J. C. Barborak and Mr. S. F. Martin for helpful comments.

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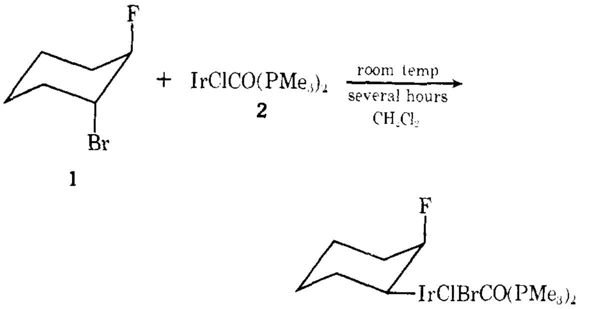
A Reinvestigation of the Claimed Oxidative Addition of *trans*-1-Bromo-2-fluorocyclohexane to *trans*-$IrClCO(PMe_3)_2$

Sir:

Recently there has been appreciable interest in the stereochemical course of the oxidative addition of alkyl halides to low-valent transition-metal complexes. Because both inversion[1] and retention[2] of configuration at carbon have been reported in reactions with square planar Ir(I) complexes, interest in the reactions of iridium compounds has been especially keen.

Osborn, *et al.*,[1] reported that the addition of *trans*-1-bromo-2-fluorocyclohexane[3] (**1**) to *trans*-$IrClCO(PMe_3)_2$[4] (**2**) occurs with inversion of configuration (eq 1).



(1)

Structural and stereochemical assignments were made spectroscopically (ir and ^{19}F nmr) on reaction mixtures without isolation of products. In the present study, this work (eq 1) has been reinvestigated and in fact it has been found that no reaction occurs at all under the reported or much more severe reaction conditions.

At the time the claimed addition was reported, studies in our laboratory with acyclic halides and Ir(I) complexes indicated such a low order of reactivity that reaction of **1** with **2** (eq 1) would be very surprising. The absence of well-characterized products[1] on which to base the claimed reaction, the low reactivity of Ir(I) observed in our studies, and the current interest in these transformations prompted a reinvestigation of the study.

Under vacuum, *trans*-1-bromo-2-fluorocyclohexane (**1**) (0.25 mmol) in 0.3 ml of CD_2Cl_2[5] was transferred to an equimolar amount of *trans*-$IrClCO(PMe_3)_2$ (**2**) in an nmr tube[5] containing a capillary of TMS as standard and the tube was sealed. A proton nmr spectrum was taken immediately after addition of the reactants and the region containing signals from the residual hydrogens of CD_2Cl_2 (δ = 5.88) and the protons α to bromine at C-1 (δ 4.54, broad singlet) and α to fluorine at C-2 (δ 5.0, J = 48 Hz, doublet) of the cyclohexyl derivative was time averaged and recorded. The nmr tube was then kept at room temperature for 166 hr and the nmr spectrum recorded periodically.

After 166 hr the reaction mixture still showed the yellow color of the starting Ir(I) complex. During the period of standing: (a) the relative areas of the signal of the residual hydrogens of CD_2Cl_2 and the signals of the protons of **1** α to bromine and α to fluorine remained constant; (b) the position of the methyl protons of the two PMe_3 groups (δ 2.17, J = 4 Hz, triplet) of the starting Ir(I) complex remained unchanged; and (c) no new signals appeared. The nmr tube was then opened; all volatiles were removed under vacuum and collected in a trap. Methyl iodide in CD_2Cl_2 was added to the dry, yellow Ir complex remaining in the nmr tube. After several minutes the MeI adduct of **2** was formed in 98.5% yield ($2PMe_3$, δ 2.40, J = 4 Hz; IrMe, δ 1.66, J = 6 Hz; ir (CH_2Cl_2) CO 2030 cm^{-1}). Examination of the volatiles by glpc analysis showed only starting material **1** and solvent.

An attempt was also made to bring about reaction of **2** with *cis*-1-bromo-2-fluorocyclohexane[6] (**3**), but no reaction occurred even after 336 hr at room temperature. (In CD_2Cl_2, the reaction mixture exhibited: PMe_3, δ 2.20, J = 4 Hz, triplet; H_α to bromine at C-l, δ 4.97, broad singlet; H_α to fluorine at C-2, δ 5.10, J = 78 Hz, doublet; external TMS.)

In the claimed observation of reaction 1, the carbonyl-stretching band of **2** at 1935 cm^{-1} was reported to disappear after the addition of **1** while a new band appeared at 2020 cm^{-1}. In our experiments utilizing ordinary ir cells, similar conversions occurred within a few hours. Addition of a controlled amount of oxygen (air) to **2** in the absence of **1** also brings about the observed spectral change in the carbonyl stretching region. Presumably, the reported[1] observations of such a change result from the presence of oxygen. The previous workers also reported the resonance at +88.3 ppm in the ^{19}F spectrum decreases while a new signal centered at +64.2 ppm appears (CF_3CO_2H as external reference). While we observed the signal at +88.3 ppm, no change in its intensity nor the appearance of a new signal at +64.2 ppm was observed.

An attempt was made to ascertain the reason for the previously reported spectral changes. 1-Fluorocyclohexene (**4**), which could be an impurity in the *trans*-1-bromo-2-fluorocyclohexane (**1**), produced no new products with **2** or with $HIrCl_2CO(PMe_3)_2$ (**5**) at 25° in CD_2Cl_2. Chloroform is an impurity in commercial CD_2Cl_2 and reacts rapidly with **2**. An attempt was made to use unpurified CD_2Cl_2 to initiate the reported reaction (eq 1) but no oxidative addition of **1** occurred.

While the stereochemistry at carbon for oxidative addition of alkyl halides to Ir(I) complexes may be inversion, it remains to be proven.

Pearson and Muir[2] reported that the addition of optically active $CH_3CHBrCOOC_2H_5$ to *trans*-IrClCO-$(PMePh_2)_2$ occurs with retention of configuration at

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[1] J. A. Labinger, R. J. Braus, D. Dolphin, and J. A. Osborn, *Chem. Commun.*, 612 (1970).

[2] R. G. Pearson and W. R. Muir, *J. Amer. Chem. Soc.*, 92, 5519 (1970).

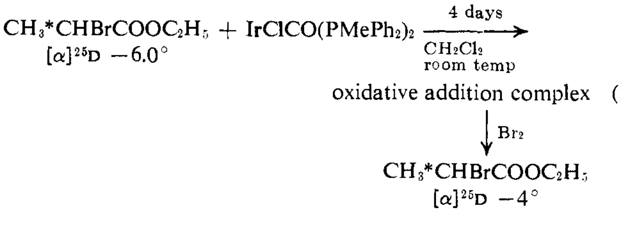
[3] A. Bowers, L. C. Ibanes, E. Denot, and R. Becerra, *ibid.*, 82, 4001 (1960).

[4] A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 1887 (1968).

[5] All samples were carefully degassed before transfer. Carbon and hydrogen analyses and spectroscopic analyses were correct for all reported compounds. Commercial CD_2Cl_2 was freed from $CDCl_3$ by vpc before use.

[6] G. Wittig and U. Mayer, *Chem. Ber.*, 96, 336 (1963).

carbon (eq 2). Since the claimed retention is based on the assumption that the bromine cleavage occurs with retention of configuration, and since bromine cleavages with inversion have been reported, it has been suggested that this claim be held in abeyance until more definitive results are obtained.[7,8]



$$\underset{[\alpha]^{25}\text{D}\ -6.0^\circ}{CH_3{}^*CHBrCOOC_2H_5} + IrClCO(PMePh_2)_2 \xrightarrow[\text{CH}_2\text{Cl}_2\ \text{room temp}]{\text{4 days}} \text{oxidative addition complex} \quad (2)$$

$$\xrightarrow{Br_2} \underset{[\alpha]^{25}\text{D}\ -4^\circ}{CH_3{}^*CHBrCOOC_2H_5}$$

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(7) G. M. Whitesides and D. J. Boschetto, *J. Amer. Chem. Soc.*, **93**, 1529 (1971); F. R. Jensen and D. D. Davis, *ibid.*, **93**, 4048 (1971); F. R. Jensen, V. Madan, and D. H. Buchanan, *ibid.*, **93**, 5283 (1971).

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Macrocyclic Transition States in Mass Spectrometry. Long-Chain α,ω-Bis(trimethylsilyl) Ethers

Sir:

Transition-state ring size is often a critical factor in mass spectrometry, and most commonly involves rings of six members,[1] although numerous examples[2] of both larger and smaller rings are available. However, it has been previously shown that interactions between remotely situated functional groups in conformationally mobile[3] long-chain molecules can lead to fragmentation reactions which proceed through large-ring transition states having no apparent ring size requirements.[4]

In order to test for an upper limit to transition-state ring size in reactions of this type, mass spectra of the trimethylsilyl ethers **1–4**[5] were examined. We wish to report evidence for intramolecular reactions between the terminal functions, which not only involve transition-state macrocycles of up to 49 members, but become increasingly favorable with increasing chain length and constitute the major fragmentation path in the spectra of **2–4**.

$$Me_3SiO(CH_2)_nOSiMe_3$$

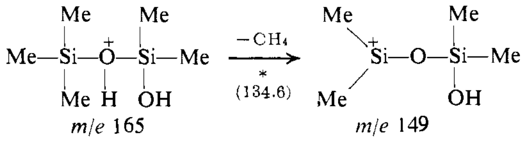
1, $n = 10$ **3**, $n = 34$
2, $n = 22$ **4**, $n = 46$

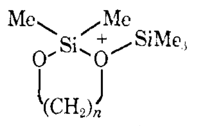
Our choice of **1–4** was dictated by knowledge that in short-chain bis(trimethylsilyl) ethers the silyl groups readily interact to form the prominent rearranged species *m/e* 147 ($Me_3SiO^+SiMe_2$).[11,12] Of much lesser importance in the short-chain homologs is *m/e* 165, which retains two hydrogens but no carbons from the polymethylene chain, and further decomposes by elimination of methane.[11] The present results (Table I) unexpectedly show the increasing prominence of *m/e* 165 and 149 with increasing chain length, while *m/e* 147 becomes less important. We view the formation of *m/e* 165 as arising from a cyclized M − CH_3 ion, earlier proposed as the precursor of *m/e* 147 from short-chain (n = 2–8) silyl ethers.[12] To shed more light on the origin of the two alkyl chain hydrogens which are retained in *m/e* 165, analogs of **2** were examined which

Table I. Abundance (% Σ_{40})[a] of Selected Ions from the Mass Spectra of **1–4**

m/e	1	2	3	4
165	0.26	2.9	5.4	7.2
149	4.6	15	16	17
147	10.5	5.2	2.8	1.9

[a] Sum of all isotopic species.





$(M-CH_3)^+$

$n = 10, 22, 34, 46$

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(1) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, pp 155–162.

(2) (a) W. Benz and K. Biemann, *J. Amer. Chem. Soc.*, **86**, 2375 (1964); S. Meyerson and L. C. Leitch, *ibid.*, **86**, 2555 (1964); (b) M. Katoh and C. Djerassi, *Chem. Commun.*, 1385 (1969); (c) A. N. H. Yeo and D. H. Williams, *Org. Mass Spectrom.*, **2**, 231 (1969).

(3) For a recent review and discussion of various effects of winding or coiling of the alkyl chain upon fragmentation, see S. Meyerson and L. C. Leitch, *J. Amer. Chem. Soc.*, **93**, 2244 (1971).

(4) For examples and leading references, see (a) J. A. McCloskey and M. J. McClelland, *ibid.*, **87**, 5090 (1965); (b) R. Brandt and C. Djerassi, *Helv. Chim. Acta*, **51**, 1750 (1968); (c) G. Eglinton, D. H. Hunneman, and A. McCormick, *Org. Mass Spectrom.*, **1**, 593 (1968); (d) G. H. Draffan, R. N. Stillwell, and J. A. McCloskey, *ibid.*, **1**, 669 (1968); (e) J. Diekman, J. B. Thompson, and C. Djerassi, *J. Org. Chem.*, **34**, 3147 (1969); (f) R. E. Wolff and A. Caspar, *Tetrahedron Lett.*, 1807 (1970); (g) E. White, V, and J. A. McCloskey, *J. Org. Chem.*, **35**, 4241 (1970).

(5) **1–4** were prepared by heating the corresponding diol (200 μg) with bis(trimethylsilyl)trifluoroacetamide (20 μl) (PCR Inc., Gainesville, Fla.) and 1% trimethylchlorosilane at 100° for 1 hr. 1,10-Decanediol was obtained commercially; the remaining diols were prepared by reduction of the corresponding C_{22}, C_{34}, and C_{46} diacids with borane in tetrahydrofuran.[6] The diacids were obtained by the method of Hünig,[7] starting with the morpholine enamines of cyclohexanone (C_{22}) and cyclododecanone[8] (C_{34}, C_{46}), by Wolff–Kishner reduction of the intermediate diketo dicarboxylic acids. All intermediate and final products were checked by gas chromatography and mass spectrometry[9] and exhibited satisfactory mass spectra.[10] Gas chromatography of **3** and **4** indicated the presence of later eluting components which did not interfere with their mass spectra. Eluting peaks of **1–4** (total ion current) were shown to be homogeneous by repeated scanning of mass spectra during elution.

(6) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 199.

(7) S. Hünig, E. Lücke, and W. Brenninger, *Org. Syn.*, **43**, 34 (1963); S. Hünig and E. Lücke, *Chem. Ber.*, **92**, 652 (1959); S. Hünig and H.-J. Buysch, *ibid.*, **100**, 4017 (1967); C. Wakselman, *Bull. Soc. Chim. Fr.*, 3763 (1967).

(8) S. Hünig, H.-J. Buysch, H. Hoch, and W. Ferdle, *ibid.*, **100**, 3996 (1967); C. Wakselman, *C. R. Acad. Sci., Ser. B*, **261**, 759 (1965).

(9) Mass spectra were recorded on an LKB 9000 instrument (70 eV, ion source 250°), utilizing the gas chromatographic inlet (3 ft, 1% SE-30 conditioned for high temperatures: **1**, 125°; **2**, 215°; **3**, 273°; **4**, 312°). Spectra were recorded on the apex of the eluting peak, free of contamination by minor, later eluting components.

(10) Full mass spectra of 1–4 have been submitted to the Archives of Mass Spectral Data, Wiley-Interscience, New York, N. Y.

(11) J. A. McCloskey, R. N. Stillwell, and A. M. Lawson, *Anal. Chem.*, 40, 233 (1968).

(12) J. Diekman, J. B. Thompson, and C. Djerassi, *J. Org. Chem.*, **33**, 2271 (1968).