Fluxional Cyclopentadienylboranes

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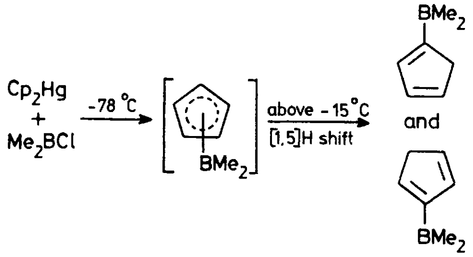
Summary Cyclopentadienyldimethylborane and pentamethylcyclopentadienyldimethylborane have been synthesized; their n.m.r. spectra indicate fluxional behaviour formally described as a [1,5]sigmatropic migration of the Me_2B species.

DURING the past decade the fluxional behaviour of various species has been studied extensively. In particular, cyclopentadienyl (Cp) derivatives of many metals and metalloids have been investigated and the fluxionality confirmed by the temperature dependence of the ^{1}H and ^{13}C n.m.r. spectra.[1] For 5-trimethylsilylcyclopenta-1,3-diene, it has been shown that a [1,5] sigmatropic migration of silicon is responsible for the time-averaged cyclopentadienyl resonance seen in the n.m.r. spectrum.[1] Many similar examples involving the [1,5] migrations of Ge, Sn, and Pb species have been studied[2] and found to rearrange by the same mechanism.

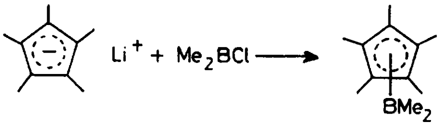
Previous to this year, all reported cyclopentadienylboranes had been vinyl isomers (1- and 2-substituted cyclopentadienes) which showed no fluxional behaviour.[3] However, rapid reversible allylic isomerizations of boron are well documented,[4] and recently Hancock and Kramer have also described irreversible [1,3] migrations of boron in allylic systems.[5] The first example of a 5-borylcyclopenta-1,3-diene, pentamethylcyclopentadienyldichloroborane, has been prepared recently by Jutzi and Seufert[6] and found to be fluxional at 40 °C. We now report the synthesis and n.m.r. spectra of the first member of the parent series, 5-dimethylborylcyclopenta-1,3-diene as well as the pentamethylcyclopentadienyl analogue. These molecules are fluxional owing to a rapid [1,5] sigmatropic migration of boron.

Reaction of cyclopentadienide salts (Na^+ or Tl^+) with Me_2BCl yields only vinyl isomers. However, Cp_2Hg reacts with Me_2BCl at −78 °C producing 5-(Me_2B)Cp which is fluxional on the n.m.r. time-scale (to −90° C, ^{1}H and ^{13}C n.m.r.).† Warming of the sample above −15 °C produces the more stable vinyl isomers by means of a [1,5] hydrogen shift (Scheme). This hydrogen migration is apparently irreversible and explains why many previous attempts to prepare 5-substituted compounds at temperatures above −15 °C yielded only the vinyl isomers.



SCHEME

In pentamethylcyclopentadienyldimethylborane, however, the hydrogen migration is no longer possible. This molecule, produced by the reaction of $LiCpMe_5$ with Me_2BCl [equation (1)], is fluxional (to −90 °C, ^{1}H and ^{13}C n.m.r.) and stable at ambient temperature. This behaviour is in accord with the previous report of Jutzi and Seufert[6] for Me_5CpBCl_2 and $Me_5CpB(NMe_2)_2$.†



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† N.m.r. data: ^{1}H (rel. to Me_4Si) 5-Me_2BCp, δ 0·59 (Me_2B) and 6·11 (Cp); 5-$Me_2BC_5Me_5$, δ 0·43 (Me_2B) and 1·65 ($CpMe_5$). ^{13}C (rel. to CD_2Cl_2) 5-Me_2BCp, δ −42·8 (br, Me_2B) and 64·6 (Cp); $Me_2BC_5Me_5$, 70·0 (ring C) and −41·3 (ring Me) p.p.m. The ^{13}C resonance for the boryl methyl groups in the $Me_2BC_5Me_5$ is not observed, presumably because it is very broad.

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