

## Fluorine Exchange in Complexes of Tungsten Hexafluoride<sup>1</sup>

Sir:

Tungsten hexafluoride forms charge transfer<sup>2</sup> and Lewis acid-base<sup>3,4</sup> complexes. Both 1:1 and 1:2 complexes of the Lewis acid-base type have been reported on the basis of analytical results for the isolated complexes.<sup>3,4</sup> In every case only a single magnetically equivalent fluorine species was observed for the complexed tungsten hexafluoride. For protons, however, stereochemical nonequivalence has been observed by magnetic resonance for eight coordinate tungsten tetrahydrides.<sup>5,6</sup> An intramolecular averaging mechanism has been suggested for the magnetic equivalence of the hydrogens at higher temperature.<sup>6</sup>

We wish to report the identification, by fluorine magnetic resonance, of the simultaneous existence of free tungsten hexafluoride, the 1:1 complex and the 1:2 complex with dimethyl sulfide. At very low temperatures nonequivalent fluorines are observed in the 1:2 complex, which is the predominant species under such conditions.

A sample initially 0.04 M in  $WF_6$  and 0.03 M in  $(CH_3)_2S$ , in vinyl chloride as solvent, has a single fluorine resonance line down to  $-40^\circ$  but yields two lines from free and complexed tungsten hexafluoride at lower temperature, as shown in Figure 1. From the relative areas and chemical shifts of these lines as a function of the ratio of reactants, equilibrium constants for formation of both complexes, and their chemical shifts, may be calculated. At  $-75^\circ$  the values determined are  $45 \pm 5$  and  $2 \pm 1$  for the equilibrium constants and  $-160 \pm 2$  and  $-90 \pm 1$  ppm for the chemical shifts of the 1:1 and 1:2 complexes. For the sample mentioned above this corresponds to an actual ratio for  $WF_6:WF_6L:WF_6L_2$  of 63.4:35.5:1.1. Satellites arising from tungsten fluorine spin coupling were observed for free tungsten hexafluoride but not for the complexes.

The 1:1 complex is not appreciably soluble at very low temperature; however, with an excess of dimethyl sulfide primarily the 1:2 complex is present and no precipitation occurs. At about  $-160^\circ$  the exchange of nonequivalent fluorines on tungsten in this complex is sufficiently slowed that a quintet is observed at  $-36.8$  ppm and a triplet at  $-118.4$  ppm with a spin coupling constant of 95 Hz. The spectrum is shown in Figure 2. There is no reasonable way for six fluorines to be arranged in an octacoordinated species to give two and four magnetically equivalent fluorine atoms (a hexagonal bipyramid is a geometric possibility). Therefore at least one intramolecular averaging mechanism is still rapid on the nmr time scale. From the temperature and concentration dependence of the exchange rate, it is hoped that information on the mechanism and activation energy for the exchange between the nonequival-

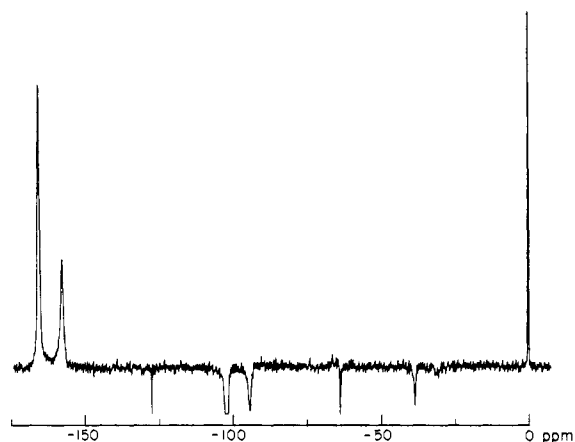


Figure 1. The  $^{19}F$  resonance spectrum of a  $WF_6-(CH_3)_2S$  sample (mole ratio 1:0.75) in  $CH_2=CHCl$  containing  $CFCl_3$  as reference at  $-75^\circ$ .

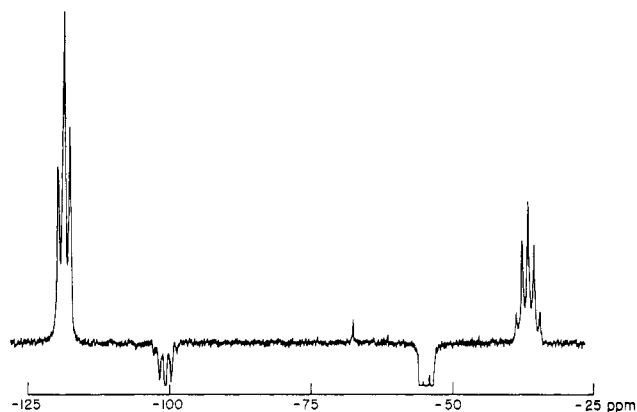


Figure 2. The  $^{19}F$  resonance spectrum of the complex  $WF_6 \cdot 2(CH_3)_2S$  at about  $-160^\circ$ .

ent fluorines can be obtained. The observation of nonequivalent fluorine atoms in an octacoordinated structure opens up the possibility of studying the stereochemistry of such complexes in solution.

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## Gas Phase Benzyl Cations from Toluene Precursors

Sir:

It is known from mass spectrometric<sup>1-4</sup> and ion photodissociation<sup>5</sup> results that extensive hydrogen scrambling occurs in the formation and fragmentation of  $C_7H_7^+$  from toluene-derived  $C_7H_8^+$ . Furthermore, those  $C_7H_7^+$  ions which subsequently fragment have been shown to undergo loss of carbon positional iden-

(1) Issued as N.R.C.C. No. 14256.

(2) (a) H. J. Clase, A. M. Noble, and J. M. Winfield, *Spectrochim. Acta, Part A*, **25**, 293 (1969); (b) R. R. McLean, D. W. A. Sharp, and J. M. Winfield, *Chem. Commun.*, 452 (1970).

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(2) H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, Chapter 10.

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tity.<sup>6,7</sup> The early view that these results indicated a tropylium ion structure for  $C_7H_7^+$  has been supplanted by proposals, based on collisional activation mass spectrometry,<sup>8</sup> on mass spectrometry of tropylium compounds,<sup>7</sup> and on radiolysis results,<sup>9</sup> that the  $C_7H_7^+$  obtained from toluene is a mixture of isomers, possibly undergoing interconversion.

A major fraction of the  $C_7H_7^+$  ions produced from toluene shows a pattern of chemical reactivity which can be rationalized only on the basis of a benzyl structure. We describe this chemistry here as satisfying evidence, complementary to that from other techniques, for the stability on a time scale of milliseconds of benzyl cations from toluene. The failure of these ions to show complete hydrogen scrambling on the icr time scale of milliseconds is, furthermore, evidence against their being in tautomeric equilibrium with a tropylium form.

Standard low electron-energy icr single and double resonance techniques<sup>10-13</sup> were employed in a "flat" icr cell configuration ( $1 \times 2.5 \times 14$  cm). Neutral gas pressures were around  $3 \times 10^{-5}$  Torr, and the electron energies were 13.5 eV ( $C_6H_5CD_3$ ,  $C_6D_5CH_3$ ,  $C-C_7H_8-C_6H_5CD_3$  mixture, and  $C_7H_7Br-C_6H_5CH_3$  mixture), 18 eV ( $C_6H_5CD_3-C_7H_7$  mixtures), and 12.8 eV ( $C_6H_4DCH_3$ ). The ratios of loss of H and D from the deuterium-labeled parent ions were in good agreement with the ratios expected from previous work<sup>4,5</sup>. The deuterium labeled compounds were available from previous studies.<sup>14</sup>

The characteristic reaction of  $C_7H_7^+$  with toluene is<sup>14</sup>



No other fragment ions other than  $C_7H_7^+$  were observed in pure toluene (at 13.5 eV), and the  $C_8H_9^+$  ion ( $m/e$  105) was the only secondary ion observed. This reaction is known from ion cyclotron double resonance experiments<sup>5</sup> and mass spectrometer results.<sup>15</sup> Assuming the xylyl structure for the  $C_8H_9^+$  ion,<sup>16</sup> reaction 1 is approximately thermoneutral, using  $\Delta H_f^\circ = 212$  kcal for  $C_7H_7^+$ .

Investigation of reaction 1 with three isotopically labeled toluene systems led to the conclusion that the product  $C_8H_9^+$  ion results from replacement of one of the ring hydrogens of the neutral toluene molecule by a  $CH_2^+$  fragment from the  $C_7H_7^+$  reactant ion.

In pure  $C_6H_5CD_3$ , the reactant ions have compositions  $C_7H_5D_2^+$  (~25%) and  $C_7H_4D_3^+$  (~75%).

(6) K. L. Rinehart, Jr., A. C. Buchholz, G. E. Van Lear, and H. L. Cantrill, *J. Amer. Chem. Soc.*, **90**, 2983 (1968).

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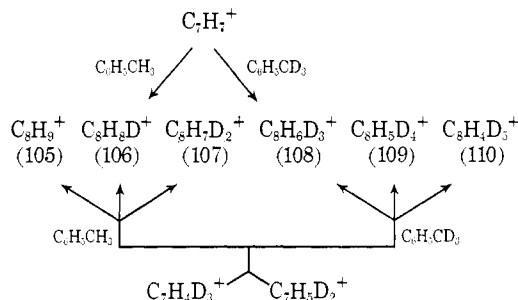
(16) J. L. Franklin, *et al.*, "Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, Washington, D. C., June 1969.

In accordance with the model given above, the only products possible, and the only ones observed (at 17 eV), were  $C_8H_6D_3^+$  (29%),  $C_8H_5D_4^+$  (45%), and  $C_8H_4D_5^+$  (26%). Double resonance results showed no substantial difference in reactivity between the two reactant species and no substantial difference in their product distributions. The relative amounts of product formed, however, indicated that, while scrambling of the hydrogens in the  $C_7(H,D)_7^+$  reactant was extensive, the methyl deuteriums of the reactant ion were statistically somewhat more likely to appear in the product than its ring hydrogens.<sup>17</sup> Qualitatively, this preference decreased somewhat at lower electron energy (29:50:21 at 13.5 eV).

Results were very similar in pure  $C_6D_5CH_3$ . Reactant ions were  $C_7D_5H_2^+$  (~65%) and  $C_7H_4D_3^+$  (~35%). The only products expected, and the only ones observed (at 13.5 eV), were  $C_8H_5D_4^+$  (25%),  $C_8H_4D_5^+$  (56%), and  $C_8H_3D_6^+$  (19%). Again, double resonance showed no substantial difference in reactivity or product distribution for the reactants, but the product peak pattern indicated that the methyl hydrogens of  $C_7(H,D)_7^+$  were statistically somewhat more likely to end up in the product than the ring deuteriums.<sup>18</sup> In both  $C_6H_5CD_3$  and  $C_6D_5CH_3$ , no product ions other than the ones reported were observable, and the fraction of product ions in these systems which violate the reaction model proposed was definitely less than 3% of the total.

A mixture of  $C_6H_5CH_3$  and  $C_6H_5CD_3$  was also examined, and the reactions occurring were fully charted by double resonance techniques. All of the major reactions observed are displayed in Scheme I; reactions not indicated had rates much slower than these.

Scheme I. Ion-Molecule Reactions Observed in a Mixture of Toluene and Toluene- $\alpha$ - $d_3$



Inspection of Scheme I shows that the observed reactions include all those, and only those, consistent with the proposed reaction model, which we regard as the only model consistent with all of these observations. The results show that of the nine hydrogens in the  $C_8H_9^+$  product, three come from the methyl group of neutral toluene, four come from the ring of neutral toluene, and two are drawn in a scrambled fashion from

(17) Complete scrambling of the  $C_7(H,D)_7^+$  hydrogens would give percentages of approximately 37:48:15, respectively, for the three observed products, assuming that the proposed reaction model is obeyed precisely. However, in view of the possibility of deviations from the assumed model, and of isotope effects on the reaction rates, a quantitative estimate of the degree of scrambling would not seem justified based on our data, and we wish only to point out that there is significant deviation from complete scrambling statistics.

(18) The product percentages are predicted to be 11:44:45 based on complete  $C_7(H,D)_7^+$  scrambling. See footnote 17.

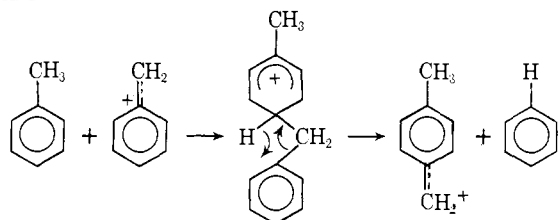
the  $C_7H_7^+$  reactant, with some preference to the hydrogens originally on the methyl group. The data do not rule out the additional possibility that the fifth ring hydrogen of the neutral toluene scrambles with the  $C_7H_7^+$  hydrogens, giving it the possibility of appearing in the product ion with low probability.

The product ion distribution for  $C_7H_6D^+$  reacting with *o*- $C_6H_4DCH_3$  indicated that the ring deuterium in the neutral reactant is abstracted with approximately statistical probability (*i.e.*, 20% of the time). Also<sup>19</sup> the  $C_7H_7^+$  ion from benzyl bromide (at 13.5 eV) reacted very rapidly with  $C_6D_5CH_3$ .

The results of these labeling experiments indicate that the identities of the hydrogens in the  $C_7H_7^+$  reactant are largely lost, although the preference for transferring the hydrogens originally on the methyl shows that hydrogen scrambling is not complete at these electron energies, and furthermore rule out a fully symmetrical structure for the reacting  $C_7H_7^+$  ion. The apparent complete retention of hydrogen identities in the neutral toluene during the reaction suggests that the reaction itself proceeds in a fashion not permitting free atom migrations, and it is reasonable to postulate that the scrambling in  $C_7H_7^+$  occurs prior to the reaction, as previous work would also imply.<sup>4,5,8</sup>

Formulating a simple, chemically reasonable mechanism satisfying the observations is apparently possible *only* on the assumption that the reactant  $C_7H_7^+$  ion has the benzyl cation structure. Toluyl or tropylium structures must at some point in the reaction be rearranged to the benzyl structure. We postulate that the reaction proceeds as in Scheme II.

Scheme II



The proposed initial attack (without positional selectivity) on a ring site of the neutral is entirely similar to the mechanism proposed<sup>20</sup> to rationalize the substituent effects in the methylene transfer to aromatic species from  $CH_3OCH_2^+$ . The evidence seems strong that the reactive  $C_7H_7^+$  species has the benzyl structure. Recent photodissociation results<sup>21</sup> indicate that  $C_7H_7^+$  formed from toluene has (on a time scale of seconds) two stable, noninterconverting forms, only one of which, presumably the benzyl form, is reactive. We may conclude with some assurance that in the gas phase the benzyl cation exists and is stable for seconds at least and that at least one other isomer (probably the tropylium structure) is also stable for seconds at least.

(19) Benzyl bromide is found by collisional activation to produce 50% benzyl cations at 70 eV (F. W. McLafferty and J. Winkler, private communication) and by analogy with other benzyl derivatives should yield a high fraction of benzyl cation at low energies. It was accordingly chosen as a convenient source of  $C_7H_7^+$  cations of probable benzyl structure.

(20) R. C. Dunbar, J. Shen, E. Melby, and G. A. Olah, *J. Amer. Chem. Soc.*, **95**, 7200 (1973).

(21) R. C. Dunbar, unpublished results.

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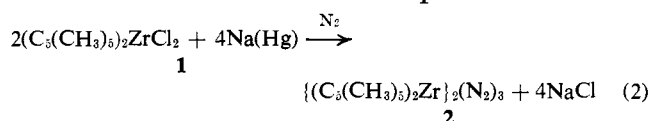
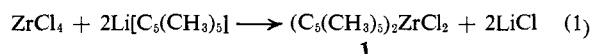
(22) Alfred P. Sloan Fellow 1973–1975.

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### Preparation of a Dinitrogen Complex of Bis(pentamethylcyclopentadienyl)zirconium(II). Isolation and Protonation Leading to Stoichiometric Reduction of Dinitrogen to Hydrazine

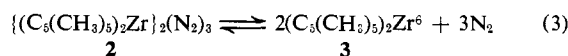
Sir:

In connection with our studies of dinitrogen complexes of group IV transition metal cyclopentadienyls, we have prepared a dinitrogen complex of bis(pentamethylcyclopentadienyl)zirconium(II) *via* the following sequence.



Lithium pentamethylcyclopentadienide is prepared from 1,2,3,4,5-pentamethylcyclopentadiene and *n*-butyllithium in 1,2-dimethoxyethane, then treated *in situ* with freshly sublimed zirconium tetrachloride. Permethylzirconocene dichloride (**1**) is isolated in good yield (50–60%) by a procedure similar to that for the analogous titanium derivative.<sup>1,2</sup> Pale yellow crystalline **1** so obtained analyzes satisfactorily<sup>3</sup> and exhibits a singlet nmr absorption at 1.99 ppm ( $CDCl_3$ ), nearly identical in position to that observed for permethyltitanocene dichloride.<sup>1</sup>

Reduction of **1** with excess sodium amalgam in toluene under 1 atm of  $N_2$  leads, over the period of 2 days at room temperature, to a dark permanganate-red dinitrogen complex, **2**. **2** is isolated in moderate yields (30–40%) as large, well-formed, metallic *green*<sup>4</sup> crystals by removal of toluene and extraction and subsequent recrystallization from pentane under 1 atm of nitrogen. **2** is moderately soluble in toluene, but only slightly soluble in pentane or diethyl ether. At room temperature in solution, **2** reversibly releases its dinitrogen *in vacuo* over a period of several hours. Quantitative measurements of the  $N_2$  released (eq 3) as well as ele-



(1) J. E. Bercaw, R. H. Marvich, L. G. Bell, and H. H. Brintzinger, *J. Amer. Chem. Soc.*, **94**, 1219 (1972).

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(3) Calculated for  $C_{20}H_{30}Cl_2Zr$ : C, 55.56; H, 6.94; Cl, 16.40; Zr, 21.10. Found: C, 55.57; H, 6.99; Cl, 16.36; Zr, 21.21.

(4) The metallic green color of these large crystals appears to be associated with a very high index of refraction. When dissolved in toluene or petroleum ether, even at  $-80^\circ$ , dark permanganate-red solutions are observed. Furthermore, the powder obtained by grinding these large green crystals appears red to transmitted but metallic green to reflected light. On the basis of these observations we conclude that the permanganate-red and metallic green compounds are compositionally identical.