The Synthesis and Crystal Structure of a Carbadibora-allyl Nickel Complex

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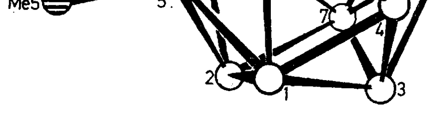
Summary The synthesis and crystal structure of the complex $[Ni(B_7C_2H_9Me_2)(PEt_3)_2]$ is described. The nickel is joined to a B_2C system in a 1,2,3-η bonding mode.

In an important series of papers Hawthorne and his co-workers[1] have shown that the chemistry of the dicarbollide ion $B_9C_2H_{11}^{2-}$ closely parallels that of the cyclopentadienyl anion in terms of bonding to transition metals. Recently the synthesis and structural characterisation of the complex $[Pt(B_3H_7)(PEt_3)_2]$ has led to the suggestion[2] that the B_3 framework may be considered analogous to a π-allyl system. A similar analogy has been drawn in the "slipped" sandwich complexes of $B_9C_2H_{11}^{2-}$ where three facial boron atoms play the role of allylic carbons.[3] We now report the first example of an η-carbadibora-allyl complex.

When tetrakis(triethylphosphine)nickel was added to a solution of the *arachno*-carborane 1,3-$B_7C_2H_{11}Me_2$[4,5] one molecule of hydrogen was evolved and red crystals of complex (I) $[Ni(B_7C_2H_9Me_2)(PEt_3)_2]$ m.p. 152—154° were formed, which in solution showed air instability. Analogous reactions between $B_7C_2H_{11}Me_2$ and $[Ni(PMe_3)_4]$, $[Pt(PEt_3)_2(stilbene)]$, $[Pt(PMe_3)_2(stilbene)]$ or $[Pt(PPh_3)_2(stilbene)]$ gave respectively (II) $[Ni(B_7C_2H_9Me_2)(PMe_3)_2]$ m.p. 184°, (III) $[Pt(B_7C_2H_9Me_2)(PEt_3)_2]$ m.p. 167°, (IV) $[Pt(B_7C_2H_9Me_2)(PMe_3)_2]$ m.p. 248°, and (V) $[Pt(B_7C_2H_9Me_2)(PPh_3)_2]$ m.p. 270°; the platinum compounds all being air-stable. The parent *arachno*-$B_7C_2H_{13}$ also reacts similarly to form, for example, (VI) $[Pt(B_7C_2H_{11})(PEt_3)_2]$, m.p. 199°.

The *X*-ray crystal structure of (I) was determined. The crystals are monoclinic, space group $P2_1/n$; $a = 9{\cdot}144(3)$, $b = 18{\cdot}954(5)$ $c = 15{\cdot}021(4)$ Å; $\beta = 90{\cdot}51(4)°$, $V = 2580$ Å^3; $D_m = 1{\cdot}13$ g cm^{-3}, $D_c = 1{\cdot}12$ g cm^{-3}, $Z = 4$, $\mu = 8{\cdot}7$ cm^{-1}. Diffraction data were collected on a Syntex $P2_1$ four-circle diffractometer using Mo-K_α radiation. The structure (Figure) was solved by conventional Patterson, Fourier and full matrix least squares techniques to a current *R* value of 10·4% for 3449 independent non-zero reflections.



Figure

The geometry of (I) is that of a *nido*-metallocarborane isoelectronic and approximately isostructural with decaborane. The open six-atom face is defined† by Ni, C(5), B(10), C(9), B(8) and B(7) with the P_2Ni system co-ordinated to C(5), B(2), and B(7) where Ni–B(7) = 2·14(1), Ni–B(2) = 2·11(1), Ni–C(5) = 2·08(1) Å; P(1)–Ni–P(2) = 102·7(2)° and C(5)–Ni–B(7) = 85·4(4)°. Nickel to phosphorus bond distances of Ni–P(1) = 2·242(3) and Ni–P(2) = 2·200(3) Å were observed.

These observations suggest that unlike the previously reported $[Co(C_2B_7H_{11})(C_5H_5)]$,[6] these complexes may be regarded as 1,2,3-η B_2C bonded compounds of Ni^{II} and Pt^{II}, analogous to the cationic species $[ML_2(C_3H_5)]^+$ (M = Ni, Pt),[7] and represent a new development in metallocarborane chemistry.

Comparison of the geometry of (I) with that of 1,3-$B_7C_2H_9Me_2$[5] suggests that in forming (I) there is little change in the geometry of the B_7C_2 system. We suggest that the formation of (I)—(VI) involves an initial oxidative-addition reaction between the d^{10} metal species and one of the acidic axial CH bonds of the carborane followed by protolysis of the resultant metal–hydrogen bond by a BHB bridged hydrogen.

Examination of the ^1H n.m.r. spectrum of (I) showed a resonance centred at τ 9·83, which is assigned to CH_{ax}, the Me(5) and Me(9) resonances being partially obscured by the ethyl resonance of the Et_3P ligands. However, the spectrum of the bis(triphenylphosphine)-platinum analogue (V) showed resonances at τ 8·40 [dd, with ^{195}Pt satellites, 3H, Me(5), $J(HP^1) \simeq J(HP^2) \simeq 4·0$ Hz, J(HPt) 16·0 Hz], 8·66 [d, 3H, Me(9), $J(HH_{ax})$ 6·0 Hz] and 9·38 [broad, 1H, H_{ax}].

These observations contrast with the report[8] that the dianion 1,3-$B_7C_2H_{11}^{2-}$ derived from 1,3-$B_7C_2H_{13}$ reacts with $CoCl_2$ to give complexes of the $B_7C_2H_9^{2-}$ ion, in which two carbons and three borons are bonded to the transition metal.

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† We have chosen to number the atoms according to IUPAC rules as a heterodecaborane rather than as a metal-ligand complex.

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