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Journal of Fluorine Chemistry 71 (1995) 185

JOURNAL OF FLUORINE CHEMISTRY

Novel halogen chemistry of atranes

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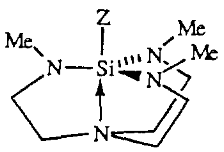
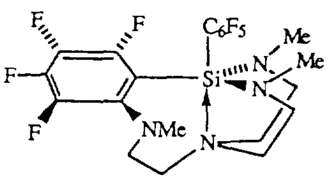
Keywords: Atranes; Halogen chemistry; NMR spectroscopy; Fluoride transfer; Hydride transfer; Transannulation

Azasilatrane (**1**) reacts with PhLi at −45 °C to give the expected substitution product **2**, and not the hydride-transfer product **3**. By contrast, **1** reacts with $C_6F_5Br/^nBuLi$ at −50 °C to provide both **4** and **5**, the latter arising from a novel fluoride-transfer process.



	Z
1	Cl
2	Ph
3	H
4	C_6F_5
5	F



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In addition, this reaction produces **6** which forms from **4** by tetrafluorobenzyne insertion as shown by trapping reactions with furan. Evidence has been adduced for the intermediacy of a species such as **7** to account for the formation of **5**. A transannular bond is observed in both **5** (2.034 Å) and **6** (2.264 Å). The seven-membered ring in **6** does not undergo inversion at room temperature on the NMR time scale even at 80 °C.

When bicyclic $P(MeNCH_2CH_2)_3N$ (**8**) is reacted with halogenonium sources, cations **9–12** are formed whose ^{31}P NMR chemical shifts are consistent with full transannulation in **9** but decreasing P←N interaction from **10–12**. The δ ^{31}P values are also linear when plotted against halogen electronegativity. While the reaction of **8** with CCl_4, CBr_4 and MeI cleanly gives cations **13–15** as their halide salts, $CHCl_3$ and CH_2X_2 (X = Br, I) react to give other products in addition to **16**, **17** and **18**, respectively. Thus, for example, products resulting from dehydrohalogenation of the hydrohalocarbon reagent are found such as cation **19** and the ylides **20** and **21**. In DMSO, cation **14** apparently disproportionates to cation **11** and ylide **22**. The dehydrohalogenation phenomenon is ascribed to the extraordinary basicity of **8**.

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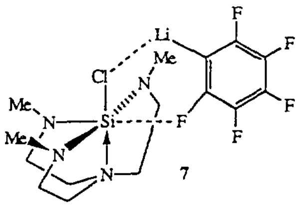

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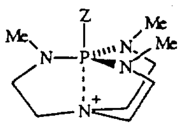
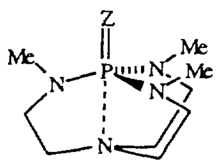


	Z		Z
9	F	15	CH_3
10	Cl	16	$CHCl_2$
11	Br	17	CH_2Br
12	I	18	CH_2I
13	CCl_3	19	H
14	CBr_3		



	Z
20	CCl_2
21	CHBr
22	CBr_2

Acknowledgements

The authors gratefully thank the donors of the Petroleum Research Fund administered by the American Chemical Society, and the National Science Foundation for grant support.

SSDI 0022-1139(94)06016-9