Diphenyl Ketimine Derivatives as a Probe for Group IV $p\pi$–$d\pi$ Bonding: The Structures of $M(NCPh_2)_4$ (M=Si, Ge, Sn)

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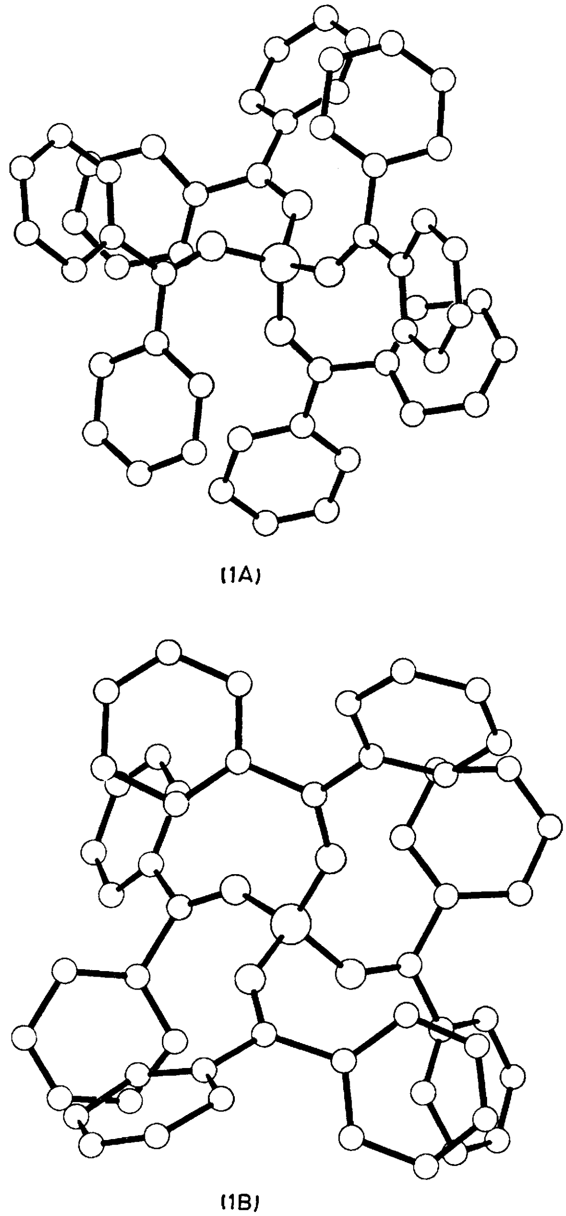
Summary The crystal structures of the three title compounds have been determined; the dramatic differences in their M–N–C bond angles suggest that Si is substantially involved in $p\pi$–$d\pi$ bonding, that Ge is partially involved, and that Sn shows no $p\pi$–$d\pi$ bonding.

An investigation of the crystal structures of the Group IV diphenyl ketimines, $M(NCPh_2)_4$ [M = Si (**1**), Ge (**2**), Sn (**3**)] has shown that they are less similar than would be expected. The M–N=C grouping is very sensitive to M–N interactions, directly indicating the extent of $p\pi$–$d\pi$ bonding. The compounds were prepared as hygroscopic yellow crystals by reaction (1).[1]

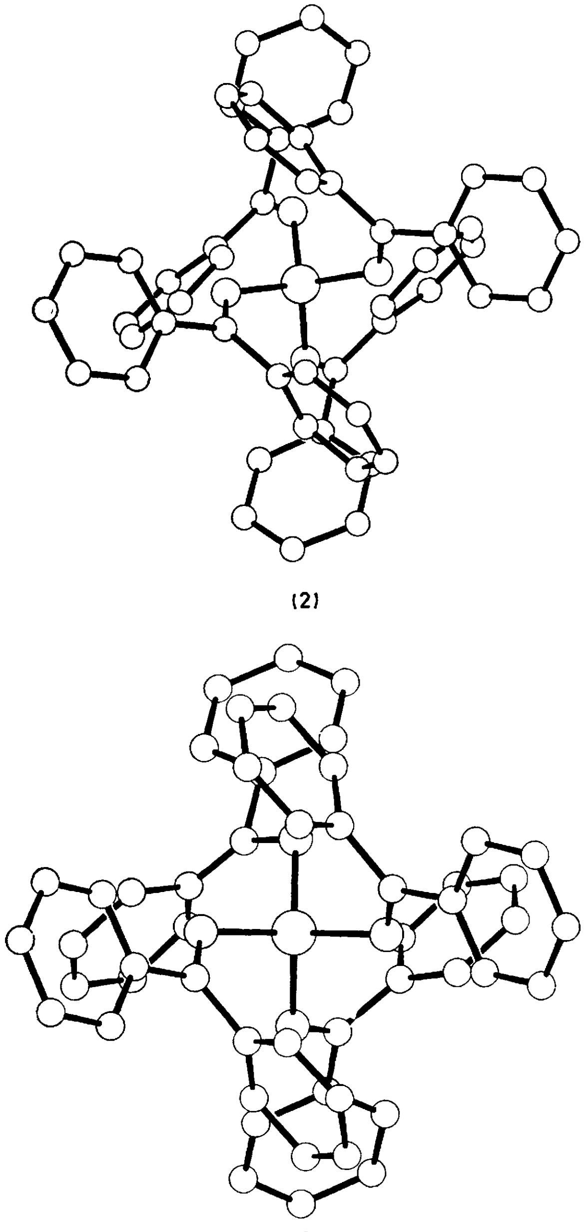
$$MCl_4 + 4Ph_2CNLi \rightarrow M(NCPh_2)_4 + 4\ LiCl \qquad (1)$$



(1A)

(1B)

Figure 1



(2)

(3)

Figure 2

TABLE

M	Average distance[a] M–N/Å	Independent M–N=C angles/°				Average
Si(**A**)	1·719(16)	136·2(1·3)	134·2(1·3)	139·5(1·3)	128·7(1·2)	134·7
Si (mean **A** and **B**)	1·717(10)					
Si(**B**)	1·716(16)	141·1(1·5)	138·6(1·3)	139·0(1·3)	139·1(1·4)	139·5
Ge	1·872(5)	123·8(6)	130·1(6)	—	—	127·0
Sn	2·06(4)	121·3(13)	—	—	—	121·3

[a] No significant deviations from the mean values.

Data were collected on a Syntex $P2_1$ diffractometer.

Crystal data: $SiC_{28}H_{40}N_4$, triclinic, a = 12·342(6), b = 18·100(8), c = 19·586(15) Å, α = 86·89(5), β = 82·72(5), γ = 84·06(4), $Z = 4$; Mo-K_α; 2327 observed reflections; space group $P\bar{1}$. There are two crystallographically independent molecules, (**A**) and (**B**), in the unit cell. The structure was solved by direct methods and refined to R = 0·058 (including H; Si, N and non-phenyl C with anisotropic temperature factors).

$GeC_{28}H_{40}N_4$, monoclinic, a = 24·050(2), b = 11·971(1), c = 18·839(3) Å, β = 130·44(8); $Z = 4$; Mo-K_α and Cu-K_α; 2189 observed reflections; space group $C2/C$ with molecular symmetry 2. The structure was solved by the heavy-atom method, and refined to R = 0·058 (including H; all other atoms with anisotropic temperature factors).

$SnC_{28}H_{40}N_4$, tetragonal, a = 18·141(7), c = 14·461(3) Å, $Z = 4$; Cu-K_α; 1329 observed reflections (collected rapidly and corrected for rapid crystal decomposition). Space group $I4_1/a$ with molecular symmetry 4. The structure was solved by the heavy-atom method and refined to R = 0·118 (including H; all other atoms with anisotropic temperature factors).

The structures of the compounds are shown in Figures 1 and 2; compounds (**2**) and (**3**) are viewed along their symmetry axes and (**1A**) and (**1B**) are viewed from equivalent directions. The most important bond parameters are given in the Table. It was initially very surprising that these compounds [particularly (**1**) and (**2**)] are not isomorphous, but this is explained by the conformation differences caused by the changing M–N=C angle. The bond angles with M = Si can be explained by a change in hybridisation at N from sp^2 towards sp, moving the lone pair partly into a p-orbital so that it can take part in $p\pi$-$d\pi$ bonding to Si (*cf.* ref. 2). With M = Ge, this bonding is less important while with M = Sn it is absent (or very slight). This pattern is confirmed by the M–N bond lengths. A predicted Si–N distance is 1·879 Å (derived from C–N=C, 1·475, C–C, 1·544 and Si–C 1·870 Å)[3] giving a shortening in (**1**) of 0·161 Å. Similarly, and perhaps more reliably, R_{Ge}–R_{Si} is 0·075 (from Si–C and Ge–C, 1·945 Å), compared to 0·155 between (**1**) and (**2**). Ge–N is calculated as 1·928 Å, again indicating less shortening in (**2**).

The observed Sn–N distance is shorter than the expected 2·11 Å, but the error in the Sn–N distance is such that not much weight can be attached to this.

It is also noticeable that the bond angles [M = Si, molecule (**A**), and M = Ge] are quite variable. This is not unexpected. Si (and still more Ge) does not require complete donation of four electron pairs. A suitable total overlap of electron density $p\pi \rightarrow d\pi$ can be obtained by combination of contributions from the four nitrogen atoms in different ways, leading to different bond angles, and the choice will depend on the packing requirements of the phenyl rings. Viewed in another way, these figures indicate that the M–N=C angle is readily distorted, and its precise value will be very dependent on packing effects.

We thank the S.R.C. for a grant for the diffractometer (N.W.A.) and a research studentship (M. P-B.).

(*Received*, 8*th January* 1975; *Com.* 022.)

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[3] Tables of Interatomic Distances, ed. L. E. Sutton, Chemical Society, London, 1965.

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