length should be shorter than the equatorial metal–ligand bond length.

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(20) Since tin and germanium have the same electronegativities, it is reasonable to expect the Lewis acid strengths of $GeCl_3^-$ and $SnCl_3^-$ to be the same, especially in light of their Lewis base strengths being the same. However, tin is larger than germanium, and overlap between platinum d orbitals and tin d orbitals might be more effective than overlap between Pt and germanium d orbitals. This contention is supported somewhat by the data in Table IV.

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(30) Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.

Table IV. Metal–Tin Distances in Metal–$SnCl_3$ Complexes

complex	d(M–Sn), Å	Σ(atomic radii),[a] Å	diff, Å	n (for d^n)	ref
$Ru_2Cl_3(CO)_5SnCl_3$	2.565	2.75	0.185	6	*b*
$[Ru(SnCl_3)_5Cl]^{4-}$	2.553, 2.579	2.75	0.197, 0.171 (0.184 av)	6	*c*
$(C_7H_7)(Me_2PPh)_2IrSnCl_3$	2.5867	2.80	0.2133	8	*d*
$(C_8H_{12})_2Ir(SnCl_3)$	2.642	2.80	0.158	8	*e*
$[Pt(SnCl_3)_5]^{3-}$	2.553, 2.572	2.80	0.247, 0.228 (0.2375 av)	8	*f*
$Pd_2(DPM)_2(SnCl_3)Cl$	2.585	2.85	0.275	9	*g*
$(\pi\text{-}C_3H_5)Pd(PPh_3)SnCl_3$	2.563	2.85	0.287	8	*h*
$(C_8H_{12})_3Pt_3(SnCl_3)_2$	2.80	2.85	0.05	?	*i*
$(\pi\text{-}C_5H_5)Fe(CO)_2(SnCl_3)$	2.467	2.85	0.383	6	*j*
$[Pt(GeCl_3)_5]^{3-}$	2.434, 2.4005	2.60	0.20, 0.166 (0.183 av)	8	*k*

[a] Slater, J. C. *J. Chem. Phys.* 1964, *41*, 3199. [b] Elder, M.; Hall, D. *J. Chem. Soc. A* 1970, 245. [c] Farrugia, L. J.; James, B. R.; Lassigne, C. R.; Wells, E. J., submitted for publication. [d] Churchill, M. R.; Lin, K. G. *J. Am. Chem. Soc.* 1974, *96*, 76. [e] Porta, P.; Powell, H. M.; Mawby, R. J.; Venanzi, L. M. *J. Chem. Soc. A* 1967, 455. [f] This work. [g] Olmstead, M. M.; Benner, L. S.; Hope, H.; Balch, A. L. *Inorg. Chim. Acta* 1979, *32*, 193. [h] Mason, R.; Robertson, G. B.; Whimp, P. O.; White, D. A. *Chem. Commun.* 1968, 1655. [i] Guggenberger, L. J. *Chem. Commun.* 1968, 512. [j] Green, P. T.; Bryan, R. F. *J. Chem. Soc. A* 1970, 1696. [k] Estes, E. D.; Hodgson, D. J. *Inorg. Chem.* 1973, *12*, 2932; geometry idealized.

Such is the case for $[Pt(SnCl_3)_5]^{3-}$, wherein the difference in these bond lengths is 0.0192 (12) Å. This difference should be compared with similar crystallographically determined differences for structurally analogous compounds. Pertinent bond distances and differences are listed in Table III.

Each of the pentacoordinate d^8 complexes exhibits axial bonds that are shorter than the equatorial bonds, wholly consistent with the theoretical predictions.[8] It is interesting to note that for $[Pt(SnCl_3)_5]^{3-}$ the axial–equatorial bond difference is the smallest of the group and is similar in magnitude to the difference found for $Fe(CO)_5$, which contains strongly π-bonding carbon monoxide. Since $SnCl_3^-$ is believed to be strongly π accepting, the small difference between the axial and equatorial platinum–tin bonds in $[Pt(SnCl_3)_5]^{3-}$ could be due to a significant amount of metal equatorial π bonding. Metal equatorial π bonding is predicted[10] to be stronger than metal–axial ligand π bonding in trigonal-bipyramidal complexes.

The data presented in Table IV corroborate this notion in the following way. For each complex, the metal–tin bond is significantly shorter than the sum of the appropriate atomic radii, suggesting some multiple-bond character in all the M–Sn bonds. Further, this difference generally increases with an increase in the electron density of the metal, the d^9 Pd(I) complex displaying the greatest difference and the d^6 Ru(II) complexes displaying smaller differences.

The complex $(C_8H_{12})_2Ir(SnCl_3)$, though containing d^8 Ir(I), also contains two strongly π-bonding cyclooctadienes, and $(C_8H_{12})_3Pt_3(SnCl_3)_2$ has the $SnCl_3$ moieties in pseudooctahedral environments such that in this complex there is probably little, if any, Pt–Sn π bonding. Each of these complexes has $SnCl_3^-$ groups with similar Cl–Sn–Cl (~95–100°) and M–Sn–Cl (~117–122°) bond angles, i.e., the Cl–Sn–Cl angles are closer to those expected for Sn–Cl bonds involving only p orbitals on Sn, leaving the M–Sn bond with considerable s character and the Sn–Cl bonds with considerable p character, consistent with Bent's rules.[30] This is an ideal situation for M–Sn π bonding.

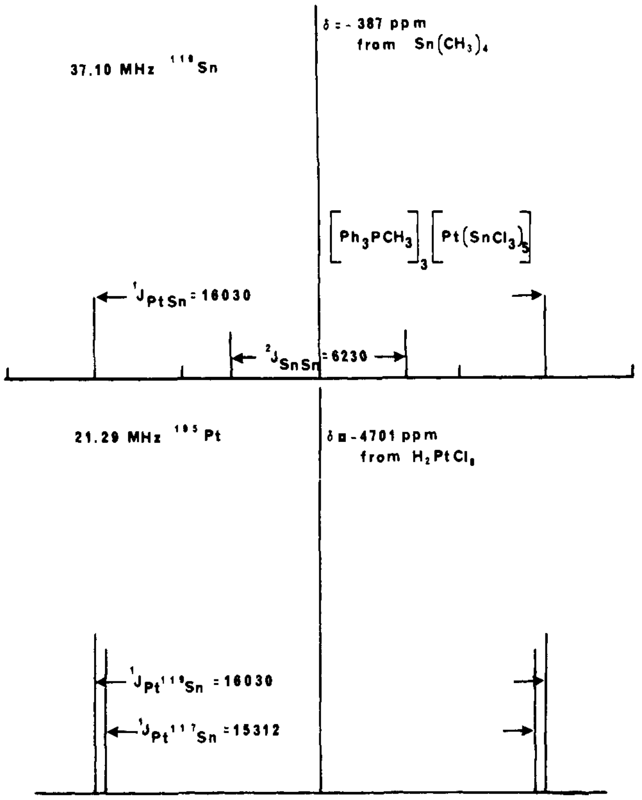

Figure 3. 37.10-MHz ^{119}Sn and 21.29-MHz ^{195}Pt NMR spectra of acetone-d_6 solutions of $[Ph_3PCH_3]_3[Pt(SnCl_3)_5]$ at 20 000-Hz sweep widths taken at 299 K.

The $[Pt(SnCl_3)_5]^{3-}$ complex maintains its integrity upon dissolution in acetone as evidenced by the ^{119}Sn and ^{195}Pt NMR spectra displayed in Figure 3. In the absence of tin site exchange, one would expect to see two different ^{119}Sn chemical shifts for the two different tin environments. For a $PtSn_5$ cluster all the tin nuclei are averaged by some rate process (e.g., Berry pseudorotation). The ^{195}Pt NMR spectrum should possess a central resonance[31] (intensity of 1) for all species containing neither ^{119}Sn ($I = {}^1/_2$, 8.58% natural abundance) nor ^{117}Sn ($I = {}^1/_2$, 7.61% natural abundance) with relative intensity of 1. The central resonance should be flanked by ^{119}Sn satellites with relative intensities of 0.23 and ^{117}Sn satellities with relative intensities of 0.20. In this spectrum, the ratio of $J_{^{119}Sn-^{195}Pt}$ to $J_{^{117}Sn-^{195}Pt}$ should be equal to the ratio of the ^{119}Sn to ^{117}Sn magnetogyric ratios, which is[32] 1.046. The ^{119}Sn NMR spectrum should contain a central resonance with relative intensity of 1 for all species not containing ^{195}Pt ($I = {}^1/_2$, 33.4% natural abundance) flanked by ^{195}Pt satellites with relative intensities of 0.25. In addition, ^{117}Sn satellites with relative intensities of 0.16 should be observed.

Hence, the observation of a single ^{119}Sn resonance as seen in Figure 3 indicates the occurrence of a site-exchange process, and the maintenance of spin correlation suggests that this

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(32) Lynden-Bell, R.; Harris, R. K. "Nuclear Magnetic Resonance Spectroscopy"; Appleton-Century-Crofts: New York, 1969.

process is intramolecular. These spectra are temperature invariant between 183 and 363 K. This is similar to what is observed in the ^{13}C NMR spectra of $Fe(CO)_5$, where a single resonance is observed even at very low temperatures,[33] but contrasts with what is observed for $Pt[P(OCH_3)_3]_5^{2+}$, where site exchange is completely stopped[3d] at 133 K. The observation of a large $^{119}Sn-^{195}Pt$ coupling constant is consistent with a considerable degree of s character in the platinum-tin bond. The near equivalence of the axial and equatorial platinum-tin bonds is consistent with the very low activation energy barrier for Berry pseudorotation in this complex.

The relative intensities of the resonances in both the ^{119}Sn and ^{195}Pt NMR spectra (Figure 3) establish the identity[31] of the $[Pt(SnCl_3)_5]^{3-}$ species in solution. No other species such as $[Pt(SnCl_3)_4]^{2-}$ or $[Pt(SnCl_3)_2Cl_2]^{2-}$ could be detected in these solutions even after they stood for nearly a year. Hence, in the absence of protic solvents, the $[Pt(SnCl_3)_5]^{3-}$ species has long-term stability. In protic solvents, the species has only short-term stability and metallic platinum is slowly precipitated from either methanol or water/HCl solutions.

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Registry No. $[Ph_3PCH_3]_3[Pt(SnCl_3)_5]$, 14302-80-8; H_2PtCl_6, 16941-12-1; K_2PtCl_6, 16921-30-5; $SnCl_2$, 7772-99-8.

Supplementary Material Available: Listings of temperature factors and observed and calculated structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

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Binding Mode of Thiocyanate in Palladium(II) Complexes: X-ray Crystal Structure of *cis*-(Isothiocyanato)(thiocyanato)bis(1-phenyl-3,4-dimethylphosphole)palladium(II)

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The crystal structure of *cis*-(isothiocyanato)(thiocyanato)bis(1-phenyl-3,4-dimethylphosphole)palladium(II) has been determined from three-dimensional X-ray diffraction techniques. The molecule crystallizes in the triclinic space group $P\bar{1}$ in a unit cell of dimensions $a = 9.902$ (2) Å, $b = 17.526$ (4) Å, $c = 8.909$ (4) Å, $\alpha = 109.10$ (2)°, $\beta = 113.02$ (2)°, $\gamma = 87.49$ (2)°, $\rho_{calcd} = 1.869$ g cm^{-3}, and $\rho_{obsd} = 1.859$ g cm^{-3}. Refinement converged to $R = 0.042$, with 3345 independent reflections. Both phosphole rings are planar, and the intracyclic phosphole bond lengths differ for the two distinct phospholes. The phosphole trans to the N-bound thiocyanate possesses more aromatic character than the phosphole trans to the S-bound thiocyanate. The two Pd-P bonds are significantly different, with that trans to the S-bound thiocyanate being longer (2.290 (2) Å) than that trans to the N-bound thiocyanate (2.248 (2) Å), reflecting the greater trans influence of thiocyanate than isothiocyanate. The thiocyanate bond distances and angles are compared to those found for analogous complexes. The data suggest that electronic effects are important in determining both the coordination geometry and thiocyanate bonding mode in $(R_3P)_2Pd(CNS)_2$ complexes. Electronic effects favor both the cis geometry about palladium and the S-bonding mode unless steric effects are large. Steric effects, however, are the discriminator for both the geometry and thiocyanate bonding mode. When steric effects become large, the favored geometry becomes trans rather than the electronically favored cis and the thiocyanate bonding mode becomes N rather than the electronically favored S-bonding mode. The thiocyanate bonding mode seems to be more responsive to small changes in steric effects than is the coordination geometry. Consequently, steric effects smaller than those necessary to stabilize the trans geometry promote N-bound thiocyanate.

Introduction

Thiocyanate[2] complexes of class "B" metal often behave in an antisymbiotic[3] manner, and this behavior has been rationalized over the years in terms of electronic and steric effects.[4-10] There has been considerable discussion concerning the relative importance of these two effects. We have shown[11] that 1-substituted-3,4-dimethylphospholes form strong bonds with palladium(II), consistent with their sterically undemanding nature and with their greater potential for metal-ligand π interaction when compared with ordinary phosphines.[12,13] Thus a study of the structures of palladium-phosphole-thiocyanate complexes of the type $L_2Pd(CNS)_2$ can provide new information about the factors affecting symbiosis in thiocyanate complexes, as well as allow us greater understanding of the nature of the palladium-phosphole bond. We

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(1) (a) University of Nevada. (b) University of Warwick. (c) CNRS-SNPE.

(2) Throughout this paper we represent metal-isothiocyanate bonding as M-NCS and metal-thiocyanate bonding as M-SCN. M-CNS is used when no specific bonding mode is implied.

(3) The term symbiosis was coined by Jorgensen (Jorgensen, C. K. *Inorg. Chem.* **1964**, *3*, 1201) and the term antisymbiosis by Burmeister and Melpolder (Burmeister, J. L.; Melpolder, J. B. *J. Chem. Soc., Chem. Commun.* **1973**, 613). The latter is more fully discussed in ref 18.

(4) Detailed discussions of the various factors that influence the thiocyanate bonding mode can be found in Burmeister and Norbury (Burmeister, J. L. In "The Chemistry and Biochemistry of Thiocyanic Acid and Its Derivatives"; Newman, A. A., Ed.; Academic Press: Condon, 1975; pp 68-130. Norbury, A. H. *Adv. Inorg. Chem. Radiochem.* **1975**, *17*, 231).

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