

attack of a cyclohexyl radical on I) which can carry the chain by abstracting a hydrogen atom from cyclohexane. Support for this theory was obtained when reaction in the presence of a radical trap, hydroquinone, gave compound VIII as the major product (61%) and IX (26%) and X (13%) as minor products.

Details of these and other reactions of perfluorodiazocompounds will appear in future publications.

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Five-Coordinate Platinum(II) Complexes

Sir:

Determination of the configuration of the $[\text{Pt}(\text{SnCl}_3)_5]^{-3}$ anion by X-ray diffraction has shown it to be a trigonal bipyramid consisting of a central platinum atom surrounded by five SnCl_3^- ligands attached through platinum-tin bonds. The complex anion thus provides the first example of a five-coordinate Pt(II) species containing only monodentate ligands. Although it might be expected that a coordination number of five should be common for platinum(II) complexes (rare gas configuration), only two such compounds have been isolated, both of which contain highly stabilizing umbrella-type polydentate ligands, e.g., tris(*o*-diphenylarsine)arsine.¹

Crystals used in the collection of diffraction intensities were of composition $[(\text{C}_6\text{H}_5)_3\text{PCH}_3]_3[\text{Pt}(\text{SnCl}_3)_5]^{-2}$ with the triclinic cell dimensions $a = 23.63 \pm 0.05$, $b = 20.90 \pm 0.05$, $c = 15.65 \pm 0.04$ Å, $\alpha = 90^\circ$, $\beta = 101.5 \pm 0.2^\circ$, $\gamma = 90^\circ$ ($\rho_c = 1.88$, $\rho_o = 1.87$ g./cm.³). Although the cell could have been based on space group $\text{P}\bar{1}$, it was more convenient to use the above cell with space group orientation $\text{C}\bar{1}$ and containing four molecules per cell.

Approximately 2500 diffraction intensities were collected with a Weissenberg counter diffractometer using Cu K α radiation. The resultant $|F_o|^{-2}$ were corrected for absorption and used to calculate three-dimensional Patterson maps. Analysis of the Pattersons showed platinum to be surrounded by five tin atoms in a trigonal bipyramidal arrangement. Possible locations for fifteen chlorine and three phosphorus atoms were obtained from Fourier maps and included in structure factor calculations along with those of the platinum and tin atoms. Preliminary refinement of this model by difference-Fourier syntheses resulted in $R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|} = 0.25$. Additional difference maps show that although further refinement of the structure is needed, the PtSn_5 configuration is correct. There remain 57 carbon and 54 hydrogen atoms which have not been included in the calculations. Although the individual Pt-Sn distances are not considered to be reliable at this time, the average is 2.54 Å.

Salts of two other complex anions, $[\text{HPt}(\text{SnCl}_3)_4]^{-3}$ and $\{\text{HPt}(\text{SnCl}_3)_2[(\text{C}_2\text{H}_5)_3\text{P}]_2\}^{-}$, have also been prepared. Based on their composition and properties, and knowledge of the structure of $[\text{Pt}(\text{SnCl}_3)_5]^{-3}$,

(1) See L. M. Venanzi, *Angew. Chem. Intern. Ed., Engl.*, **3**, 453 (1964), for a recent review.

(2) R. D. Cramer, E. L. Jenner, R. V. Lindsey, Jr., and U. G. Stolberg, *J. Am. Chem. Soc.*, **85**, 1691 (1963).

these anions must also be formulated as five-coordinate platinum(II) species. In addition, they are believed to be the first examples of anionic platinum hydrides.

Reaction of an acetone solution of $[(\text{CH}_3)_4\text{N}]_3[\text{Pt}(\text{SnCl}_3)_5]^{-3}$ (prepared in the same manner as has been described¹ for the corresponding triphenylmethylphosphonium salt) with hydrogen at 30° and 500 atm. pressure gives brownish yellow, crystalline $[(\text{CH}_3)_4\text{N}]_3[\text{HPt}(\text{SnCl}_3)_4]$, $\nu_{\text{Pt-H}}$ 2072 (s) and 2052 (sh) cm.⁻¹. Although high pressure was employed for preparative purposes, the formation of the hydride is readily followed spectroscopically at 25° and 3 atm., conditions under which the platinum-tin complexes were observed to promote the homogeneous hydrogenation of olefins.

A methanol solution of $[(\text{C}_2\text{H}_5)_3\text{P}]_2\text{PtCl}_2$ containing 2 molar equiv. of stannous chloride rapidly absorbs 1 mole of hydrogen at 25° and 1 atm. Addition of tetraethylammonium chloride affords yellow crystals of $[(\text{C}_2\text{H}_5)_4\text{N}][\text{PtH}(\text{SnCl}_3)_2[(\text{C}_2\text{H}_5)_3\text{P}]_2]$, $\nu_{\text{Pt-H}}$ 2108 cm.⁻¹. The same compound is obtained more conveniently by addition of $(\text{C}_2\text{H}_5)_4\text{NSnCl}_3$ to a methanol solution of $[(\text{C}_2\text{H}_5)_3\text{P}]_2\text{PtH}(\text{SnCl}_3)$.⁵

Further studies are in progress on the properties of the SnCl_3^- ligand and the role of the five-coordinate hydrides in homogeneous hydrogenations.

(3) Satisfactory analytical data have been obtained for all new compounds described herein.

(4) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 5075 (1962).

(5) R. V. Lindsey, Jr., G. W. Parshall, and U. G. Stolberg, *J. Am. Chem. Soc.*, **87**, 658 (1965).

R. D. Cramer, R. V. Lindsey, Jr.
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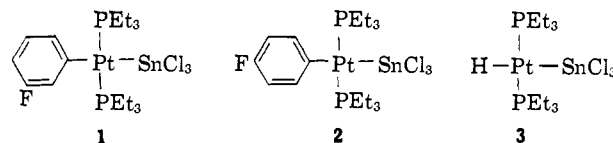
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SnCl_3^- . A Strongly *trans*-Activating Ligand

Sir:

In the preceding communication,¹ we described novel five-coordinated platinum(II) complexes containing SnCl_3^- groups bonded to platinum through tin. The unusual ability of SnCl_3^- to stabilize five-coordinate platinum has prompted us to characterize this ligand more fully, particularly with respect to its electronic properties. For this purpose, we have carried out spectroscopic studies on the new complexes 1-3.



Previous studies in this laboratory² have shown that the F^{19} n.m.r. shielding parameters of fluorophenylplatinum complexes are sensitive criteria of the σ -donor and π -acceptor properties of the ligand *trans* to the phenyl group. The F^{19} n.m.r. absorption peaks of 1 and 2 were found at -0.23 and $+6.96$ p.p.m., respectively, relative to fluorobenzene in dilute solutions in acetone. The negative shielding parameter of 1 characterizes SnCl_3^- as a weak σ -donor, and the difference

(1) R. D. Cramer, R. V. Lindsey, Jr., C. T. Prewitt, and U. G. Stolberg, *J. Am. Chem. Soc.*, **87**, 658 (1965).

(2) G. W. Parshall, *ibid.*, **86**, 5367 (1964).

Table I

Spectrum	Cl	Br	I	NCS	SnCl ₃	CN
N.m.r., $\delta_{\text{Pt-H}}(\tau)$	26.9	25.6	22.7	23.2	19.2	17.8
Infrared, $\nu_{\text{Pt-H}}(\text{cm.}^{-1})$	2183	2178	2156	2112	2105	2041

between the two parameters (7.19 p.p.m.) suggests that it is a strong π -acceptor.

As a result of this combination of properties, five SnCl₃⁻ ligands may be coordinated about platinum to give [Pt(SnCl₃)₅]⁻³ without excessive buildup of electron density on the central metal atom. In addition, the formation of π -bonds from the filled 5p- and d-orbitals of the platinum to the vacant 5d-orbitals of the tin atoms would be expected to stabilize the trigonal bipyramidal configuration,³ as has now been established for [Pt(SnCl₃)₅]⁻³.

These same electronic properties are characteristic of such strongly *trans*-activating ligands as carbon monoxide. Accordingly, we have also examined the *trans* effect of the SnCl₃⁻ ligand by criteria expounded by Chatt and co-workers.^{4a,b} These investigators showed that the *trans* series, obtained by ranking ligands (X) in terms of their ability to shift the Pt-H infrared stretching frequency and H¹ n.m.r. frequency in *trans*-[(C₂H₅)₃P]₂PtHX compounds, conforms closely to that established earlier by ligand-exchange reactions.⁵

By similar examination of 3, we now place the SnCl₃⁻ anion between NCS⁻ and CN⁻, the two most powerful ligands in the Chatt series, as shown in Table I (all values from ref. 4 except those for SnCl₃⁻).

This strong *trans*-activation undoubtedly plays an important role in the catalytic activity⁶ and facile ligand-exchange reactions⁷ observed for platinum metal-tin chloride complexes.

trans-Hydrido(trichlorotin)bis(triethylphosphine)-platinum(II) was prepared by reaction of equimolar quantities of *trans*-[(C₂H₅)₃P]₂PtHCl and SnCl₂·2H₂O in concentrated methanolic solution at 25°. White needles precipitated which, after recrystallization from methanol, melted at 100–101°. *Anal.* Calcd.: C, 21.91; H, 4.75; Pt, 29.7; Sn, 18.1. Found: C, 21.86; H, 4.70; Pt, 29.8; Sn, 17.8. The proton magnetic resonance spectrum of the ethyl groups showed equivalent coupling of the CH₃ protons to the two P³¹ nuclei in the complex, a condition characteristic of the *trans* configuration.⁸ The methyl resonance appeared as a five-line pattern ($J_{\text{P}_2\text{-CH}_3} = 16$ c.p.s., $J_{\text{CH}_2\text{-CH}_3} = 7.8 \pm 0.2$ c.p.s.) which was partially collapsed to a 1:2:1 triplet by irradiation of the methylene signal.

The *m*- and *p*-fluorophenylplatinum complexes 1 and 2 were prepared similarly by treatment of the corresponding chloro compounds, FC₆H₄Pt(PEt₃)₂Cl, with stannous chloride in acetone. The presence of a coordinated SnCl₃⁻ group in complexes 1–3 was con-

(3) R. J. Gillespie, *J. Chem. Soc.*, 4672 (1963).

(4) (a) J. Chatt, L. A. Duncanson, and B. L. Shaw, *Chem. Ind. (London)*, 859 (1958); (b) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 5075 (1962).

(5) F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, 4, 381 (1962).

(6) R. D. Cramer, E. L. Jenner, R. V. Lindsey, Jr., and U. G. Stolberg, *J. Am. Chem. Soc.*, 85, 1691 (1963).

(7) A. G. Davies, G. Wilkinson, and J. F. Young, *ibid.*, 85, 1692 (1963).

(8) J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, 279 (1963).

firmed by the presence of a doublet infrared vibration at 330 cm.⁻¹ assignable to Sn-Cl stretching. This absorption seems to be typical of complexes bearing the SnCl₃⁻ ligand including [Pt(SnCl₃)₅]⁻³

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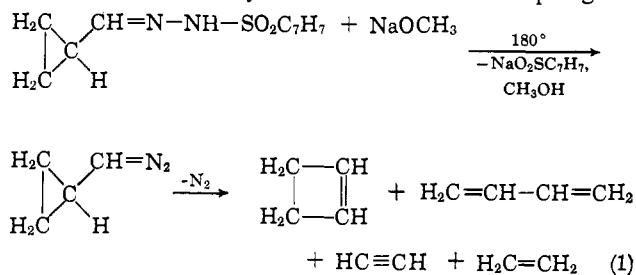
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Intramolecular Processes in Carbenic and Cationic Decomposition of Cyclopropanecarboxaldehyde *p*-Tosylhydrazone

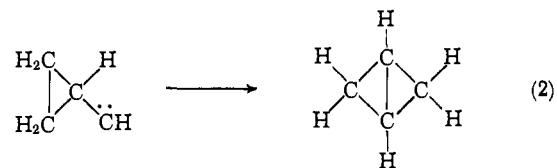
Sir:

Aldehyde and ketone *p*-tosylhydrazones react with bases in aprotic solvents at 90–180° to give diazo compounds which decompose by carbenic processes.^{1a,b} In proton-donor solvents decomposition of *p*-tosylhydrazones by bases occurs primarily by cationic mechanisms involving diazonium and/or carbonium ion intermediates.¹

Cyclopropanecarboxaldehyde *p*-tosylhydrazone (I) has been reported² to react with sodium methoxide in aprotic solvents to give (eq. 1) cyclobutene (60–67%) by ring expansion, 1,3-butadiene by reorganization, and ethylene and acetylene by fragmentation, along with unidentified hydrocarbons. In attempting to



prepare cyclobutene from I and sodium methoxide in Diethyl Carbitol or triglyme, Frey^{3a} informed us that the principal product (~80%) of their experiment was a hydrocarbon isomeric with cyclobutene and 1,3-butadiene. The hydrocarbon was subsequently identified^{3b} as bicyclo[1.1.0]butane, and it was suggested^{2b} that this product is formed (eq. 2) by intramolecular insertion of cyclopropylcarbene into one of its four equivalent secondary carbon-hydrogen bonds. We



wish to report our additional studies on base-catalyzed decomposition of I and emphasize the importance of experimental conditions on the paths and the apparent carbenic and cationic mechanisms of reaction of this system.

The effects of the number of equivalents of sodium methoxide and of the proton-donor capacity of sol-

(1) (a) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, 81, 5512 (1959); (b) J. W. Powell and M. C. Whiting, *Tetrahedron*, 7, 305 (1959).

(2) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, 82, 1002 (1960).

(3) (a) H. M. Frey, private communication, Sept. 30, 1963; (b) H. M. Frey and I. D. R. Stevens, *Proc. Chem. Soc.*, 144 (1964).