Carborane Analogues of Cobalticinium Ion

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THE preparation of ferrocene and ferricinium ion analogues in which one[1] or both[2] of the cyclopentadienyl rings were replaced by $B_9C_2H_{11}^{2-}$ units has recently been reported.

We now report the synthesis of stable compounds which are analogous to the cobalticinium cation in which a single Co^{III} is simultaneously bound to the open faces of two $B_9C_2H_{11}^{2-}$ units or to one $B_9C_2H_{11}^{2-}$ and one $C_5H_5^-$ unit.

The $B_9C_2H_{12}^-$ ion[3] and its *C*-substituted derivatives appear to have the geometry of an eleven-particle icosahedral fragment. They are readily converted into $B_9C_2H_{11}^{2-}$, (I), by the abstraction of a proton with sodium or sodium hydride in tetrahydrofuran solution. Addition of this solution (2 moles) to a solution of anhydrous $CoCl_2$ (1·5 moles) in tetrahydrofuran gave rise to a precipitate of cobalt metal (0·5 g.-atom) and sodium chloride (3 moles); the solution becoming deeply coloured. In contrast to cobaltocene,[4] a suspension of $Co(NH_3)_6Cl_2$ was also reduced to cobalt metal giving the Co^{III} product (II). ($M = Co^{III}$.)

The compounds were isolated as their cæsium or tetramethylammonium salts in yields as high as 92%. The salts[5] of unsubstituted (II) are yellow [λ_{max} (ϵ): 216 (36,000), 293 (45,000), 345 (2,200), 445 (440)].

Polarography of (II) gave reversible one-electron reductions at the unusually high[6] potentials of −1·42 v (unsubstituted) −1·16 v (*CC'*-dimethyl-), and −1·28 v (*C*-phenyl-). Chemical reduction was possible with n-butyl-lithium to give an intensely purple cobaltocene analogue $[(B_9C_2H_{11})_2Co^{II}]^{2-}$ which was rapidly oxidised to (II) by air. The ^{11}B n.m.r. spectrum of (II) extended over 35 p.p.m., but has not yet been conclusively interpreted apart from showing a gross similarity to the iron derivative,[2] $[(B_9C_2H_{11})_2Fe^{II}]^{2-}$.

The neutral compound (III) was prepared from an equimolar mixture of $C_5H_5^-$ and $B_9C_2H_{11}^{2-}$ ions and anhydrous $CoCl_2$ in tetrahydrofuran solution. The crude material was obtained in a yield of 72%, considerably higher than that

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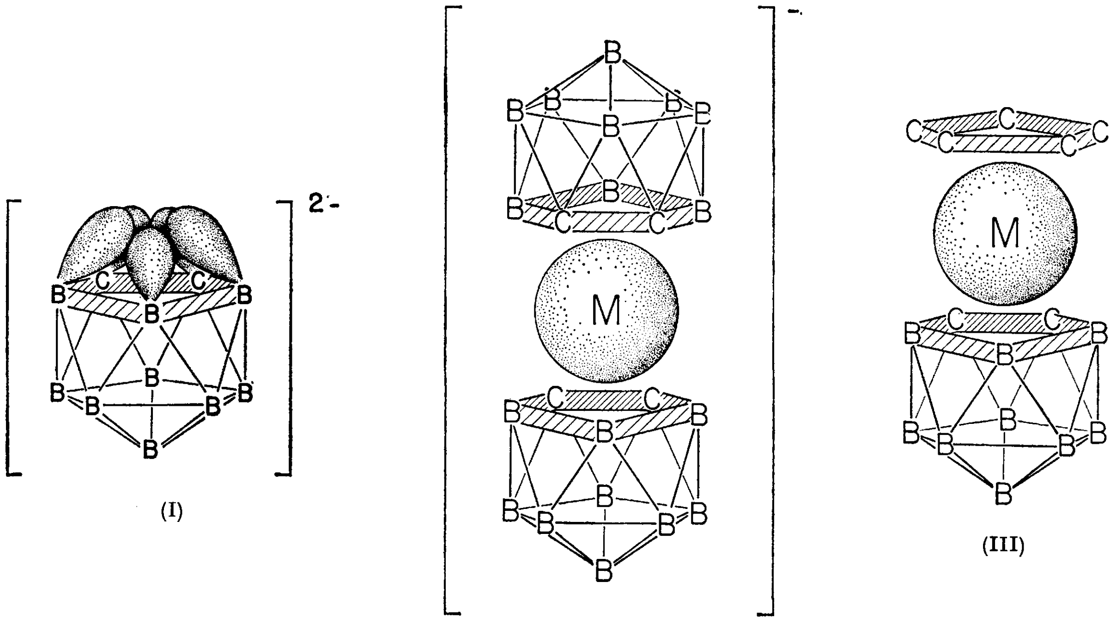
[1] M. F. Hawthorne and R. L. Pilling, *J. Amer. Chem. Soc.*, 1965, in press.
[2] M. F. Hawthorne, D. C. Young, and P. A. Wegner, *J. Amer. Chem. Soc.*, 1965, **87**, 1818.
[3] M. F. Hawthorne and R. A. Wiesboeck, *J. Amer. Chem. Soc.*, 1964, **86**, 1642.
[4] J. F. Cordes, *Chem. Ber.*, 1962, **95**, 3084.
[5] Satisfactory analyses and equivalent weights were obtained for the new compounds reported.
[6] Against standard calomel electrode.

predicted on a purely statistical basis. Recrystallisation from a hexane–dichloromethane mixture gave yellow plates m.p. 247—248°,[7] [λ_{max} (ϵ) 208 (54,000), 273 (33,600), 320 (545), 422 (400)].



(I)

(II)

(III)

Structures of (I), (II), *and* (III) *with H-atoms omitted and showing the* sp^3 *hybrid atomic orbitals assumed to be present in* $B_9C_2H_{11}^{2-}$.

The structure (III) was assigned by analogy with the similar Fe^{III} derivative[1] of known structure.[8] This is consistent with the ^1H n.m.r. which shows a broad carborane C–H resonance of relative intensity 2·0 at $-4{\cdot}25$ p.p.m.[9] and a sharp singlet of relative intensity 5·0 at $-5{\cdot}74$ p.p.m. assigned to the cyclopentadienyl protons. Cobalticinium derivatives exhibit proton resonances at $-4{\cdot}5$ to $-4{\cdot}75$ p.p.m.[10]

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[7] Uncorrected m.p.

[8] A. Zalkin, D. H. Templeton, and T. E. Hopkins, *J. Amer. Chem. Soc.*, 1965, in press.

[9] Relative to tetramethylsilane.

[10] M. L. H. Green, L. Pratt, and A. Wilkinson, *J. Chem. Soc.*, 1959, 3753.