Metallocarboranes: New Syntheses

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Summary The preparation and synthetic utility of the complexes $Tl_2R^1R^2C_2B_9H_9$ is described; the *closo*-carborane $Me_2C_2B_9H_9$ undergoes a polyhedral expansion reaction on treatment with d^{10} metal complexes of Ni, Pd, or Pt.

Two general methods have been developed for the synthesis of *closo*-metallocarboranes. The first and most widely used approach involves treatment of the open faced *nido*-carborane dianions (3)-1,2- and (3)-1,7-$C_2B_9H_{11}^{2-}$ with transition-metal halides.[1] More recently[2] the addition of two electrons to the *closo*- species $B_nC_2H_{n+2}$ (n = 6, 8, and 10) to form dianions, which react with $CoCl_2$ in the presence of sodium cyclopentadienide to form $B_nC_2H_{n+2}Co(\pi\text{-}C_5H_5)$ complexes, has been described.

Addition of an aqueous solution of thallium(I) acetate to an aqueous alkaline solution of (3)-1,2-$C_2B_9H_{12}^-$ or its *C*-alkyl derivatives causes the precipitation of the new complexes (I),† $Tl_2R^1R^2C_2B_9H_9$ ($R^1 = R^2$ = H, pale yellow; R^1 = H, R^2 = Me, yellow; $R^1 = R^2$ = Me, bright yellow).

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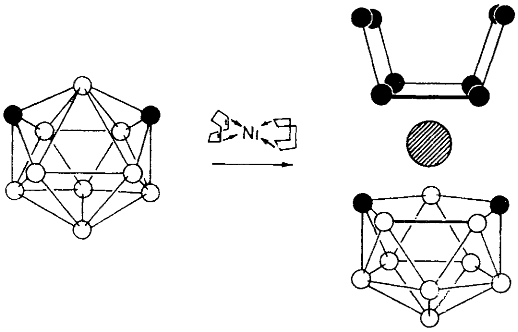
† Satisfactory analytical data were obtained for these compounds and all other new complexes mentioned.

One of the thallium atoms can be readily replaced by, for example, the tetraphenylarsonium cation, suggesting the presence in (I) of the icosahedral ions $[TlR^1R^2C_2B_9H_9]^-$. Compounds (I), which are stable in air and water and may apparently be stored indefinitely without special precautions, are useful intermediates for the synthesis of *closo*-metallocarboranes. Reaction in tetrahydrofuran with halogeno-derivatives of the transition metals, for example, $FeCl_2$, $CoCl_2$, $Pt(1,5\text{-}C_8H_{12})Cl_2$, and *cis*-$Pd(PPh_3)_2Cl_2$, leads to the formation in high yield of the corresponding π-(3)-1,2-dicarbollyl derivatives. The only thallium derivative of boron hydrides or carboranes to have been previously described is the complex $[Me_2Tl]^+[Me_2TlB_{10}H_{12}]^-$.[3]



FIGURE

We have also considered the possibility of the direct insertion of a nucleophilic metal species into the *closo*-carboranes $B_nC_2H_{n+2}$ (n = 6, 8, and 10). However, the highly reactive species $Ni(PEt_3)_4$ and $Pt(PEt_3)_3$ failed to react with either $1,2\text{-}C_2B_{10}H_{12}$ or $1,2\text{-}Me_2C_2B_{10}H_{10}$. In contrast, the eleven atom carborane *closo*-$1,8\text{-}Me_2C_2B_9H_9$[4,5] readily undergoes a novel polyhedral expansion reaction, on treatment with, for example, $Ni(1,5\text{-}C_8H_{12})_2$, $Ni(1,5\text{-}C_8H_{12})(PEt_3)_2$, $Pd(Bu^tNC)_2$, $Pt(PEt_3)_3$, or $Pt(PMe_2Ph)_3$ at room temperature or below in toluene to give, respectively, the crystalline complexes $(1,5\text{-}C_8H_{12})Ni[Me_2C_2B_9H_9]$ (II), $(Et_3P)_2Ni[Me_2C_2B_9H_9]$ (III), $(Bu^tNC)_2Pd[Me_2C_2B_9H_9]$ (IV), $(Et_3P)_2Pt[Me_2C_2B_9H_9]$ (V), and $(PhMe_2P)_2Pt[Me_2C_2B_9H_9]$ (VI). The suggested structure for these complexes is one in which the metal atom, formally in the (2+) oxidation state, occupies the vacant icosahedral site above a *nido*-1,7-$Me_2C_2B_9H_9$ fragment (Figure).

Physical data collected on these compounds were consistent with the suggested structure. For example, the brown crystalline complex (II), m.p. 207—210° (decomp.), had i.r. bands at 2550s and 2520sh (BH) cm^{-1}, and no other bands between 2800 and 1600 cm^{-1}. The mass spectrum showed a parent envelope centred at m/e 327 with partial cut-off at the m/e 330, corresponding to $^{60}Ni^{12}C_{12}{}^{11}B_9{}^1H_{27}$; the 100 MHz ^1H n.m.r. spectrum consisted of an unresolved multiplet centred at τ 4·36 (4H, CH=), a broad multiplet at 7·4 (8H, CH_2), and a singlet at 7·20 (6H, Me); the 80·2 MHz ^{11}B n.m r spectrum contained doublets of relative area 1:2:2:1:3 at + 20·1 (150), + 23·4 (150), +27·3 (160), +28·7 (150), and +32·1 (160) [chemical shift, p.p.m. relative to $B(OMe)_3$ (J_{BH}, Hz)]. The suggested (3)-1,7-structure has six types of boron atom in the ratio 2:2:2:1:1:1 as have the (3)-1,2-, (3)-5,6-, and (3)-5,11-isomers. As the other five possible isomers have boron ratios of 2:2:2:2:1 or 1:1:1:1:1:1:1:1:1 these were therefore excluded. Strong support for the (3)-1,7-structure came from an alternative synthesis of (V) from *cis*-$Pt(PEt_3)_2Cl_2$ and $[(3)\text{-}1,7\text{-}Me_2C_2B_9H_9]^{2-}$.

The formation of (II)—(VI) formally corresponds to an oxidative-elimination reaction at the metal centre.

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