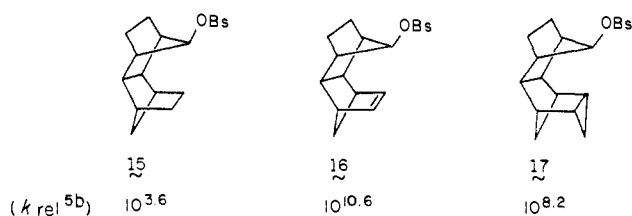


make at this time. We note, however, that **7**, **8**, and **9** share the common feature of slightly enhanced (two- to fivefold) reactivity over the group consisting of **1**–**ODNB**, **10**, and **11**. In every case, the additional bicyclic moiety is endo fused (at C₄,C₅) to the 7-substituted norbornenyl framework, but methano bridging as in the latter series increases the angle separating the remaining two-carbon bridges in this appendage.¹¹ Diminution in intrabridge nonbonded interactions may possibly ensue.^{12,13}

Accordingly, the present situation differs in a significant way from the behavior of somewhat related doubly bridged laticyclic systems such as **15**–**17**^{14–16}

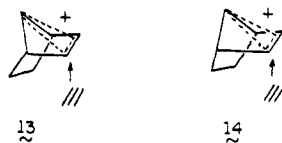


where remote stabilizing influences are convincingly manifested in kinetic acceleration. One is led to conclude that abrupt changes in electron-deficiency demand markedly affect the need for laticyclic interaction, so much so that the additional π bridge in cations possessing (2 + 2 + 0) topology contributes little to anchimeric assistance.¹⁷

(11) M. J. Goldstein, S. Natowsky, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, **56**, 294 (1973).

(12) Factors other than steric compression which may contribute to the enhanced rates of ionization include differences in the field and orbital electronegativity inductive effects for oxa, methylene, etheno, and ethano bridges and differences in the geometries of the 7-norbornenyl moieties in the more highly bridged systems.

(13) When apprised of our results, L. M. Loew and R. Hoffmann initiated an EH search of possible interactions which might arise upon approach of an acetylene molecule to the underside of "normal" and "bent" 7-norbornenyl cations as in **13** and **14**, respectively. Their



calculations have revealed that even at intra- π distances as small as 3 Å, no meaningful interaction is generated in either model (private communication).

(14) S. Winstein and R. L. Hansen, *J. Amer. Chem. Soc.*, **82**, 6206 (1960).

(15) S. Winstein and R. L. Hansen, *Tetrahedron Lett.*, **4** (1960).

(16) M. A. Battiste, J. Haywood-Farmer, H. Malkus, P. Seidl, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 2144 (1970).

(17) Research supported in part by grants from the National Science Foundation and Chevron Research Co. whom we thank.

Leo. A. Paquette,* Ian R. Dunkin

*Department of Chemistry, The Ohio State University
Columbus, Ohio 43210*

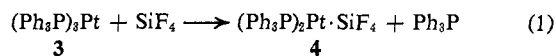
Received November 19, 1973

Some Chemistry of Silicon Tetrafluoride with Transition Complexes in Glass Vessels

Sir:

The close correspondence between the activation parameters for addition of triphenylphosphine and of silicon hydrides to the reactive intermediate hydrido-carbonylbis(triphenylphosphine)iridium(I) (**1**) led to the hypothesis that the primary interaction between the

addend and the Ir^I, on the approach to the transition state, was a π acceptance of electrons by the former from the latter.¹ An obvious test of the validity of this hypothesis would be the demonstration of coordinate bond formation between a π -acid possessing no lone pairs and a π -basic metal. To explore the possibility of such bond formation, a study of the reaction of SiF₄ with hydridocarbonyltris(triphenylphosphine)iridium(I) (**2**) was undertaken. Encouragement to continue this approach was provided by a report that SiF₄ formed a coordination complex with a bis(triphenylphosphine)platinum(0) moiety, by displacement of triphenylphosphine from tris(triphenylphosphine)platinum(0) (**3**) (eq 1).² Such a reaction would be



difficult to rationalize on grounds other than that Pt⁰ behaves more as a π -base than as a σ -acid.

Reaction of **2** with a slight excess of SiF₄ in benzene at room temperature gave a pale yellow, coarse crystalline precipitate, **5**, over a period of several hours. After recrystallization from benzene, **5** gave strong bands in the infrared at 875, 780, 477, and 445 cm⁻¹ (KBr disk), due to Si–F modes. The compound also gave a singlet at ϕ 136.4 due to ¹⁹F resonance, in methylene chloride solution. These physical parameters were indistinguishable from those reported for **4**.² They are also in accord with values reported for SiF₅⁻ salts.^{3–5} The similarity of the infrared spectrum of **5** in the $\nu_{\text{Ir-H}}$ (2100 s, 2140 sh cm⁻¹) and $\nu_{\text{C-O}}$ (2000 cm⁻¹) regions to the spectra of the dihydride resulting from addition of silicon hydrides to **2**⁶ was striking. The presence of the 1,2-dihydrido-3,4,5-tris(triphenylphosphine)carbonyl-iridium(III) cation (**6**) in **5** was confirmed by observation of its 60-MHz pmr spectrum at high field in methylene chloride [H(1), τ 20.5; H(2), τ 22.2; $J_{\text{H-H}} = 4$ Hz; $J_{\text{H1-P3,5}} = 20$ Hz; $J_{\text{H2-P4}} = 100$ Hz; $J_{\text{H1-P4}} = 20$ Hz].⁷ After establishment of the presence of the latter cation in **5**, it became virtually certain that the silicon was present as SiF₅⁻.

The compound **5** consistently gave a sharp resonance due to free benzene in its pmr spectrum. That this benzene was present as benzene of crystallization was suggested by the fact that the crystals melted sharply at 92°, resolidified, and decomposed without further melting at 170°. After melting, the crystals lost weight and the features in the infrared and pmr spectra due to benzene of crystallization disappeared. Chemical analysis, weight loss, and pmr integral measurements all suggested the presence of roughly three molecules of free benzene per iridium. Although **5** consistently gave good C, H, and P analyses for the pentafluorosilicate of **6**, the Si and F analyses were always poor.

Since no successful structure determination for SiF₅⁻

(1) J. F. Harrod, C. A. Smith, and Khin Aye Than, *J. Amer. Chem. Soc.*, **94**, 8321 (1972).

(2) T. R. Durkin and E. P. Schram, *Inorg. Chem.*, **11**, 1048 (1972).

(3) H. C. Clark, K. R. Dixon, and J. G. Nicolson, *Inorg. Chem.*, **8**, 450 (1969).

(4) I. Wharf and M. Onyszchuk, *Can. J. Chem.*, **48**, 2250 (1970).

(5) H. C. Clark, K. R. Dixon, and W. J. Jacobs, *J. Amer. Chem. Soc.*, **90**, 2259 (1968).

(6) J. F. Harrod, D. F. R. Gilson, and R. Charles, *Can. J. Chem.*, **47**, 2205 (1969).

(7) D. Commereuc, I. Douek, and G. Wilkinson, *J. Chem. Soc. A*, 1771 (1970); L. Malatesta, G. Caglio, and M. Angoletta, *J. Chem. Soc.*, 6974 (1965); L. Vaska, *Chem. Commun.*, 614 (1966); M. S. Fraser and W. H. Baddeley, *J. Organometal. Chem.*, **36**, 377 (1972).

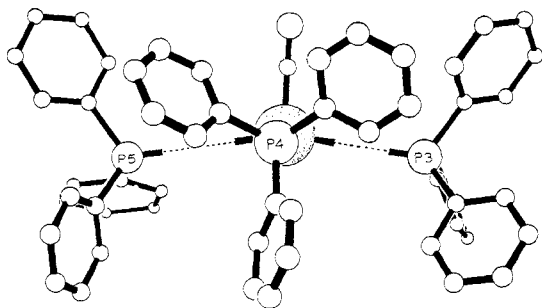


Figure 1. Molecular structure of $[\text{IrH}_2\text{CO}(\text{PPh}_3)_3]^+$.

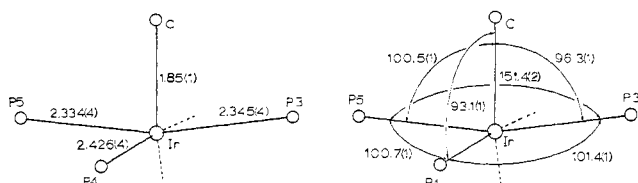


Figure 2. Bond lengths and angles for $[\text{IrH}_2\text{CO}(\text{PPh}_3)_3]^+$.

has appeared in the literature, a structure determination of **5** by X-ray diffraction was undertaken. In addition to providing confirmation of the structure of **5**, the successful solution of this problem has provided parameters for SiF_5^- , shown the crystal to contain 3.5 benzene molecules per formula unit, and revealed considerable distortions in the cation from ideal octahedral geometry.

The compound **5** crystallizes in space group $P\bar{1}$ (no. 2) with $a = 16.69$ (3), $b = 12.78$ (2), $c = 16.65$ (2) Å, $\alpha = 101.15$ (1)°, $\beta = 95.66$ (1)°, $\gamma = 101.60$ (1)°, $Z = 2$, and $V = 3378.7$ Å³. The observed and calculated densities are respectively 1.387 and 1.385 g cm⁻³. A hemisphere of data limited by a maximum 2θ of 35° was collected on a Picker-Nuclear FACS-1 diffractometer. Conventional heavy-atom methods for structure solution followed by full-matrix least-squares refinement, using 3855 observations, have reduced the R value to 5.8%. The phenyl rings have been refined as rigid groups with atoms having individual isotropic thermal parameters; the remaining nonhydrogen atoms have been refined anisotropically.

The cation, depicted in Figure 1, shows the predicted configuration. Selected bond lengths and angles are shown in Figure 2. The angles in particular show that the coordination sphere of the Ir does not have perfect mirror symmetry, possibly as a result of disymmetric steric interactions between triphenylphosphine groups. The chirality (right-handed screw on Figure 1) of the triphenylphosphine group associated with P4 will be transmitted to the other phosphines, P3 and P5, since the nine phenyl rings must mesh comfortably, thus rendering them inequivalent.

The SiF_5^- anion is depicted in Figure 3 with its various observed parameters. This ion is not significantly distorted from a trigonal bipyramid, and there is no discernible difference between axial and equatorial Si-F bond lengths. It should be noted that the anion, though not disordered as might have been expected, did show a very large apparent vibrational motion which limited the accuracy of the structure determination and led to the marked differences between the observed and corrected bond lengths. Predictably, the mean

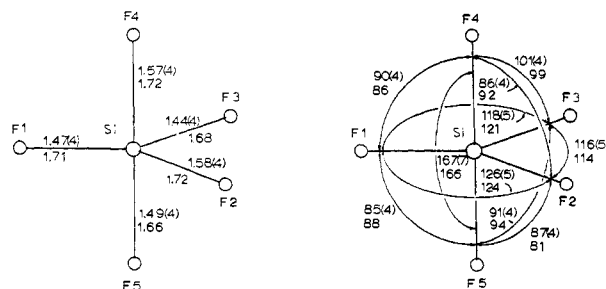


Figure 3. Bond lengths and angles for SiF_5^- . Upper figures are uncorrected for thermal motion. Lower figures have been corrected.

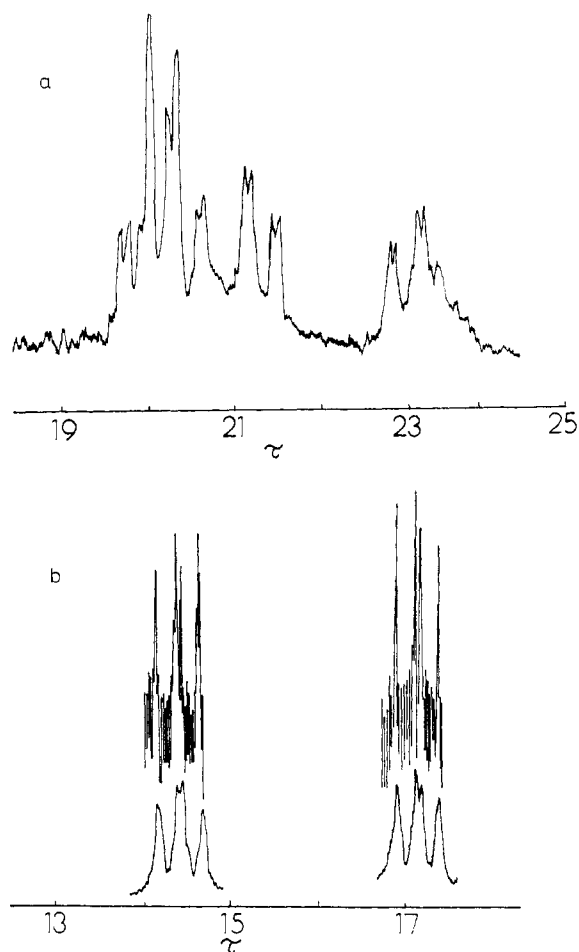


Figure 4. (a) The pmr spectrum of $[\text{IrH}_2\text{CO}(\text{PPh}_3)_3]\text{SiF}_5$. (b) The pmr spectrum of $[\text{PtH}(\text{PPh}_3)_3]\text{SiF}_5$. The resonance due to the ^{195}Pt isotope at τ 20.9 and 23.5 is not shown.

Si-F bond distance, 1.69 Å, lies between the values for SiF_4 (1.54) and SiF_6^{2-} (1.71),⁸ closer to the latter value.

The compound **5** may be alternatively synthesized rapidly and quantitatively by addition of concentrated aqueous HF to a stirred suspension of high surface area silica in a benzene-methanol solution of **2**. The same method, using **3** instead of **2**, yields hydridotris(triphenylphosphine)platinum(II) pentafluorosilicate (**7**) identical with the initial product **4** obtained on reaction of **3** with SiF_4 by the method of Durkin and Schram.² The rather weak $\nu_{\text{Pt-H}}$ exhibited by **7** led the latter

(8) R. J. H. Voarhoeve, "Organohalosilanes," Elsevier, New York, N. Y., 1967, p 302; J. H. Hoard and W. B. Vincent, *J. Amer. Chem. Soc.*, **62**, 3126 (1940).

authors to conclude that this hydride was present as an impurity. In our hands **7** is obtained virtually pure, its structure being confirmed by the virtual identity of the high field pmr spectrum to that of $[(Et_3P)_3PtH]^+$ ⁹ and the identity of the ¹⁹F spectrum and Si-F modes in the infrared region to those of other SiF_5^- salts. Although refluxing **7** in tetrahydrofuran with excess triphenylphosphine resulted in disappearance of the hydride, as previously reported,² the SiF_5^- spectrum remained unchanged. The compound **5** was unaffected by the latter treatment. Although the dehydrofluorination of **7** by tetrahydrofuran to yield **4** could not presently be ruled out, the physical evidence would seem to point equally strongly to the conclusion that the purported silicon tetrafluoride adduct is a pentafluorosilicate.

The high field pmr spectrum of **5** is essentially that expected, but certain anomalies in line shapes suggest some effects due to a less than perfect equivalence of P3 and P5; see Figure 4a. The spectrum of **7** was simpler and more easily resolved (Figure 4b). It suggests that the ideal square planar structure does not exist in solution for this compound and that the two phosphorus atoms cis to the proton are not exactly equivalent. Several possible causes of this inequivalence, such as the diastereotopic packing of triphenylphosphine ligands, referred to above, or unsymmetrical association of ion pairs, are presently being explored.

In addition to the reactions described above, it has also been shown that BF_3 reacts with **2** and **3** to give the tetrafluoroborate analogs of **5** and **7**. Evidently, great care must be taken when interpreting the results of reactions of covalent fluorides with basic metal complexes when the reactions are carried out in glass apparatus.

Acknowledgment. Financial support for this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Research Council of Canada is gratefully acknowledged.

(9) H. C. Clark and K. R. Dixon, *J. Amer. Chem. Soc.*, **91**, 596 (1969).

P. Bird*

Department of Chemistry, Sir George Williams University
Montreal, Quebec, Canada

J. F. Harrod,* Khin Aye Than

Department of Chemistry, McGill University
Montreal, Quebec, Canada

Received September 20, 1973

A Facile Synthesis of Arene Oxides at the K Regions of Polycyclic Hydrocarbons

Sir:

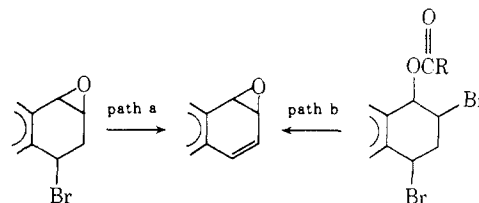
The establishment of arene oxides as primary intermediates in oxidative metabolism of aromatic substrates¹ has generated substantial interest in their pharmacology and biochemistry. To date, arene oxides have been implicated as causative agents in the carcinogenic, toxic, and mutagenic activity² displayed by many aromatic hydrocarbons. The broad interest in

(1) Plants, animals, and certain microorganisms employ this pathway with the eventual secondary formation of phenols, cysteine conjugates, dihydrodiols, and catechols. For a review, see J. W. Daly, D. M. Jerina, and B. Witkop, *Experientia*, **28**, 1129 (1972).

(2) The biological activity of arene oxides has been reviewed: D. M. Jerina and J. W. Daly, *Science*, in press.

the biological effects of these compounds has prompted development of versatile and convenient entries into this class of unstable oxiranes.³ K-Region arene oxides have been accessible through closure of the corresponding dialdehydes with tris(dimethylamino)phosphine⁴ and, more recently, by dehydration of trans dihydrodiols with the dimethyl acetal of dimethylformamide.⁵ Non-K-region arene oxides have been prepared by dehydrohalogenation of tetrahydrobromo epoxide precursors^{6,7} (Scheme I, path a). A related but improved

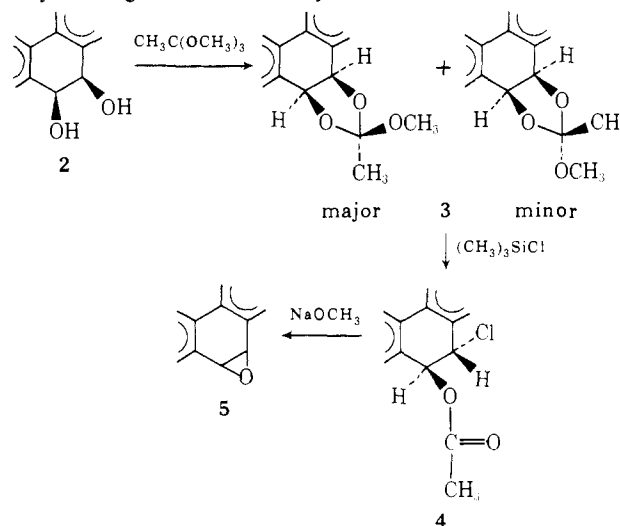
Scheme I. Synthesis of Non-K-Region Arene Oxides via Dehydrohalogenation Routes



procedure employs halohydrin esters as precursors⁸ (Scheme I, path b). The use of halohydrin esters has now been extended to the preparation of K-region arene oxides and provides facile access in high yield. This approach has been exemplified by the synthesis of K-region oxides of the six hydrocarbons (**1a-f**) listed in Table I.⁹

The general synthetic route (Scheme II) consists of (i)

Scheme II. Synthesis of K-Region Arene Oxides via Dehydrohalogenation of Chlorohydrin Acetates



formation of a 2-alkoxy-1,3-dioxolane (**3**) from the cis dihydrodiol (**2**) at the K region,¹⁰ (ii) transformation into a

(3) For reviews see (a) E. Vogel and H. Gunther, *Angew. Chem., Int. Ed. Engl.*, **6**, 385 (1967); (b) D. M. Jerina, H. Yagi, and J. W. Daly, *Heterocycles*, in press.

(4) M. S. Newman and S. Blum, *J. Amer. Chem. Soc.*, **86**, 5559 (1964).

(5) S. H. Goh and R. G. Harvey, *J. Amer. Chem. Soc.*, **95**, 242 (1973).

(6) E. Vogel and F. G. Klarner, *Angew. Chem., Int. Ed. Engl.*, **7**, 374 (1968).

(7) J. F. Waterfall and P. Sims, *Biochem. J.*, **128**, 265 (1972).

(8) H. Yagi and D. M. Jerina, *J. Amer. Chem. Soc.*, **95**, 243 (1973).

(9) The best overall yields were obtained for the oxides of hydrocarbons **1c** and **1f** which have been considered the two most difficult types of K-region oxides to synthesize.⁵

(10) While most of the cis dihydrodiols were prepared through the action of OsO_4 on the hydrocarbon in benzene solvent with a 2 molar equiv of pyridine as described by J. W. Cook and R. Schoental, *J. Chem. Soc.*, 170 (1948), diols **2e** and **2f** were obtainable in much higher yield and purity when the reaction with OsO_4 was run for 5 days in pyridine followed by destruction of the osmate ester with aqueous $NaHSO_3$ as described by J. S. Baran, *J. Org. Chem.*, **25**, 257 (1960).