

Figure 1. The asymmetric unit (two formula units of $[(C_2H_5)_4N^+]_3 \cdot [B_9C_2H_{11} \cdot Co \cdot B_8C_2H_{10} \cdot Co \cdot B_8C_2H_{10} \cdot Co \cdot B_9C_2H_{11}]^{3-}$) projected on (100). Cobalt and nitrogen atoms are in black; carbon atoms of the carborane systems are shaded.

86.70, $\gamma = 102.98^\circ$.³ The observed density, $\rho_{\text{obsd}} = 1.19 \pm 0.01 \text{ g cm}^{-3}$ (by flotation in aqueous zinc iodide solution), is consistent with that calculated for $M = 1073.72$ and $Z = 4$ ($\rho_{\text{calcd}} = 1.194 \text{ g cm}^{-3}$).

While good-sized crystals could easily be obtained, optical examination showed many to be hollow; all crystals examined gave unusually weak diffraction patterns. X-Ray data complete to $\sin \theta = 0.63$ (Cu $K\alpha$ radiation)⁴ were collected with a 0.01 incrementing Super-Pace Buerger Automated Diffractometer using a stationary-background, ω -scan, stationary-background counting sequence. All data were corrected for absorption ($\mu = 64.46 \text{ cm}^{-1}$) and the structure was solved, with considerable difficulty, by a combination of Patterson, Fourier, and least-squares refinement techniques. The asymmetric unit consists of two well-defined $[B_9C_2H_{11} \cdot Co \cdot B_8C_2H_{10} \cdot Co \cdot B_8C_2H_{10} \cdot Co \cdot B_9C_2H_{11}]^{3-}$ anions and six poorly defined $[(C_2H_5)_4N^+]$ cations. The present discrepancy index, after several cycles of positional and isotropic thermal parameter refinement for the 144 independent nonhydrogen atoms, is $R_F = 14.1\%$ for 3994 independent nonzero reflections. Refinement is continuing. The crystallographic asymmetric unit is shown in Figure 1. (Carbon atoms of the icosahedral cages are identified by the following properties: (i) on electron density maps they appear as larger peaks than do the boron atoms; (ii) when all light atoms of the icosahedral cages are specified as boron atoms, refinement leads to negative isotropic thermal parameters for the carbon atoms; (iii) interatomic C-C and C-B distances are significantly shorter than B-B distances.)

(3) We have recently discovered a monoclinic modification, space group $P2_1/c$, with $a = 19.998$, $b = 14.110$, $c = 21.369 \text{ \AA}$, $\beta = 101.52^\circ$, $Z = 4$. Crystallographic studies on this polymorph are presently in progress.

(4) The use of copper radiation was necessary in order to resolve adjacent reflections and to obtain diffraction data of reasonable intensity.

The two crystallographically independent $[B_9C_2H_{11} \cdot Co \cdot B_8C_2H_{10} \cdot Co \cdot B_8C_2H_{10} \cdot Co \cdot B_9C_2H_{11}]^{3-}$ ions show essentially identical features. The terminal formal cobalt(III) ions are each linked to a C_2B_3 face of a $B_9C_2H_{11}^{2-}$ ligand and to a C_2B_3 face of a $B_8C_2H_{10}^{4-}$ ligand; the central cobalt(III) ion is bonded to C_2B_3 faces of two $B_8C_2H_{10}^{4-}$ ligands. Average dimensions within the anions are (in \AA): $Co \cdots Co = 3.80$, $Co-C = 2.05$, $Co-B = 2.14$, $C-C = 1.60$, $C-B = 1.75$, and $B-B = 1.83$.

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Vapor Phase Fluorination with Xenon Difluoride. Facile Substitution of Fluorine into Aromatic Compounds¹

Sir:

We wish to report that XeF_2 is an efficient and well-behaved fluorinating agent for aromatic compounds in the vapor phase. In particular we have shown that it causes facile substitution of fluorine into such molecules as benzene, nitrobenzene, and substituted fluorobenzenes.

Specific instances of fluorination by XeF_2 have already been reported from this and other laboratories.^{2,3} Shieh, Yang, and Chernick^{2a} studied the addition reactions of xenon fluorides with several olefins, e.g., XeF_4 with perfluoropropylene and XeF_2 and XeF_4 with ethylene and propylene. Recently Hyman, *et al.*, used XeF_2 to carry out substitution of benzene neat and in CCl_4 solution,^{2b} and toluene, fluorobenzene, and benzo-trifluoride in CCl_4 solution.^{2c}

Our previous work³ showed that a very smooth and efficient addition of two fluorine atoms occurred when XeF_2 vapor was heated at $100-200^\circ$ with octafluoronaphthalene or hexafluorobenzene vapor. Similar results were subsequently obtained with decafluorobiphenyl, so this vapor phase addition reaction is presumably general for perfluoroaromatics. We have since addressed ourselves to the possibility, suggested by the work of Hyman, *et al.*,^{2b,c} that fluorine substitution of aromatic hydrocarbons might be general with the use of XeF_2 under appropriate conditions, such as vapor phase and moderate temperature. The compounds we have used are benzene, nitrobenzene, *o*-

(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

(2) (a) T. Shieh, N. C. Yang, and C. L. Chernick, *J. Amer. Chem. Soc.*, **86**, 5021 (1964); (b) M. J. Shaw, H. H. Hyman, and R. Filler, *ibid.*, **91**, 1563 (1969); (c) M. J. Shaw, J. A. Weil, and H. H. Hyman, Paper FLUO-2, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969.

(3) Annual Report, Nuclear Engineering Department, Brookhaven National Laboratory, BNL 50082 (S-70), Dec 31, 1967, p 33.

Table I. Results of Fluorination Experiments with C₆H₆

Mol ratio, XeF ₂ /C ₆ H ₆	Temp, °C	Ratio, substn/addn	Ratio, substn/polymerization	Distribn of substn products
0.21	145	>>110	2.1	Mono-F/di-F = 18, tri-F insignificant C ₆ H ₄ F ₂ , <i>p</i> : <i>o</i> = 6.5
2.2	165	6.6	0.7	Mono:di:tri = 6.1:6.3:1.0 ^a C ₆ H ₄ F ₂ , <i>p</i> : <i>m</i> : <i>o</i> = 14.5:1.8:1.0 ^b

^a C₆H₃F₃ estimate based on ir because of complete overlap of glc peaks. ^b *m*-C₆H₄F₂ estimate based on ir because of complete overlap of glc peaks.

Table II. Results of Fluorination Experiments With Substituted Benzenes

Starting compd	Mol ratio, XeF ₂ /starting compd	Temp, °C	Substn products	Distribn of substn products	Ratio, substn ^a /addn
C ₆ H ₅ NO ₂	0.29	120	<i>o</i> -, <i>m</i> -, and <i>p</i> -	<i>p</i> : <i>m</i> : <i>o</i> = 1:8.0:1.8	>>100
	0.95	167	C ₆ H ₄ FNO ₂	<i>p</i> : <i>m</i> : <i>o</i> = 1.5:8.2:1	16.5
<i>p</i> -C ₆ H ₄ F ₂	0.60	100	1,2,4-C ₆ H ₃ F ₃ and 1,2,4,5-C ₆ H ₂ F ₄	Tri-F/tetra-F ~ 8 ^b	0.3 ^b
	4.2	166	1,2,4-C ₆ H ₃ F ₃ and 1,2,4,5-C ₆ H ₂ F ₄	<i>c</i>	≲0.1 ^c
<i>o</i> -C ₆ H ₄ F ₂	0.56	100	1,2,4-C ₆ H ₃ F ₃ and 1,2,4,5-C ₆ H ₂ F ₄	Tri-F/tetra-F = 42	33
1,2,4,5-C ₆ H ₂ F ₄	0.27	100	None detected		
	4.8	164			
C ₆ HF ₅	0.40	100	C ₆ F ₆		0.06

^a Determined by glc, taking the sensitivities of addition products to be the same as those of substitution products. ^b C₆H₃F₃ estimate based on ir because of complete overlap of glc peaks. ^c Amount of C₆H₃F₃ not determined. Addition products predominated over tetra-F.

and *p*-difluorobenzene, 1,2,4,5-tetrafluorobenzene, and pentafluorobenzene.

XeF₂ was prepared by exposing xenon-fluorine mixtures to sunlight in a Pyrex bulb in the manner of Streng and Streng^{4a} as given by Williamson.^{4b} It was stored in evacuated Monel U-tubes. The organic compounds were obtained commercially and were pure enough (≥98% apparent purity by glc) to be used as received. Reagents were transferred using a metal vacuum system and reactions were carried out in prefluorinated nickel or Monel containers. Temperatures were in the range 100–200° to ensure that reactants were in the vapor phase. Typically 1–2 mmol of organic and a similar amount of XeF₂ were allowed to react overnight in a vessel of 150-cc volume. After the reaction period, the vessel was cooled to –78° and HF and xenon pumped off.⁵ The organic products were transferred under vacuum to a glass container and processed by glc. Fractions were collected for purification of individual compounds using other glc columns as required. Subsequent identification was made by ir and mass spectrometry.

The relative distribution of products was easily maintained by controlling the temperature and ratio of reactants. Representative results are summarized in Tables I and II. By addition products is meant any compounds with more than six substituents on the ring. They were generally not characterized because we wished only to know definitely that they were addition products. This was readily ascertained by their glc retention times which were much shorter than those of any substitution products. Dimers and higher polymers constituted a brown tarry residue, which was investigated only in several experiments with C₆H₆.

(4) (a) L. V. Streng and A. B. Streng, *Inorg. Chem.*, **4**, 1370 (1965); (b) S. M. Williamson, *Inorg. Syn.*, **11**, 147 (1968).

(5) Xenon can be recovered from the HF–Xe mixture by trapping the HF cryogenically, using a suitable hydrocarbon slush (*e.g.*, isooctane or methylcyclohexane), or chemically, in a soda-lime or NaF scrubber.

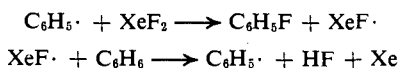
In fluorination of the latter (Table I), substitution predominated over all other types of reaction, particularly when it is considered that some of the addition products and polymeric products were partially substituted. This was especially true at low XeF₂:C₆H₆ mole ratios where formation of addition products was negligible. As the XeF₂:C₆H₆ ratio increased, both addition and multiple substitution increased with respect to monosubstitution, though overall substitution still predominated over addition at a XeF₂:C₆H₆ mole ratio of 2.2.

Comparison with the reaction in CCl₄ solution^{2b} is instructive. The latter in an experiment with the mole ratio XeF₂:C₆H₆ = 0.27 gave no detectable addition products or C₆H₄F₂, and a ratio of substitution to polymerization of 0.8. Our experiment with XeF₂:C₆H₆ = 0.21 (Table I) yielded essentially no addition products, appreciable amounts of difluorobenzenes, and a ratio of substitution to polymerization of 2.1. Under these particular conditions then, substitution in the vapor phase is more efficient (with respect to other processes) and proceeds to a higher degree.

Difluorobenzenes were readily substituted to the tetrafluoro stage (Table II) but 1,2,4,5-C₆H₂F₄ yielded no C₆HF₅ (or C₆F₆). C₆HF₅ was fluorinated to C₆F₆, but in a yield much lower than that of addition products. The ease of substitution was greatly decreased when the aromatic ring was already highly substituted with fluorine. In fact even at the difluoro stage, *p*-C₆H₄F₂ showed somewhat more addition than substitution. To fully substitute benzene by this method, then, may be possible but will presumably be inefficient.

Hyman, *et al.*,^{2b,c} provide good evidence that substitution in the liquid phase proceeds *via* cation radicals and requires HF as a catalyst. In the vapor phase, it seems likely that the mechanism is free radical. Our XeF₂ was undoubtedly contaminated with a small amount of HF but we did no experiments to determine

whether HF has any significant effect on the reaction. At the temperatures used, a significant amount of F₂ and Xe is in equilibrium with XeF₂. Thus elemental fluorine, as well as XeF₂, is available to initiate reaction. Once phenyl radicals are formed, a sequence such as



would be expected to operate. With nitrobenzene, meta orientation by the NO₂ group is observed as expected. In the case of a fluorine atom on the ring, para orientation is favored and there appears to be as much of an inhibiting effect for ortho as for meta substitution.

It is concluded that vapor-phase reaction with XeF₂ leads to facile, easily controlled substitution of aromatic compounds. The method appears to be general and may offer some advantages in ease of handling over reaction in solution. The main limitation is the low volatility of the higher aromatics, and for these substances reaction in inert solvent will be preferable. However, vapor phase reaction will still be feasible for compounds like naphthalene and biphenyl at temperatures below 200°.⁶

Acknowledgment. We are indebted to Mr. R. Smol for expert technical assistance.

(6) For example, the vapor pressure of biphenyl is 100 mm at 180° and that of naphthalene is nearly 300 mm. Nitrobenzene (bp 211°) was successfully substituted at 120° where its vapor pressure is only 50 mm.

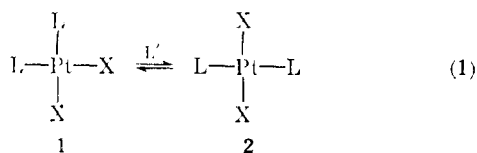
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Ligand-Complex Interaction in Tetragonal Planar Complexes and the Mechanism of Catalyzed Isomerization¹

Sir:

Associative interactions appear to be very important in the chemistry of tetragonal planar complexes.² Both substitution reactions and homogeneous catalysis can be understood in terms of associative mechanisms. Through study of isomerization of platinum(II) complexes (eq 1), we have obtained considerable insight into the nature of association in tetragonal planar complexes. The results are also of importance to the problem of fluxional changes in structure of coordination compounds.



When *cis*-bis(trialkylphosphine)dichloroplatinum(II) (1: X = Cl, L = R₃P) complexes are mixed in cyclohexane with a catalytic amount of phosphine (L'), the rate of isomerization can be measured spectro-

(1) Research supported by Grant No. GP-13453 from the National Science Foundation.

(2) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 1st ed, Wiley, New York, N. Y., 1957; 2nd ed, 1967; C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1966.

photometrically.³ When L' = L or L' ≠ L, well-behaved, first-order rates are observed and each system has a unique second-order rate constant evaluated from first-order rate constants over a range of [L']. For example, at 30°, when L = L' = (n-C₃H₇)₃P, k₂ = 2.60 × 10² M⁻¹ sec⁻¹, but when L = (n-C₃H₇)₃P and L' = (n-C₄H₉)₃P, k₂ = 4.50 × 10² M⁻¹ sec⁻¹. Or, when L = L' = (n-C₄H₉)₃P, k₂ = 4.50 × 10² M⁻¹ sec⁻¹; but when L = (n-C₄H₉)₃P and L' = n-C₄H₉P-(C₆H₅)₂, k₂ = 1.84 × 10² M⁻¹ sec⁻¹.⁴ Since the total amount of L is greater by at least a factor of 20 than L', exchange of L and L' would lead to either: (1) curved plots if the rate of exchange were comparable to the rate of isomerization, or (2) nearly identical rates in the two sets quoted above if exchange were rapid compared to isomerization. Consequently, *isomerization must proceed much faster than exchange; the phosphines do not mix during isomerization.*

The mechanisms proposed previously for isomerization will not accommodate this discovery. The double displacement mechanism⁵ (L' displacing X followed by X displacing L) must lead to exchange at every isomerization. Pseudorotation³ through trigonal-bipyramidal associated states must involve identity of L and L' at some point.

We conclude that association⁶ of L' and 1 must result in a distorted pentacoordinate state in which L' occupies a unique position. This distorted state must be able to undergo fluxional change which interconverts the positions of L and X and, therefore, enables isomerization of 1 into 2. Attractive models may be found in the recent determinations of the structure of pentacoordinate complexes with d⁸ electronic configurations.⁸ An interesting trend has emerged in the form of frequent deviations from regular pentacoordinate geometry so that it is often impossible to classify the structure as either trigonal bipyramidal or tetragonal pyramidal. During association and the fluxional change causing isomerization, L' must retain its identity—perhaps due to a long Pt-L' bond, as in the complex studied by Meek and Ibers,^{8c} or in Ni(PR₃)₃(CN)₂,^{8c} where one phosphine is unique and has a long Ni-P bond.

The activation enthalpy for isomerization is low, only 3 kcal/mol,³ and it is considerably higher in displacement reactions.⁹ The activation entropy is similar for substitution and isomerization and indicates the importance of association.^{2,3} Therefore, isomerization appears to be a low energy process proceeding through a distorted pentacoordinate state. Since some barrier to fluxional change would be expected, the pentacoordinate state may be similar in geometry to that

(3) P. Haake and R. M. Pfeiffer, *Chem. Commun.*, 1330 (1969); for spectra, see P. Haake and T. A. Hylton, *J. Amer. Chem. Soc.*, **84**, 3774 (1962).

(4) There are many more results of this kind; these are two of the most striking.

(5) Discussed in ref 2 and in L. Cattalini and M. Martelli, *J. Amer. Chem. Soc.*, **90**, 4272 (1968).

(6) We have observed kinetic evidence for association with L' = tricyclohexylphosphine; the observations are similar to those reported in a displacement reaction.⁷

(7) P. Haake, *Proc. Chem. Soc. London*, 278 (1962).

(8) Among the recent reports are: (a) F. K. Ross and G. Stucky, *Inorg. Chem.*, **8**, 2734 (1969); (b) L. P. Haugen and R. Eisenberg, *ibid.*, **8**, 1072 (1969); (c) J. K. Stalick and J. A. Ibers, *ibid.*, **8**, 1084, 1090 (1969); (d) M. DiVaira and P. O. Orioli, *ibid.*, **8**, 2729 (1969); (e) D. W. Meek and J. A. Ibers, *ibid.*, **8**, 1915 (1969).

(9) Reference 2 and G. Carturan and D. S. Martin, *ibid.*, **9**, 261 (1970).