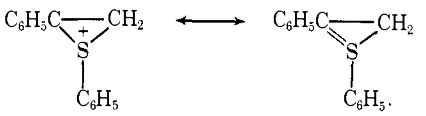
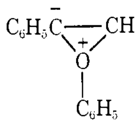
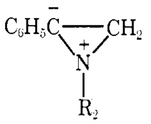


XVa XVb

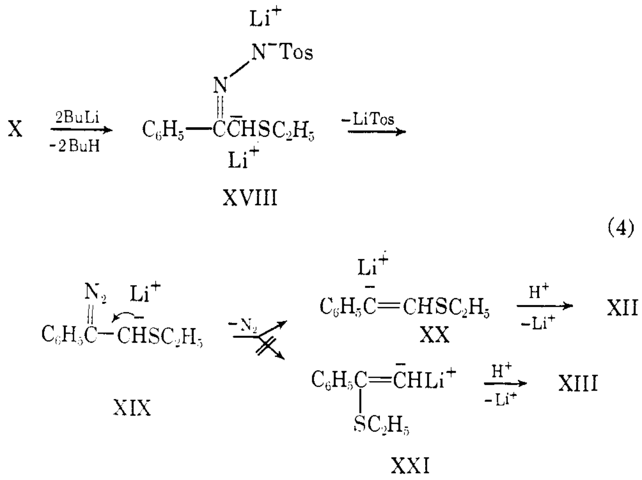


XVI



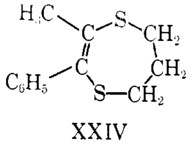
XVII

used.[9] Reaction of X with butyllithium (2.1-3.1 equiv) in decalin at 120° and neutralization result in exclusive formation of XII; the thioethoxy group does not migrate. It is probable that X, in the presence of excess butyllithium, collapses primarily as its dianion (XVIII, eq 4) to XIX which then decomposes to XX rather than to XXI.[9] Conversion of X to XVIII is indicated by its reaction with butyllithium (3.0 equiv) in tetrahydrofuran at 0° and neutralization by deuteriotrifluoroacetic acid (3 equiv) to give N,2-dideuterio-2-ethylmercaptoacetophenone p-tosylhydrazone[10] (99% isotopic purity). Further evidence for the mechanism sequence proposed is derived by demonstration that the dry salt obtained from 3 equiv of butyllithium and X decomposes thermally to an intense red intermediate which loses nitrogen and then gives XII after neutralization.

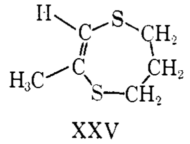


(4)

Salts of 2-benzoyl-2-methyl-1,3-dithiane p-tosylhydrazone (XXII, mp 145°) and 2-formoyl-2-methyl-1,3-dithiane p-tosylhydrazone (XXIII, mp 123°) decompose to 2-methyl-3-phenyl-1,4-dithia-2-cycloheptene (XXIV) and 2-methyl-1,4-dithia-2-cycloheptene (XXV), respectively. Ring expansion rather than methyl migration in these systems again reflects the marked ability of β-thioether groups to undergo carbenic rearrangement. The structure of XXIV is assigned from its nmr and its hydrogenation over nickel to 1-phenylpropane; XXV is established from its nmr signals (τ) at 8.15 (doublet, area 3, $J \sim 1$ cps), 7.85 (multiplet, area 2), 6.55 and 6.60 (superimposed triplets, area 4), and 4.32 (quartet, area 1).



XXIV



XXV

The effects of other neighboring groups in carbenic rearrangement are being investigated.

Acknowledgment. This research was supported by the National Science Foundation.

John H. Robson, Harold Shechter
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

Received August 28, 1967

---

[9] (a) W. Kirmse, B. G. von Bülow, and H. Schepp, *Ann.*, **691**, 41 (1966), also report that decomposition of salts of p-tosylhydrazones is altered in excess (7-8 equiv) sodium amide or sodium hydride. For additional description and discussion of the effects of excess butyllithium on the decomposition of p-tosylhydrazones, see R. H. Shapiro and M. J. Heath, *J. Am. Chem. Soc.*, **89**, 5734 (1967); G. Kaufmann, F. Cook, H. Shechter, J. Bayless, and L. Friedman, *ibid.*, **89**, 5736 (1967). (b) The present mechanism involving p-tosylhydrazone dianions differs from that of Kirmse, *et al.*

[10] The deuterium content and positions were established by nmr methods.

New Polyhedral Transition Metal Complexes Containing the $B_7C_2H_9^{-2}$ Ligand

Sir:

The recent discovery of polyhedral transition metal complexes in which the metal is "sandwich" bonded to two 11-particle icosahedral carborane fragments[1] (dicarbollide ion, $B_9C_2H_{11}^{-2}$) led us to investigate routes to similar structures which contain smaller $B_nC_2H_{n+2}^{-2}$ ligands. In this and the accompanying communication we report the synthesis of representative polyhedral species which contain the $B_7C_2H_9^{-2}$ and $B_6C_2H_8^{-2}$ ligands coordinated to transition metals.

The previously described $B_7C_2H_{13}$ carborane[2] reacts with 2 moles of sodium hydride in diethyl ether to produce the $B_7C_2H_{11}^{-2}$ ion. Treatment of this ion with cobalt(II) chloride in diethyl ether solvent results in the formation of hydrogen, cobalt metal, and the very stable complex $(B_7C_2H_9)_2Co^-$ (I), which contains cobalt in the formal oxidation state +3. Yields of I were 51%. The salts of $Co^{III}[B_7C_2H_9]_2^-$ are brown [λ_{max} mμ (ϵ): 224 (16,000), 261 (sh) (8950), 290 (sh) (7900), and 373 (5050)]. *Anal.* Calcd for $(CH_3)_4N(B_7C_2H_9)_2Co$: C, 27.41; H, 8.63; B, 43.15; N, 4.00; Co, 16.81; equiv wt, 351. Found: C, 27.12; H, 8.60; B, 43.22; N, 4.30; Co, 16.93; equiv wt, 340. The formula weight of the tetraethylammonium salt was determined: calcd for $(C_2H_5)_4N(B_7C_2H_9)_2Co$, 405; found, 407 (osmometric), assuming 100% dissociation in acetone solution.

$$2B_7C_2H_{11}^{-2} + 1.5Co^{+2} \longrightarrow 0.5Co^0 + 2H_2 + (B_7C_2H_9)_2Co^-$$

The 60-Mc/sec ^1H nmr spectrum of the tetramethylammonium salt of I contained a sharp singlet of intensity 12 at τ 6.22 and two broad singlets, each of intensity 2, at τ 3.40 and 4.80. The former resonance was assigned to the methyl protons of the cation and the two smaller resonances to two dissimilar sets of protons attached to the carbon atoms of the complex. The 32-Mc/sec ^{11}B nmr spectrum of I consisted of a low-field doublet and an overlapped array of six distinct doublets which correspond to seven distinct types of B atoms in the complex.

---

[1] (a) M. F. Hawthorne, D. C. Young, and P. A. Wegner, *J. Am. Chem. Soc.*, **87**, 1818 (1965); (b) M. F. Hawthorne and T. D. Andrews, *Chem. Commun.*, 443 (1965).

[2] F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **88**, 607 (1966).

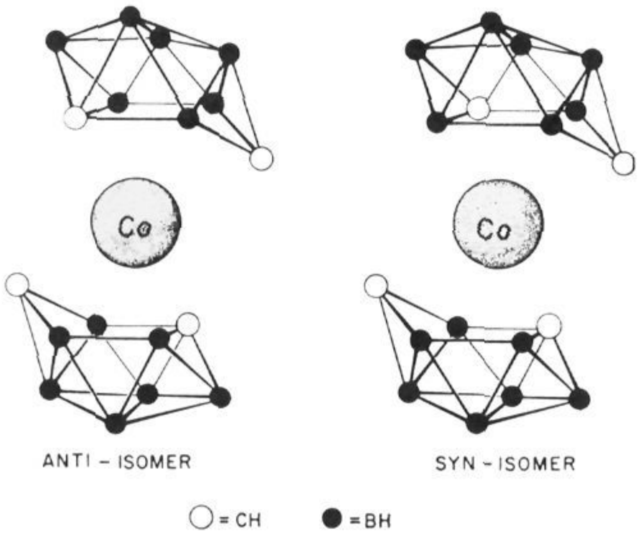


Figure 1. Possible isomer structures of the $(B_7C_2H_9)_2Co^-$ ion.

These nmr results prove that the $B_7C_2H_9^{-2}$ ligand has very low symmetry with all carbon and boron atoms in unique environments.

A mixed complex (II) of formal cobalt(III) was prepared in 36% yield from the reaction of cobalt(II) chloride with the $B_7C_2H_{11}^{-2}$ ion and a fivefold excess of the $C_5H_5^-$ ion in diethyl ether. The red complex (II) was easily purified by sublimation or by recrystallization from hexane, mp 158–159°. *Anal.* Calcd for $(B_7C_2H_9)Co(C_5H_5)$: C, 36.12; H, 6.06; B, 32.80; Co, 25.31. Found: C, 36.10; H, 6.09; B, 32.90; Co, 25.07. High-resolution mass spectroscopy unequivocally verified the formulation $CoB_7C_7H_{14}$: calcd for $^{59}Co^{11}B_7{}^{12}C_7{}^1H_{14}$, 234.108; found, 234.109. The electronic spectrum was determined in acetonitrile [λ_{max} mμ (ϵ): 270 (15,400), 315 (4800), 365(sh) (1800), and 502 (345)].

$$C_5H_5^- + 1.5Co^{+2} + B_7C_2H_{11}^{-2} \longrightarrow H_2 + 0.5Co^0 + (C_5H_5)Co(B_7C_2H_9)$$

The 60-Mc/sec ^1H nmr spectrum of II contained a sharp cyclopentadienyl resonance at τ 3.9. The protons associated with the carbon atoms of the $B_7C_2H_9^{-2}$ ligand were very broad and appeared at τ 2.31 and 6.23. The 32-Mc/sec ^{11}B nmr spectrum resembled that obtained with the complex I and consisted of seven discrete doublets.

Since the nmr results, composition, and charge type of both I and II indicate that each carbon and boron atom carries one proton and that cobalt(III) couples two ligands (identical in the case of I), it is attractive to formulate the gross structures of I and II as species in which the metal ion completes a polyhedral surface containing one or two $B_7C_2H_9^{-2}$ fragments. This being the case, one would expect the complex polyhedron to resemble the well-known $B_{10}H_{10}^{-2}$,[3] $B_9CH_{10}^-$,[4] and $B_8C_2H_{10}$[5] structures. Ruling out the possibility of carbon-atom nearest neighbors and giving cobalt a coordination number of 5, including two carbon atoms (one at an apex position since the ^{11}B nmr spectrum indicated one apical boron atom at low field),[6] we were led to propose structures such as those shown in Figures 1 and 2. Preliminary X-ray diffraction results obtained by using tetraethylammonium(I) confirm[7] this gross structure of I and place the carbon-atom positions as shown in the antiisomer of Figure 1.

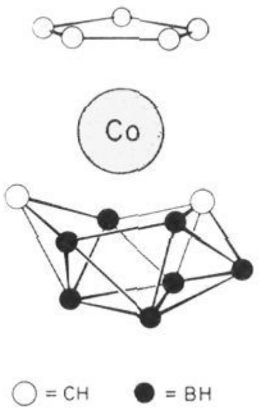


Figure 2. Proposed structure of $(C_5H_5)Co(B_7C_2H_9)$.

While only the complexes of formal cobalt(III) were presented here, further preliminary work suggests that many other polyhedral complexes may be prepared which incorporate the $B_7C_2H_9^{-2}$ ligand. Further work is in progress.

Acknowledgment. This research was supported in part by the Office of Naval Research.

M. Frederick Hawthorne, T. Adrian George
Department of Chemistry, The University of California
Riverside, California 92502

Received November 8, 1967

---

[3] M. F. Hawthorne and A. R. Pitochelli, *J. Am. Chem. Soc.*, **81**, 5519 (1959).

[4] W. H. Knoth, *ibid.*, **89**, 1274 (1967).

[5] F. N. Tebbe, P. M. Garrett, D. C. Young, and M. F. Hawthorne, *ibid.*, **88**, 609 (1966).

[6] W. N. Lipscomb, A. R. Pitochelli, and M. F. Hawthorne, *ibid.*, **81**, 5833 (1959).

[7] We are indebted to D. H. Templeton, A. Zalkin, and D. St. Clair for the communication of these preliminary results.

The $B_6C_2H_8^{-2}$ Ligand in a New Polyhedral Transition Metal Complex Containing Manganese

Sir:

The accompanying communication[1] describes the preparation of two polyhedral cobalt complexes which contain the $B_7C_2H_9^{-2}$ ligand and in which the transition metal completes a bicapped Archimedean antiprism. We now wish to describe the preparation of what may prove to be a polyhedral complex which assumes a tricapped trigonal prism configuration with a $B_6C_2H_8^{-2}$ ligand in conjunction with a transition metal.

The reaction of $BrMn(CO)_5$[2] with the $B_7C_2H_{11}^{-2}$ ion[1] in tetrahydrofuran solution at the reflux temperature led to the formation of $Mn_2(CO)_{10}$, unidentified solids, H_2, CO, and a 48% yield of a new anion (I). The $Mn_2(CO)_{10}$ and sodium I were separated by using column chromatography on silica gel with hydrocarbon solvents. The tetramethylammonium or $BH_2(py)_2^+$ salts of I were prepared by precipitation from water and recrystallized from organic solvents. Salts of I were stable indefinitelu in the solid state in air but decomposed slowly in solytion. The anion I was characterized as $B_6C_2H_8Mn(CO)_3^-$. *Anal.* Calcd for $CsB_6C_2H_8Mn(CO)_3$: B, 17.54; C, 16.27; H, 2.17; Cs, 36.03; Mn, 14.88. Found: B, 17.91; C, 16.22; H, 2.13; Cs, 34.85; Mn, 14.54. Calcd for $(CH_3)_4NB_6C_2H_8Mn(CO)_3$: equiv wt, 309.7. Found: equiv wt, 312. Calcd for $(C_2H_5)_4NB_6C_2H_8Mn(CO)_3$: formula wt, 366. Found: formula wt, 369, assuming 100% dissociation in acetone solution (osmometric). An infrared spectrum of the tetramethyl-

---

[1] M. F. Hawthorne and T. A. George, *J. Am. Chem. Soc.*, **89**, 7114 (1967).

[2] E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1501 (1959).