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 perfluorodiazo compounds will appear in future publications.

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Five-Coordinate Platinum(II) Complexes

Sir:

Determination of the configuration of the $[Pt(SnCl_3)_5]^{-3}$ 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-diphenylarsinophenyl)arsine.[1]

Crystals used in the collection of diffraction intensities were of composition $[(C_6H_5)_3PCH_3]_3[Pt(SnCl_3)_5]^2$ with the triclinic cell dimensions $a = 23.63 \pm 0.05$, $b = 20.90 \pm 0.05$, $c = 15.65 \pm 0.04$ Å., $\alpha = 90°$, $\beta = 101.5 \pm 0.2°$, $\gamma = 90°$ ($\rho_c = 1.88$, $\rho_o = 1.87$ g./cm.^{3}). Although the cell could have been based on space group $P\bar{1}$, it was more convenient to use the above cell with space group orientation $C\bar{1}$ and containing four molecules per cell.

Approximately 2500 diffraction intensities were collected with a Weissenberg counter diffractometer using Cu Kα 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 $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.25$. 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, $[HPt(SnCl_3)_4]^{-3}$ and $\{HPt(SnCl_3)_2[(C_2H_5)_3P]_2\}^-$, have also been prepared. Based on their composition and properties, and knowledge of the structure of $[Pt(SnCl_3)_5]^{-3}$,

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 $[(CH_3)_4N]_3$-$[Pt(SnCl_3)_5]^3$ (prepared in the same manner as has been described[1] for the corresponding triphenylmethylphosphonium salt) with hydrogen at 30° and 500 atm. pressure gives brownish yellow, crystalline $[(CH_3)_4$-$N]_3[HPt(SnCl_3)_4]$, ν_{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 $[(C_2H_5)_3P]_2PtCl_2$[4] 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 $[(C_2H_5)_4N][PtH(SnCl_3)_2[(C_2H_5)_3P]_2]$, ν_{Pt-H} 2108 cm.$^{-1}$. The same compound is obtained more conveniently by addition of $(C_2H_5)_4NSnCl_3$ to a methanol solution of $[(C_2H_5)_3P]_2PtH(SnCl_3)$.[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).

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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**.
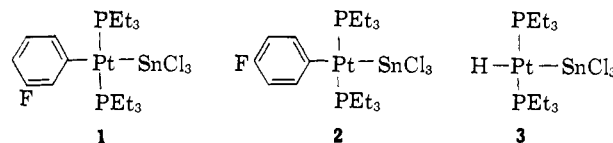
Previous studies in this laboratory[2] have shown that the F^{19} n.m.r. shielding parameters of fluorophenylplatinum complexes are sensitive criteria of the σ-donor and π-acceptor properties of the ligand *trans* to the phenyl group. The F^{19} n.m.r. absorption peaks of **1** and **2** were found at −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) 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).

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