Reactions at Functional Silicon Centres in Compounds Containing Carbon–Zinc Bonds

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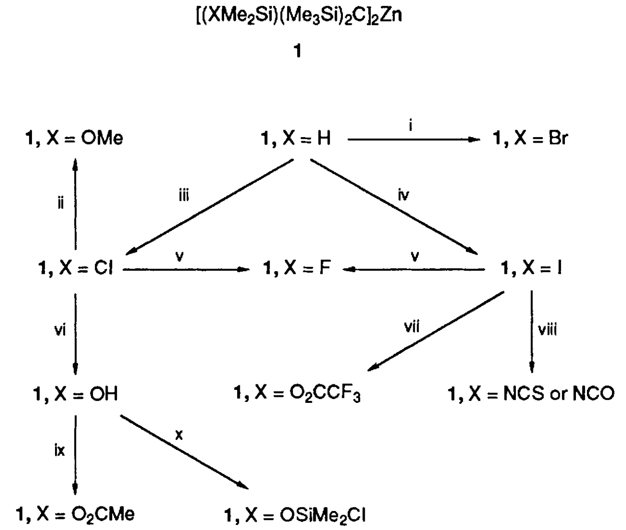
Substitutions at the Si–X bonds in the compounds $[(XMe_2Si)(Me_3Si)_2C]_2Zn$, some involving powerful electrophiles, take place without cleavage of the C–Zn bonds.

Some years ago we reported the remarkable chemical and thermal stability of the substituted-dimethylzinc $[(Me_3Si)_3C]_2Zn$, illustrating its robustness by, among other ways, purifying it by steam distillation.[1] We have now found that the C–Zn bonds in the related species **1** are, for steric reasons, so resistant to attack that substitutions, often involving powerful electrophiles, can be carried out at the Si–X bonds without breakdown of the molecule. The reactions have been used to prepare a range of remarkable organozinc compounds containing functional groups that could not normally coexist with Zn–C bonds.

The entry into the series of compounds was provided by the reaction with $ZnBr_2$ of the organolithium reagent $(HMe_2Si)(Me_3Si)_2CLi$, itself made by reaction of $(HMe_2Si)(Me_3Si)_2CCl$ with BuLi in Et_2O–tetrahydrofuran at −110 °C. The hydride **1**, X = H, thus obtained was treated with ICl, Br_2 or I_2, respectively, to give the halides **1**, X = Cl, Br or I, and from these the compounds **1** with X = F, OH, OMe, O_2CCF_3, O_2CMe, NCS, NCO and $OSiMe_2Cl$ were obtained, directly or indirectly, by standard organosilicon reactions, as shown in Scheme 1. It is noteworthy that the C–Zn bonds are unaffected by such vigorous electrophiles as halogens, CF_3CO_2H, MeCOCl, Me_2SiCl_2 and the hydrogen halides generated in many of the reactions shown in Scheme 1.

The identities of the compounds, all crystalline solids, were established in the usual ways, including elemental analysis, NMR spectroscopy [some typical δ_H values for solutions in CCl_4, are (for Me_3Si, Me_2Si, and X, respectively); (X =) H,



Scheme 1 *Reagents*: i, Br_2–CCl_4; ii, MeOH; iii, ICl (2.5 molar proportion in CCl_4); iv, I_2–CCl_4; v, $AgBF_4$–CH_2Cl_2; vi, H_2O–tetrahydrofuran; vii, Ag_2O/CF_3CO_2H; viii, AgSCN or AgOCN in CH_2Cl_2; ix, MeCOCl; x, Me_2SiCl_2

0.21, 0.28 (d), 4.36 (septet); OH, 0.21, 0.30, 2.67 (br); OMe, 0.18, 0.24, 3.34; F, 0.34, 0.42 (d); I, 0.37, 1.06] and mass spectrometry (in all cases strong peaks were observed for the $[M - Me]^+$ ions, and in most cases weaker peaks for the $[M]^+$ ions), and for **1**, X = Cl, OH, OMe and O_2CCF_3, by X-ray crystallography.

A feature of interest is that the preparation of **1**, X = $OSiMe_2Cl$, opens up the possibility of obtaining linear and cyclic polysiloxanes incorporating stable Si–C–Zn–C–Si linkages in their backbones.

Many of the related compounds $[(XMe_2Si)(Me_3Si)_2C]_2M$ with M = Hg or Cd have been made analogously.

We thank the SERC for support and for the award of Research Studentship (to A.H.), Dr P. D. Lickiss for valuable discussions, Dr A. G. Avent and Dr G. Lawless for help with the NMR spectra, and Mr A. M. Greenway for the mass spectra.

Received, 20th June 1990; Com. 0/02766I

References

1 C. Eaborn, N. Retta and J. D. Smith, *J. Organomet. Chem.*, 1980, **190**, 101.