Paramagnetic Borabenzene Cobalt Complexes

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Summary Novel paramagnetic borabenzene cobalt complexes have been synthesized by the reaction of $Co(C_5H_5)_2$ with organoboron dihalides and boron trihalides.

BORABENZENE (C_5H_5B) (**1**) is unknown. We have previously reported the formation of cyclopentadienyl-(1-phenylborabenzene)cobalt cation (**2**),[1] the first known derivative of (**1**). 1-Phenylborabenzenide (**3**) has since become accessible through the work of Ashe and Shu.[2]

We report here a novel class of paramagnetic borabenzene cobalt complexes (**4**) and (**5**) which are obtained by treating bis(cyclopentadienyl)cobalt in hexane or toluene with organoboron dihalides and boron trihalides at temperatures between −80° and 20°. In a typical preparation $PhBBr_2$ (or $PhBCl_2$) in hexane is added to $Co(C_5H_5)_2$ (*ca.* 1 : 3 ratio) in hexane at 20°. Bis(cyclopentadienyl)cobalt salts precipitate instantly and the solution turns deep red. After hydrolysis the organic layer contains (**4a**) as the main product, a small amount of (**5a**), and some unchanged $Co(C_5H_5)_2$. Chromatography on alumina (4% water; eluant: hexane) and crystallization from hexane at low temperature yields pure (**4a**) (dark brown needles; m.p. 70—71°) and (**5a**) (dark red, lustrous plates; m.p. 191—192°). Similarly, with $MeBBr_2$, (**4b**) (m.p. 28°) and (**5b**) (m.p. 98°) are obtained. The stoicheiometry of the main reaction is given by equation (1).

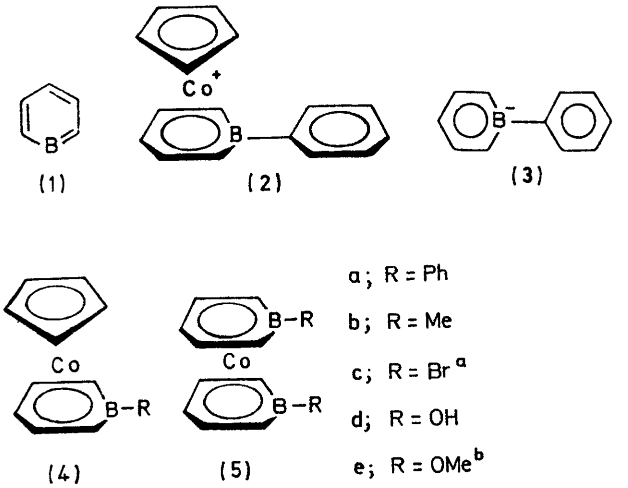

FIGURE (**4c**) and (**5c**) were not isolated, but their identity was inferred from the products; (**4e**) was identified by mass spectroscopy only.

$$3\,Co(C_5H_5)_2 + RBBr_2 \rightarrow 2\,[Co(C_5H_5)_2]Br + Co(C_5H_5)(C_5H_5BR) \qquad (1)$$

R = Ph, Me.

Excess of BBr_3 reacts with bis(cyclopentadienyl)cobalt (ratio ⩾1·3 : 1) roughly according to equation (2). The salts may be filtered off and the deep red filtrate contains (**5c**) as the sole product. Upon hydrolysis (**5d**) (sublimes with partial decomposition at 150—180° in a high vacuum) is formed. Recrystallization from absolute methanol yields (**5e**) (m.p. 98°). At a 1 : 1 ratio of the reactants, however, a mixture of unchanged $Co(C_5H_5)_2$, (**4c**), and (**5c**) is produced, which may be separated by chromatography on alumina (5% water; eluant: Et_2O); $Co(C_5H_5)_2$, (**4d**) (sublimes at 80—100° in a high vacuum and decomposes above 170° without melting), and (**5d**) are successively eluted.

$$5\,Co(C_5H_5)_2 + 6\,BBr_3 \rightarrow 4\,[Co(C_5H_5)_2][BBr_4] + Co(C_5H_5BBr)_2 \qquad (2)$$

The new complexes of type (**4**) and (**5**) have a number of unusual properties in common with bis(cyclopentadienyl)-cobalt. They possess one electron in excess of the inert gas configuration. They are therefore paramagnetic, giving no n.m.r. spectra under normal conditions. Preliminary measurements using the method of Evans[3,4] gave a magnetic moment of 1·8 ± 0·1 B.M. for (**5e**). As for $Co(C_5H_5)_2$ no tendency to form diamagnetic dimers is observed. The ionization potentials are remarkably low (Table). Comparison with the value of $Co(C_5H_5)_2$ shows that the neutral C_5H_5BR radical is a much better electron acceptor in bonding to the metal than is the C_5H_5 radical. Compounds of type (**4**) are far more air sensitive than those of type (**5**). Thermal instability due to the labilizing influence of the extra electron is again more pronounced in the borabenzene(cyclopentadienyl)cobalt complexes (**4**) than in the bis(borabenzene)cobalt complexes (**5**).

TABLE

Ionization potentials determined by electron impact

Compound	I.p. in eV
$Co(C_5H_5)_2$	$6{\cdot}2_1$[a]
(**4a**)	$6{\cdot}6_3$[b]
(**4b**)	$6{\cdot}5_6$
(**5a**)	$7{\cdot}2_5$
(**5b**)	$7{\cdot}1_5$
(**5e**)	$7{\cdot}0_2$

[a] See ref. 5. [b] Relative errors are less than 0·1 eV.

(**4a**), (**4b**), (**4d**), (**5a**), (**5b**), (**5d**), and (**5e**) have been characterized by elemental analyses and mass spectra. Additional structural information may be inferred from the simple one-electron redox relationship [equation (3)] between (**2**) and (**4a**).† Since it is known from ^1H- and

$$(\mathbf{4a}) \underset{Co(C_5H_5)_2}{\overset{Fe^{3+}}{\rightleftharpoons}} (\mathbf{2}) \qquad (3)$$

^{11}B-n.m.r. data that the 1-phenylborabenzenide ligand (**3**) acts as a *hexahapto*-ligand in (**2**),[1] it seems likely that the

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† Similar redox reactions may be effected with all complexes (**4**) and (**5**), thus making accessible a variety of cationic borabenzene cobalt complexes.

same situation occurs in all complexes (**4**) and (**5**). *X*-Ray work on (**5b**) and (**5e**) intended to confirm this assumption is currently in progress.[6]

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