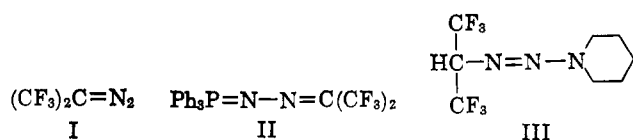


Bis(trifluoromethyl)diazomethane. Evidence for a Novel Radical Chain Reaction

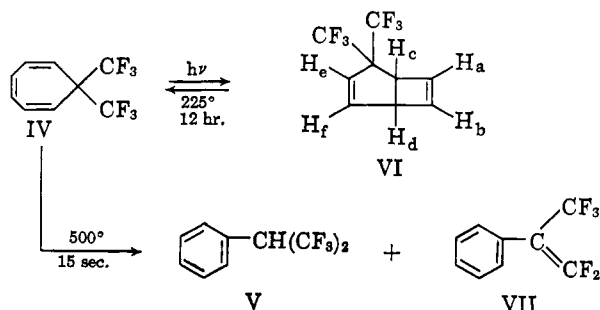
Sir:

We wish to report the synthesis of the first example of a perfluorinated diazo compound,^{1,2} bis(trifluoromethyl)diazomethane (I), by lead tetraacetate oxidation of the corresponding hydrazone³ in benzonitrile. The pale yellow diazo compound, b.p. 12–13°, was characterized by a band at 2240 cm.⁻¹ in its infrared spectrum, by a sharp singlet at +60.3 p.p.m. from FCCl₃ in its F¹⁹ n.m.r. spectrum, and by analysis. *Anal.* Calcd. for C₃F₆N₂: F, 64.02. Found: F, 63.88, 64.07.⁴ Compound I is neither impact nor static sensitive and is stable to long storage at -78°; however, I partly decomposes with loss of nitrogen after several weeks at room temperature. On pyrolysis of I at 150 or 200° over quartz in a helium atmosphere (0.5-min. contact time), hexafluoropropene and tetrakis(trifluoromethyl)ethylene were isolated as the major products. Further characterization was provided by the reaction of I with triphenylphosphine to form the phosphazine II (m.p. 137–138°) and with piperidine⁵ to give the triazene III (b.p. 66–68° (10 mm.); n_D²⁵ 1.3990). Unlike most diazo compounds, I is not sensitive to acids.



When compound I was heated at 200° for 8 hr. in an autoclave with excess benzene, 7,7-bis(trifluoromethyl)-1,3,5-cycloheptatriene (IV, 88%; b.p. 141°; λ_{max} 276 mμ (ε 3200), Raman bands at 3050, 1620, and 1565 cm.⁻¹; see Table I) and hexafluoroisopropylbenzene⁵ (V, 12%) were isolated in 70% combined yield. This reaction is believed to be the first addition of a perfluorocarbene [:C(CF₃)₂] to an aromatic system.

Photolysis of I (5.6 g.) for 40 hr. with a G.E. H85A3 lamp through Pyrex glass in 40 ml. of dry benzene gave 2 g. of product which, after gas chromatographic purification, was shown to contain 40% IV, 5% V,



(1) See, however, S. P. Makanov, A. J. Yakubovich, *et al.*, *Dokl. Akad. Nauk SSSR*, **141**, 357 (1961). This paper claims the preparation of Ph₃P=CF₂ by the reaction of Ph₃P with CF₃NO and NH₃. Difluorodiazomethane, CF₂N₂, is postulated as an intermediate.

(2) Syntheses of partly fluorinated diazo compounds have been reported: (a) H. Gilman and R. G. Jones, *J. Am. Chem. Soc.*, **65**, 1458 (1943); (b) R. Fields and R. N. Haszeldine, *J. Chem. Soc.*, 1881 (1964); (c) F. Weygand, H. Dworschak, K. Koch, and St. Konstas, *Angew. Chem.*, **73**, 409 (1961).

(3) W. J. Middleton and C. G. Krespan, Abstracts, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964, p. 24K.

(4) All new compounds reported here gave satisfactory analyses.

(5) W. A. Sheppard, private communication.

Table I. Nuclear Magnetic Resonance Data for (CF₃)₂C=N₂ Reaction Products

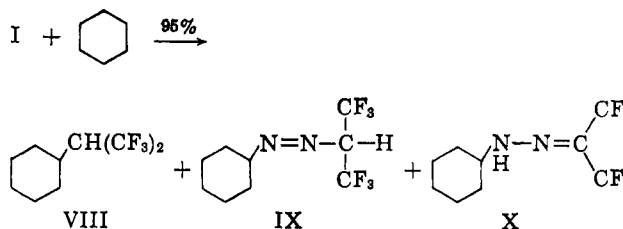
Compound	F ^{19a}	H ^{1b}
IV	Singlet, 4.42 at ca. ^c -120° to 140°	Mult. (4 H), 3.6; mult. (2 H), 4.6
VI	Pair of quartets (<i>J</i> = 9.5), 5.96, 1.5; low-field quartet split further	3.58 (H _a), 3.95 (H _b), 6.12 (H _c), 6.27 (H _d), 3.58 (H _e), 4.48 (H _f); <i>J</i> _{ab} = 2.5, <i>J</i> _{ef} = 6.0; all other <i>J</i> ≈ 0 (spin-spin decoupling employed) ^d
VIII	Doublet (<i>J</i> = 9), -3.31	Septet (<i>J</i> = 9) (1 H), 7.28 (split further into doublets, <i>J</i> = 2); mult. (11 H), 8-9
IX	Doublet (<i>J</i> = 7), 3.98	Septet (<i>J</i> = 7), 5.75 (1 H); broad (1 H), 6.35; mult. (10 H), 8-8.8.
X	Pair of quartets (<i>J</i> = 6), 0.177, 0.976, low-field further split	Mult. (1 H), 2.86; broad (1 H), 6.65; mult. (10 H), 8-9.

^a P.p.m. from external CFCl₂CFCl₂ in CCl₄. ^b τ (in CCl₄). ^c Freezing point of ether solution to boiling point neat. ^d Suggested assignments.

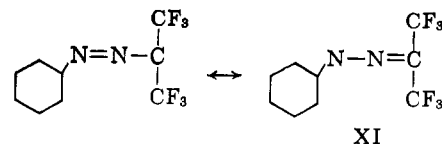
and 55% of a photodiene, b.p. 139° (no ε >35 ultraviolet; infrared bands at 1565 and 1618 cm.⁻¹ for cyclobutene and cyclopentene, respectively), assigned bicyclic structure VI on the basis of analysis and spectral data (Table I).

The benzene adducts IV and VI were shown to be interconvertible and to undergo pyrolytic rearrangement to the benzene derivatives V and VII.⁶

A unique reaction was observed when compound I was heated with excess cyclohexane at 150° for 8 hr. In addition to the carbene insertion product VIII, hexafluoroisopropylcyclohexane, b.p. 72° (72 mm.) (12%), the major products IX (52%), b.p. 79° (50 mm.), -N=N- at 1570 cm.⁻¹ and no -NH in infrared, and X (36%), b.p. 104° (50 mm.), -NH at 3450 cm.⁻¹ and -N=C at 1600 cm.⁻¹ in infrared, had *retained nitrogen*.



Anal. Calcd. for C₉H₁₂F₆N₂: N, 10.68. Found for IX: N, 10.78, 10.84. Found for X: N, 10.88. (See Table I for n.m.r. data.) These products can best be explained by the assumption that in favorable competition with the carbene insertion into cyclohexane, there is a radical chain reaction proceeding through the resonance-stabilized radical XI (formed from the



(6) W. A. Sheppard has demonstrated the conversion of V to VII on pyrolysis.

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.

David M. Gale, William J. Middleton, Carl G. Krespan

Contribution No. 1036, Central Research Department
E. I. du Pont de Nemours and Co., Wilmington 99, Delaware

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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*-diphenylarsinophenyl)arsine.¹

Crystals used in the collection of diffraction intensities were of composition $[(\text{C}_6\text{H}_5)_3\text{PCH}_3]_3[\text{Pt}(\text{SnCl}_3)_5]^{-3}$ 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 $[(\text{CH}_3)_4\text{N}][\text{HPt}(\text{SnCl}_3)_4]$, $\nu_{\text{Pt-H}}$ 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 $[(\text{C}_2\text{H}_5)_3\text{P}]_2\text{PtCl}_2$ 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 $[(\text{C}_2\text{H}_5)_4\text{N}][\text{PtH}(\text{SnCl}_3)_2[(\text{C}_2\text{H}_5)_3\text{P}]_2]$, $\nu_{\text{Pt-H}}$ 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.
C. T. Prewitt, U. G. Stolberg

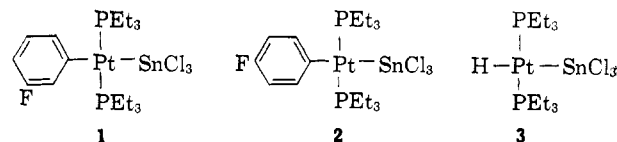
Contribution No. 1037, Central Research Department
Experimental Station, E. I. du Pont de Nemours and Company
Wilmington, Delaware

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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).