

## Preparation and Properties of $[\pi-(C_6H_5)_4C_4]Pd[\pi-B_9C_2H_{11}]$

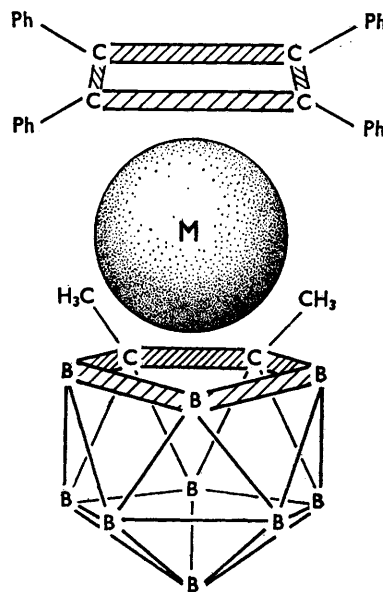
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THE recent discovery of the (1)-2,3- and (1)-2,4-dicarbollide ions,  $[B_9C_2H_{11}]^{2-}$ , has led to the preparation of numerous "sandwich" complexes in which a transition-metal ion fills the open pentagonal face of two dicarbollide ions.<sup>1,2</sup> Mixed sandwich compounds<sup>3,4</sup> containing a cyclopentadienide ring and a dicarbollide cage have also been reported as have carbonyl metal dicarbollide complexes such as  $\pi-B_9C_2H_{11}Re(CO)_3$ .<sup>5,6</sup>

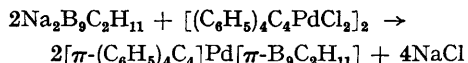
We now wish to expand further the scope of reported dicarbollide ion reactions by describing representative compounds which contain a tetraphenylcyclobutadiene ring and a dicarbollide ion symmetrically sandwich bonded to  $Pd^{II}$  (Figure). Two such derivatives,  $[\pi-(C_6H_5)_4C_4]Pd[\pi-B_9C_2H_{11}]$  (I), m.p. 308–309°, and  $[\pi-(C_6H_5)_4C_4]Pd[\pi-B_9C_2H_9-(CH_3)_2]$  (II), m.p. >325° decomp., have been prepared. The latter compound bears methyl groups at the two carborane carbon atoms of the dicarbollide cage. The formation of (I) and (II), which are structurally analogous to the recently synthesized  $(\pi-(C_6H_5)_4C_4)Pd[\pi-C_5H_5]$  cation,<sup>7</sup> yields further evidence that the scope of dicarbollide ion chemistry is at least as broad as that of the cyclopentadienide ion.

The palladium complexes were formed according



FIGURE

to the following equation using the disodium (1)-2,3-dicarbollide salt prepared in pure tetrahydrofuran.



The  $[(\text{C}_6\text{H}_5)_4\text{C}_4\text{PdCl}_2]_2$  complex was prepared by the method of Maitlis.<sup>8</sup> The yields of the desired dicarbollide products were of the order of 10%. The major product of these reactions was a black solid which spontaneously ignites when dry and in the presence of air. Both (I) and (II) were isolated by column chromatography and were further purified by recrystallization from methylene chloride/hexane. Both of the palladium derivatives are readily soluble in chlorinated hydrocarbons, slightly soluble in benzene, and very sparingly soluble in alkanes.

The empirical formulae of (I) and (II) were determined by elemental analyses and osmometric molecular weight data obtained in benzene

solution. The infrared spectra of (I) and (II) contained a B-H stretching band near  $2500\text{ cm}^{-1}$  and a monosubstituted phenyl absorption at  $700\text{ cm}^{-1}$ . The  $^1\text{H}$  n.m.r. spectrum of (II) in methylene chloride shows a multiplet in the phenyl region  $\tau$  2.30, 2.49 (rel. area = 10.3) and a methyl resonance at  $\tau$  8.53 (rel. area = 3) while (I) in the same solvent shows a phenyl resonance centred at  $\tau$  2.55 (rel. area = 13.7) and a broad carborane hydrogen absorption at  $\tau$  7.31 (rel. area = 1). The  $^{11}\text{B}$  n.m.r. spectrum of (I) is broad and structureless while that of (II) is a broad multiplet with resonances at  $\delta = -4.65, 5.70, 10.76$  [ $\text{BF}_3:\text{O}(\text{C}_2\text{H}_5)_2 = 0$ ].

A single crystal X-ray study by Pettersen, Zalkin, and Templeton has confirmed the sandwich structure of (II) and a detailed analysis of the structure will be reported at a later date by those authors.

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