Insertion of an Acetylene into the Pt–Sn Bond of (PEt₃)₂(SnCl₃)₂(μ-Cl)₂Pt₂

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The chlorine-bridged dimer $(PEt_3)_2(SnCl_3)_2(\mu\text{-Cl})_2Pt_2$ reacts with 2 equiv of hexafluorobut-2-yne to give a product, $C_{20}H_{30}Cl_8F_{12}P_2Pt_2Sn_2$, which preserves the dichloro bridge and contains two Pt—C=C—Sn moieties. The crystals of this product are triclinic of space group $P\bar{1}$ with one chlorine-bridged centrosymmetric dimer in a unit cell of dimensions $a = 9.501$ (2) Å, $b = 12.952$ (3) Å, $c = 9.263$ (2) Å, $\alpha = 108.77$ (2)°, $\beta = 106.99$ (2)°, and $\gamma = 90.13$ (2)°. The structure was solved by the heavy-atom method and refined by the full-matrix least-squares calculations: $R = 0.0374$ for 3253 reflections with $I > 3\sigma(I)$ collected by diffractometer. The unique Pt atom has close to square-planar geometry with the PtC_4Sn plane approximately normal (78.3°) to the $PtCl_2PC$ coordination plane. Principal dimensions are as follows: Pt—Cl(1) (trans to PEt₃) = 2.415 (2) Å, Pt—Cl(1)' (trans to C) = 2.396 (2) Å, Pt—C(2) = 1.982 (6) Å, C(2)=C(3) = 1.339 (9) Å, C(3)—Sn = 2.127 (6) Å, Sn—Cl(11) = 2.306 (2) Å, Sn—Cl(12) = 2.288 (2) Å, Sn—Cl(13) = 2.302 (2) Å, and Pt—P = 2.230 (2) Å. Atom Cl(12) of the SnCl₃ moiety is constrained to lie slightly off the normal to the Pt coordination plane with Pt⋯Cl(12) = 3.430 (2) Å. The C(3)–Sn–Cl(12) angle (129.0 (2)°) is considerably enlarged over the anticipated tetrahedral value as a result of Pt⋯Cl repulsion. The other C(3)–Sn–Cl angles are just less than tetrahedral (107.4 and 108.4 (2)°). The structure of this product, in which the dichloro bridge is maintained, suggests that it may be formed by a process that utilizes the leaving properties and nucleophilicity of the SnCl₃ ligand.

Introduction

Although metal–metal bonds are known to display widely varying degrees of chemical reactivity, many react with unsaturated substrates, such as olefins or acetylenes, to give products based on the M–C–C–M' skeleton.[1] Such species can be derived from both homogeneous and heterogeneous metal–metal bonds.[2] We now describe the preparation and characterization of the first such product derived from a Pt–Sn bond.

Experimental Section

Infrared spectra were recorded on a Beckman IR-12 spectrophotometer as Nujol mulls using KBr plates in the 4000–400 cm⁻¹ region. Proton, ³¹P, and ¹⁹F NMR spectra were obtained on a Varian A-60 or a Bruker WP-60 Fourier transform spectrometer with Me₄Si, H₃PO₄, or CFCl₃ as internal reference lock signals, respectively. Analyses were performed by MHW Laboratories, or Guelph Chemical Laboratories, Guelph, Ontario, Canada.

Preparation of Bis(triethylphosphine)bis(trichlorotin)-bis(μ-chloro)diplatinum(II) ((Et₃P)₂(SnCl₃)₂(μ-Cl)₂Pt₂, I). When a twofold excess of powdered SnCl₂·2H₂O was added with constant stirring to a dichloromethane solution of bis(triethylphosphine)dichlorobis(μ-chloro)diplatinum, {PtCl₂(PEt₃)}₂,[3] a color change from yellow to orange-red occurred within a few minutes. Stirring was continued at room temperature for 2 h, after which the solution was filtered, the filtrate was reduced in volume, and hexane was added to give orange crystals of I. The ³¹P NMR spectrum showed δ(P) 12.263 ($J(PtP) = 3479$, $J(SnP) = 232$ Hz). Anal. Calcd for $C_{12}H_{30}P_2Sn_2Cl_8Pt_2$: Cl, 24.73. Found: C, 24.5.

Reaction of I with Hexafluorobut-2-yne. Excess hexafluorobut-2-yne (C₄F₆) was condensed under vacuum into a tube containing a dichloromethane solution of I. The tube was sealed and kept at room temperature for 10 days, during which time orange-yellow crystals appeared. These were separated by decantation, and a further crop was obtained on concentrating the mother liquor. The yield of a product identified as Pt₂-

$(SnCl_3)_2Cl_2(PEt_3)_2(C_4F_6)_2$ was 78%: IR $\nu(C=C)$ 1575 (s), CF_3 1150 (vs), 1235 (vs) cm⁻³; ³¹P NMR, showed two sets of resonances with an intensity ratio of 3:1, δ(P₁) 8.041 ($J(PtP) = 4072$, $J(SnP) = 147$ Hz), δ(P₂) 6.634 ($J(PtP) = 4084$, $J(SnP) = 19.5$ Hz?); ¹⁹F NMR (in acetone-d₆), showed two sets of resonances, δ(F) –49.687 (J-(PtF) 24 Hz), δ(F₂) –50.825 ($J(PtF) = 13$ Hz). Anal. Calcd for $C_{20}H_{30}Cl_8F_{12}P_2Pt_2Sn_2$: C, 16.32; H, 2.04; Cl, 19.30. Found: C, 16.64; H, 2.01; Cl, 19.19.

Crystal Structure Analysis. Crystal Data: $C_{20}H_{30}Cl_8$-$F_{12}P_2Pt_2Sn_2$, $M_r = 1471.5$, triclinic, $a = 9.501$ (2) Å, $b = 12.952$ (3) Å, $c = 9.263$ (2) Å, $\alpha = 108.77$ (2)°, $\beta = 106.99$ (2)°, $\gamma = 90.13$ (2)°, $V = 1026.28$ Å³, $Z = 1$, $D_{calcd} = 1.43$ g cm⁻³, $F(000) = 680$, Mo radiation, $\lambda = 0.71069$ Å, $\mu(Mo\ K\alpha) = 54.2$ cm⁻¹, space group $P\bar{1}$. Accurate cell parameters were obtained by a least-squares refinement of the setting angles of 25 reflections (with θ between 10 and 15°) measured on an Enraf-Nonius CAD4 automatic diffractometer. Intensity data were collected with a small (0.11 × 0.14 × 0.41 mm) crystal to a maximum θ of 25°, and 3610 unique data were obtained. After corrections for Lorentz and polarization effects, the data with $I > 3\sigma(I)$ (3253) were labeled observed and used in structure solution and refinement.

Structure Solution and Refinement. The coordinates of the Pt atom were obtained from an analysis of a three-dimensional Patterson function and the remaining non-hydrogen atoms were located in a heavy-atom-phased Fourier summation. Refinement was by full-matrix least-squares calculations, initially with isotropic and then with anisotropic vibration parameters. A difference map, computed at an intermediate stage in the refinement, revealed maxima (0.41–0.73 e Å⁻³) in positions expected for all hydrogen atoms; these were then allowed for in geometrically idealized positions (C–H = 0.95 Å) and only an overall isotropic thermal parameter was refined for them in the final rounds of calculations.

In the final refinement cycles a weighting scheme of the form $\omega = 1/[\sigma^2(F) + pF^2]$ was employed where the final p parameter was 2.87×10^{-3}. Scattering factors used in the structure factor calculations were taken from ref 4 and 5, and allowance was made for anomalous dispersion.[6] Refinement converged with $R = 0.037$ and $R\omega = [\Sigma\omega\Delta^2/\Sigma\omega F_o^2]^{1/2} = 0.039$. A final difference map was

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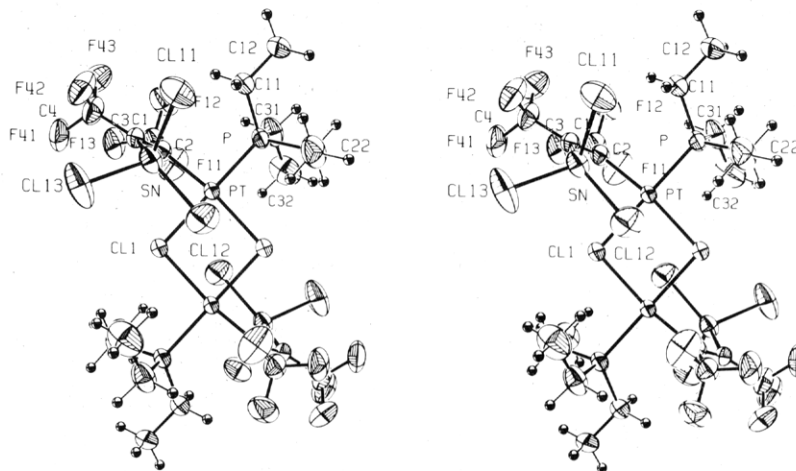(6) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, 53, 1891.

Figure 1. Stereoview of the dimer with the crystallographic numbering scheme.

Table I. Final Fractional Coordinates (Pt and Sn, ×10⁵; others, ×10⁴) for C₂₀H₃₀Cl₈F₁₂P₂Pt₂Sn₂ with Standard Deviations in Parentheses

Table I. Final Fractional Coordinates (Pt and Sn, $\times 10^5$; others, $\times 10^4$) for $C_{20}H_{30}Cl_8F_{12}P_2Pt_2Sn_2$ with Standard Deviations in Parentheses

| atom	x/a	y/b	z/c
Pt	46572 (2)	13825 (2)	2653 (3)
Sn	61371 (5)	24958 (4)	43057 (6)
Cl(1)	6772 (2)	370 (1)	766 (2)
Cl(11)	4803 (3)	3714 (2)	5653 (3)
Cl(12)	4804 (3)	857 (2)	3704 (3)
Cl(13)	8278 (3)	2364 (3)	6176 (3)
P	2717 (2)	2316 (1)	−280 (2)
F(11)	6092 (7)	2361 (5)	−1501 (6)
F(12)	5937 (6)	4011 (4)	−173 (7)
F(13)	7967 (5)	3316 (4)	316 (6)
F(41)	9300 (5)	3777 (4)	3681 (7)
F(42)	7989 (6)	4577 (4)	5105 (6)
F(43)	7825 (6)	4887 (4)	2947 (7)
C(1)	6539 (8)	3106 (6)	−58 (9)
C(2)	6092 (6)	2714 (5)	1163 (7)
C(3)	6761 (6)	3171 (5)	2743 (8)
C(4)	7982 (8)	4089 (7)	3614 (10)
C(11)	2918 (7)	3714 (5)	1118 (10)
C(12)	1572 (8)	4322 (6)	769 (11)
C(21)	1014 (6)	1650 (6)	−299 (10)
C(22)	1039 (9)	1606 (8)	1296 (13)
C(31)	2305 (9)	2429 (7)	−2281 (10)
C(32)	2084 (14)	1345 (10)	−3607 (12)
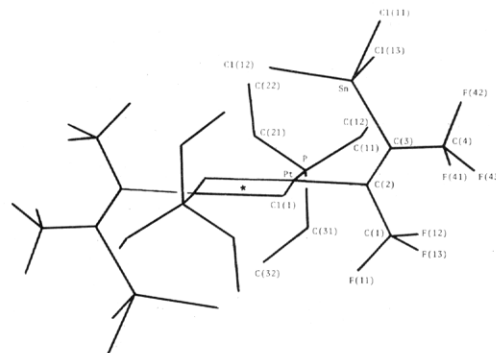
Figure 2. Line drawing of the dimer.

devoid of any significant features.

Results and Discussion

Under mild reaction conditions, the chlorine-bridged dimer I reacts with 2 equiv of acetylene to give a crystalline, well-characterized product. The infrared and NMR spectroscopic data (a) show that a vinylic group (i.e., C=C) has been formed and (b) suggest that in solution two species may be present in a 3:1 ratio. Unambiguous

Table II. Interatomic Distances (Å) and Angles (deg) for C₂₀H₃₀Cl₈F₁₂P₂Pt₂Sn₂[a]

Table II. Interatomic Distances (Å) and Angles (deg) for $C_{20}H_{30}Cl_8F_{12}P_2Pt_2Sn_2$[a]

Bond Lengths

Pt–Cl(1)	2.415 (2)	Sn–C(3)	2.127 (6)	C(2)–C(3)	1.339 (9)
Pt–Cl(1)′	2.396 (2)	P–C(11)	1.827 (7)	C(3)–C(4)	1.497 (8)
Pt–P	2.230 (2)	P–C(21)	1.825 (6)	C(4)–F(41)	1.308 (9)
Pt–C(2)	1.982 (6)	P–C(31)	1.834 (8)	C(4)–F(42)	1.319 (9)
Sn–Cl(11)	2.306 (2)	C(1)–C(2)	1.539 (8)	C(4)–F(43)	1.352 (10)
Sn–Cl(12)	2.288 (2)	C(1)–F(11)	1.317 (9)	C(11)–C(12)	1.513 (9)
Sn–Cl(13)	2.302 (2)	C(1)–F(12)	1.327 (9)	C(21)–C(22)	1.490 (12)
		C(1)–F(13)	1.303 (8)	C(31)–C(32)	1.504 (13)

Bond Angles

Cl(1)–Pt–Cl(1)′	85.1 (1)	Pt–P–C(31)	111.9 (3)	C(2)–C(3)–C(4)	128.9 (6)
Cl(1)–Pt–P	177.9 (1)	C(11)–P–C(21)	105.7 (3)	C(2)–C(3)–Sn	118.2 (4)
Cl(1)–Pt–C(2)	86.6 (2)	C(11)–P–C(31)	106.3 (4)	C(4)–C(3)–Sn	112.8 (5)
P–Pt–C(2)	93.1 (2)	C(21)–P–C(31)	104.8 (4)	C(3)–C(4)–F(41)	113.6 (7)
Pt–Cl(1)–Pt′	94.9 (1)	C(2)–C(1)–F(11)	111.3 (5)	C(3)–C(4)–F(42)	111.0 (6)
Cl(11)–Sn–Cl(12)	101.5 (1)	C(2)–C(1)–F(12)	111.2 (6)	C(3)–C(4)–F(43)	112.3 (6)
Cl(11)–Sn–Cl(13)	107.6 (1)	C(2)–C(1)–F(13)	112.5 (6)	F(41)–C(4)–F(42)	106.9 (7)
Cl(12)–Sn–Cl(13)	101.4 (1)	F(11)–C(1)–F(12)	107.0 (7)	F(41)–C(4)–F(43)	107.0 (6)
C(3)–Sn–Cl(11)	108.4 (2)	F(11)–C(1)–F(13)	107.0 (6)	F(42)–C(4)–F(43)	105.4 (7)
C(3)–Sn–Cl(12)	129.0 (2)	F(12)–C(1)–F(13)	107.4 (6)	P–C(11)–C(12)	114.2 (5)
C(3)–Sn–Cl(13)	107.4 (2)	C(1)–C(2)–Pt	116.2 (5)	P–C(21)–C(22)	113.7 (5)
Pt–P–C(11)	114.7 (2)	C(1)–C(2)–C(3)	121.7 (5)	P–C(31)–C(32)	113.9 (6)
Pt–P–C(21)	112.7 (2)	Pt–C(2)–C(3)	121.6 (4)		

[a] The primed atoms are obtained from those in the coordinate table by the symmetry operation $1 - \bar{x}, \bar{y}, \bar{z}$.

structural information is provided by the crystal structure analysis.

The molecular structure and atomic numbering scheme for $C_{20}H_{30}Cl_8F_{12}P_2Pt_2Sn_2$ are given in Figures 1 and 2 which was prepared with the aid of ORTEP.[7] The final values of the positional parameters with their standard deviations are shown in Table I, Table II gives interatomic distances, bond angles, and torsion angles, and Table III has details of mean plane calculations.

The crystal structure contains discrete, dimeric, and centrosymmetric molecules separated by normal van der Waals contacts. The Pt coordination is distorted square planar with cis angles at Pt in the range 85.1–95.1 (2)°. The plane containing the carbon atoms C(1), C(2), C(3), and C(4), Pt, and Sn (Figures 1 and 2) is approximately normal (78.3°) to the PtCl₂PC coordination plane. Atom Cl(12) of the SnCl₃ moiety is constrained to lie above the Pt atom with Pt···Cl(12) = 3.430 (2) Å; the C(3)–Sn–Cl(12) angle (129.0 (2)°) is considerably enlarged over the tetrahedral value as a result of Pt···Cl repulsion.

This is the first determination of a structure with Pt—C≡C—Sn moiety; there are no molecules with this system currently listed in the Cambridge Crystallographic Data Base.

The Pt–C bond length (1.982 (6) Å) is comparable to those found in [Pt₃(hfb)₄(cod)₂][8] (average value 2.06 (3) Å). The Sn–C bond length (2.127 (2) Å) also compares well with the mean value (2.137 (8) Å) for the Sn–C bonds of (C₆H₅)₃Sn(OH).[9] In the hfb moiety the C–C single bond distances are 1.539 and 1.497 (8) Å and the C(2)–C(3) double bond distance is 1.339 (9) Å. The geometry of the trifluoromethyl groups is approximately tetrahedral, and the bond lengths are unexceptional (Table II).

Apart from this being the first well-characterized species containing the Pt—C≡C—Sn moiety, the formation of this compound has several other unusual aspects. Superficially, it would appear that its formation requires preferential insertion of the acetylene into the Pt–Sn bond without cleavage of the bridge.
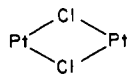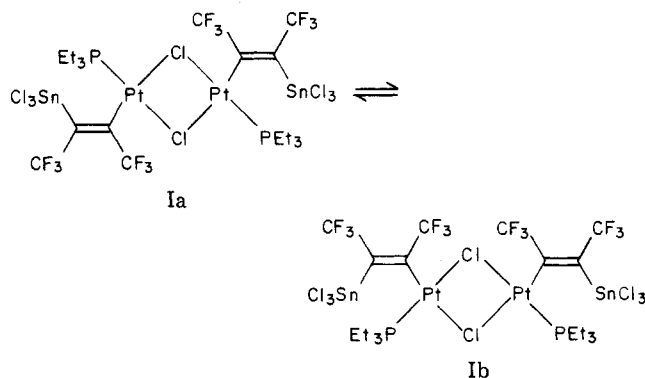

This appears unreasonable, not only on the basis of energetic considerations but also in view of the well-established ease of cleavage of such a bridge by a variety of reagents. A more reasonable speculation is that SnCl₃⁻ functions as a good leaving group, thus generating a cationic platinum acetylene species (see eq 1). Nucleophilic

$$\text{(1)}$$
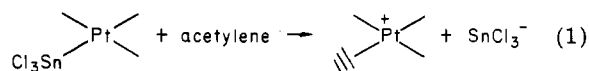
attack by SnCl₃⁻ on the coordinated acetylene will then generate the observed product. This explanation that emphasizes both the behavior of SnCl₃ as a good leaving group and its nucleophilicity is consistent with the role of the –SnCl₃ ligand in other reactions,[10] e.g., Pt–Sn-catalyzed hydroformylation. Whether the reaction proposed above would occur with or without cleavage of the platinum–chlorine bridge, perhaps by the acetylene, is by no means clear, although reformation of the bridge is obviously possible.

There is also evidence from the ³¹P NMR spectrum that the platinum–chlorine bridge is labile. In the centrosymmetric structure observed, the two phosphorus nuclei are in the same environment and hence are magnetically equivalent. The spectrum, however, shows two sets of resonances, in a 3:1 intensity ratio. Both sets show couplings to ¹⁹⁵Pt and ¹¹⁹Sn, although the assignment for this latter coupling is questionable since the satellites are of very low intensity. It seems likely, therefore, that in solution an equilibrium occurs as

Ia

Ib

Crystallization from solution then gives only the trans form Ia.

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