Synthesis of Transition Metal-Monocarbon Carborane Complexes

Sir:

We wish to report the facile synthesis of complexes of the $B_{10}H_{10}CH^{3-}$ and $B_{10}H_{10}CNH_2R^{2-}$ ions with several transition metals.[1] The syntheses are based on two general reactions very closely related to the preparative methods recently described for the (3)-1,2-dicarbollyl sandwich complexes:[2,3] (1) $Na_3B_{10}H_{10}CH$ and anhydrous metal chloride, and (2) $CsB_{10}H_{12}CH$, aqueous sodium hydroxide, and metal chloride.

Table I. Analyses

Compound	Calculated, % C	H	N	B	Metal	Found, % C	H	N	B	Metal
$[(CH_3)_4N]_3Co(B_{10}H_{10}CH)_2$	30.91	10.74	7.72	39.78	10.84	30.99	10.80	7.58	39.73	10.6
$Cs_2Ni(B_{10}H_{10}CH)_2$	4.09	3.78	...	36.84	10.00	3.77	3.90	...	36.55	9.8
$[(CH_3)_4N]_3Fe(B_{10}H_{10}CH)_2$	31.05	10.80	7.78	40.07	10.30	30.92	10.98	7.59	...	9.8
$(CH_3)_4NCo(B_{10}H_{10}CNH_2C_2H_5)_2$	24.83	9.59	8.69	44.70	12.18	25.09	9.63	8.67	...	12.6
$Ni(B_{10}H_{10}CNH_2C_3H_7)_2$	22.01	8.76	6.42	49.45	13.44	22.05	9.08	6.40	...	12.9

The $B_{10}H_{10}CH^{3-}$ ion is readily prepared as a sparingly soluble sodium salt (I) by deamination and deprotonation of $B_{10}H_{12}CN(CH_3)_3$ with sodium metal in tetrahydrofuran (THF).[4] Addition of I to a solution of anhydrous $CoCl_2$ in THF yielded a precipitate of cobalt metal and sodium chloride. The $Co^{III}(B_{10}H_{10}CH)_2^{3-}$ ion (II) was isolated as either the cesium or tetramethylammonium salt. The salts of II are diamagnetic and yellow [λ_{max} (ϵ): 279 (36,600) and 422 mμ (382)].

The second type of reaction is illustrated by the synthesis of the $Ni^{IV}(B_{10}H_{10}CH)_2^{2-}$ ion (III). An aqueous mixture of $NiCl_2$ (13.5 mmoles), $CsB_{10}H_{12}CH$ (22.1 mmoles), and sodium hydroxide (270 mmoles) was heated at 40° with air injection for 20 hr. The yellow, diamagnetic cesium salt of III could be isolated in yields as high as 82% from this reaction. By this method one can also obtain good yields of II and salts of the red $Fe^{III}(B_{10}H_{10}CH)_2^{3-}$ ion (IV).

Preliminary X-ray data on $Cs_2Ni^{IV}(B_{10}H_{10}CH)_2$ yield the cell parameters: $a = 20.25$, $b = 12.77$, $c = 14.64$ A, $z = 8$, d(calcd) 2.08, d(found) 2.04. The ^{11}B nmr spectra of II and III extend over 29 ppm and are grossly similar to one another but have not been completely interpreted. The paramagnetic ion (IV) has a ^{11}B nmr spectrum which extends over approximately 300 ppm and does not appear to show $^{11}B-^{1}H$ coupling.[5]

Treatment of $B_{10}H_{12}CNH_2C_3H_7$[6] with $NiCl_2$ in aqueous base gives in good yield, orange, diamagnetic $Ni^{IV}(B_{10}H_{10}CNH_2C_3H_7)_2$ (V). The mass spectrum of V cuts off sharply at m/e 444 corresponding to the parent ion, $^{12}C_8{}^{1}H_{38}{}^{14}N_2{}^{11}B_{20}{}^{62}Ni^+$. Orange, diamagnetic $(CH_3)_4NCo^{III}(B_{10}H_{10}CHNH_2C_2H_5)_2$ (VI) was obtained in the same manner. Methylation of V with sodium bicarbonate and methyl iodide gives dark orange $Ni^{IV}[B_{10}H_{10}NH(CH_3)C_3H_7]_2$. The ^{11}B nmr spectra of these amine derivatives extend over 29 ppm and are similar to those of the unsubstituted complexes but are not as well resolved. Analyses of the compounds are given in Table I.

The striking similarity in properties of the metal complexes reported in this paper and their isoelectronic dicarbollide analogs leads us to suggest that the transition metal in these compounds is π-bonded to the open face of two monocarbon carborane (carbollide) icosahedral fragments. Thus the Co^{III} species II and VI are apparent analogs of the cobalticinium ion and the Fe^{III} species IV analogous to the ferricinium ion. A single crystal X-ray study now in progress should lend support to this postulate.

Salts of the $(B_{10}H_{10}CH)Mn(CO)_3^{2-}$ and $Cu^{III}(B_{10}H_{10}CH)_2^{3-}$ ions have also been obtained from $BrMn(CO)_5$ and copper(II) acetylacetonate, respectively, by the anhydrous route with $Na_3B_{10}H_{10}CH$. The ^{11}B nmr spectra of these ions which extend over 20 ppm are similar to one another but dissimilar to the spectra of the nickel and cobalt derivatives.

Further synthetic and structural studies of these new carbollyl–transition metal complexes are in progress and will be reported at a later date.

Acknowledgment. The authors wish to thank Mr. J. Nemeth for the microanalyses, Dr. Donald F. Gaines, University of Wisconsin, for the 32-Mc ^{11}B nmr, and the National Science Foundation for support under Grant GP-4982.

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Received April 5, 1967

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[1] We are indebted to Dr. Knoth, who recently advised us of his work in this area: W. H. Knoth, *J. Am. Chem. Soc.*, **89**, 3342 (1967).

[2] M. F. Hawthorne, D. C. Young, and P. A. Wegner, *ibid.*, **87**, 1818 (1965).

[3] L. F. Warren, Jr., and M. F. Hawthorne, *ibid.*, **89**, 470 (1967).

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

[5] A similar broad, decoupled spectrum was observed for the $Fe^{III}(B_9C_2H_{11})_2^-$ ion; see ref 2.

[6] D. E. Hyatt, D. A. Owen, and L. J. Todd, *Inorg. Chem.*, **5**, 1749 (1966).

Transition Metal Complexes of $B_{10}H_{10}CNH_3^{2-}$ and $B_{10}H_{10}CH^{3-}$

Sir:

A series of sandwich complexes of transition metals with the $B_9C_2H_{11}^{2-}$ anion has been reported by Hawthorne and co-workers.[1] These complexes are formally analogous to metallocenes because the metal in both cases is bonded to a pentagonal face which can contribute three bonding molecular orbitals and six electrons.[2,3]

This communication reports the preparation of similar metal complexes of $B_{10}H_{10}CNH_3^{2-}$ and $B_{10}H_{10}$-

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[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); (c) L. F. Warren, Jr., and M. F. Hawthorne, *J. Am. Chem. Soc.*, **89**, 470 (1967).

[2] M. F. Hawthorne and R. C. Pilling, *ibid.*, **87**, 3987 (1965).

[3] A. Zalkin, D. H. Templeton, and T. E. Hopkins, *ibid.*, **87**, 3988 (1965).

Table I. Representative Analyses

Compound	Calculated, %					Found, %				
	B	C	H	N	M	B	C	H	N	M
$Cs_3(B_{10}H_{10}CH)_2Cr \cdot H_2O$[a]	29.6	3.3	3.3	...	...	30.2	3.5	3.1	...	...
$[(CH_3)_3NH]_2(B_{10}H_{10}CH)_2Mn$	49.5	21.9	9.7	6.4	12.5	49.5	22.6	9.5	6.2	11.7
$Cs_3(B_{10}H_{10}CH)_2Co \cdot H_2O$[a]	29.3	3.2	3.2	...	8.0	29.6	3.0	3.3	...	8.0
$[(CH_3)_4N]_3(B_{10}H_{10}CH)_2Co$	46.0	25.5	9.8	6.0	12.6	45.4	25.6	9.9	6.2	12.2
$Cs_2(B_{10}H_{10}CH)_2Ni$	36.8	...	...	...	10.0	36.7	...	...	...	10.1
$(CH_3)_4N(B_{10}H_{10}CNH_3)_2Fe$	51.0	17.0	9.0	9.9	13.1	50.0	17.1	9.5	9.7	13.3
$[(CH_3)_4N]_2B_{10}H_{10}CNH_2CoB_{10}H_{10}CNH_3$	...	23.9	9.9	11.2	11.8	...	23.9	10.2	11.0	11.9
$[B_{10}H_{10}CNH(CH_3)_2]_2Ni$	53.0	17.6	8.4	6.8	14.3	53.0	17.7	8.9	7.2	14.3
$[(CH_3)_4N]_2(B_{10}H_{10}COH)_2Ni$	43.1	24.0	9.2	5.6	11.8	42.9	24.0	9.4	5.8	11.7

[a] The presence of water of hydration was established by infrared analysis.

CH^{3-} by the reactions of $B_{10}H_{12}CNH_3$[4] and $B_{10}H_{12}CH^-$[4] with transition metal halides under basic conditions.[5] The facile, essentially one-step, preparation of $B_{10}H_{12}CNH_3$ from decaborane and sodium cyanide makes the $B_{10}H_{10}CNH_3^{2-}$–metal complexes particularly accessible; $B_{10}H_{12}CH^-$ is prepared in two steps from $B_{10}H_{12}CNH_3$.[4]

Cobalt, nickel, manganese, and iron complexes have been prepared from both $B_{10}H_{12}CNH_3$ and $B_{10}H_{12}CH^-$; in addition a chromium complex has been prepared from the latter. These species have the general formulas $(B_{10}H_{10}CNH_3)_2M$ and $(B_{10}H_{10}CH)_2M$. The over-all charge is dependent on the formal valence of the metal and, for the aminated complexes, also on the degree of protonation of the nitrogen. For example, the complex of Co(III) with the aminated ligand has been isolated as salts of the $B_{10}H_{10}CNH_2CoB_{10}H_{10}CNH_3^{2-}$ and $(B_{10}H_{10}CNH_3)_2Co^-$ anions.

It has been shown[1c] that the $B_9C_2H_{11}^{2-}$ ligand stabilizes relatively high metal oxidation states; *e.g.*, $(B_9C_2H_{11})_2Ni^-$, which is a Ni(III) complex, can be oxidized to a Ni(IV) species, $(B_9C_2H_{11})_2Ni$. The $B_{10}H_{10}CNH_3^{2-}$ and $B_{10}H_{10}CH^{3-}$ ligands also stabilize high oxidation states; in fact, they may be superior to $B_9C_2H_{11}^{2-}$ in this respect because in their complexes Ni(IV) is the *preferred* oxidation state (*i.e.*, the isolated products contain Ni(IV) without the need for an additional oxidation step). Furthermore, the yellow-orange, diamagnetic $(B_{10}H_{10}CH)_2Co^{3-}$ anion, which contains Co(III), is oxidized by ceric ion to an almost black, paramagnetic $(B_{10}H_{10}CH)_2Co^{2-}$ ion, which formally contains Co(IV). The formal oxidation states in the manganese, iron, cobalt, and chromium complexes as isolated are IV, III, III, and III, respectively. Analyses of representative compounds are given in Table I.

The preparations of the complexes are simple and consist of adding *n*-butyllithium to a mixture of a metal(II) halide (except that $CrCl_3$ is used to prepare the chromium compound) and $B_{10}H_{12}CNH_3$ or a salt of $B_{10}H_{12}CH^-$ in tetrahydrofuran. An even more convenient preparation of the cobalt and nickel complexes consists of treating $CoCl_2$ or $NiCl_2$ with $B_{10}H_{12}CNH_3$ or $B_{10}H_{12}CH^-$ in aqueous sodium hydroxide. The isolated Fe(III) products are formed by spontaneous air oxidation of the analogous Fe(II) species; oxidation of the other metals to the states observed in the isolated products occurs with concurrent reduction of excess metal halide. The two-electron oxidations (M(II) → M(IV)) may involve both air oxidation and disproportionation.

The iron-, nickel-, chromium-, and cobalt(III) complexes are quite stable in air and are not readily decomposed by acids, consistent with the behavior reported[1] for the $B_9C_2H_{11}^{2-}$ metal complexes. The manganese complexes decompose slowly in acetonitrile solution; the products have not been identified.

Although the structures of the complexes have not been unequivocally established, it is quite reasonable to assume they are analogous to those of the $B_9C_2H_{11}^{2-}$ metal sandwich species.[1–3] This assumption is based on the isoelectronic relationship of $B_9C_2H_{11}^{2-}$ with $B_{10}H_{10}CH^{3-}$ and $B_{10}H_{10}CNH_3^{2-}$ and on the chemical similarities noted above for their respective metal complexes. The proposed structure is shown in Figure 1.

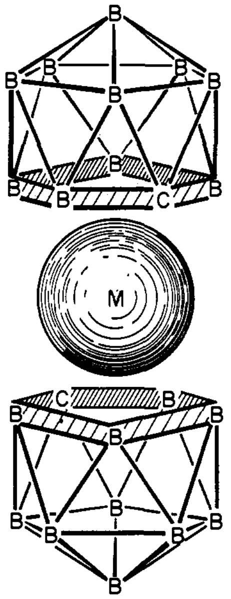

Figure 1. Proposed skeletal structure for metal sandwich complexes of $B_{10}H_{10}CH^{3-}$ and its derivatives

The metal complexes derived from $B_{10}H_{12}CNH_3$ are of particular interest, not only because of the facile preparation of this aminocarborane, but also because the amine group provides convenient access to other C-substituted complexes. For example, the reactions of $(B_{10}H_{10}CNH_3)_2Ni$ with nitrous acid and with dimethyl sulfate have given $(B_{10}H_{10}COH)_2Ni^{2-}$ and $[B_{10}H_{10}CNH(CH_3)_2]_2Ni$, respectively. An N-alkylated analog, $(B_{10}H_{10}CNH_2CH_2C_6H_5)_2Ni$, has also been pre-

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[4] W. H. Knoth, *J. Am. Chem. Soc.*, **89**, 1274 (1967).

[5] Closely related work has been reported: D. E. Hyatt, J. L. Little, J. T. Moran, F. R. Scholer, and L. J. Todd, *ibid.*, **89**, 3342 (1967).

pared by the reaction of $B_{10}H_{12}CNH_2CH_2C_6H_5$[4] with $NiCl_2$ in aqueous sodium hydroxide.

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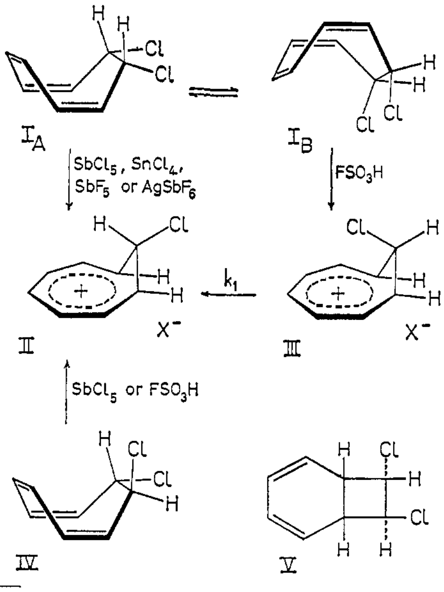
Received April 5, 1967

endo- and *exo*-8-Chlorohomotropylium Salts

Sir:

The occurrence of an 8-halohomotropylium ion as an intermediate in the halogenation of cyclooctatetraene is conceivable. It would explain the unique features of this reaction.[1] To provide evidence for this mechanistic possibility, we prepared *exo*- and *endo*-8-chlorohomotropylium salts. von Rosenberg, Mahler, and Pettit[2] obtained stable homotropylium salts by the reaction of cyclooctatetraene with strong acids. Further studies in the laboratories of Winstein[3] and Pettit[4] confirmed the homoaromatic character of the cationic species.

We treated *cis*-7,8-dichlorocycloocta-1,3,5-triene[5] (IA and IB) with antimony pentachloride in dichloromethane at −15° and isolated the crystalline, colorless *exo*-8-chlorohomotropylium hexachloroantimonate (II, $X^- = SbCl_6^-$) in 95% yield.[6] The salt (mp 82–85° dec in a sealed tube) is stable at room temperature but decomposes on exposure to moist air. Structural assignment is based on the nmr spectrum (CD_3NO_2).[7] The homoaromatic protons at positions 2–6 are centered at τ 1.1 (multiplet); protons 1 and 7 give rise to a triplet at τ 2.82 with $J_{12} = J_{18} = 8.2$ cps. The aromatic ring current shifts the triplet of the *endo*-8-H to τ 8.20.



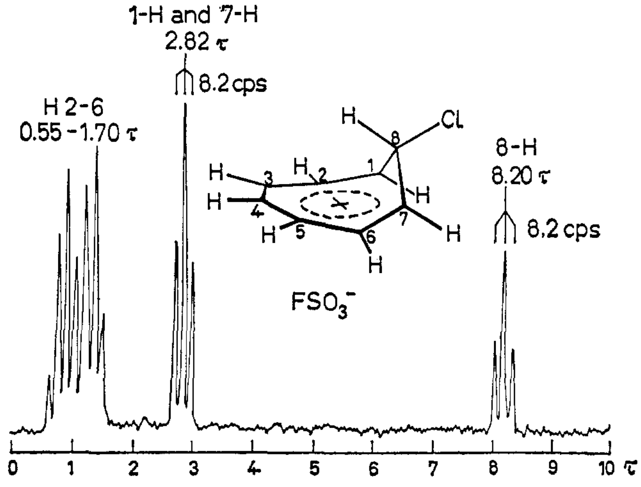


Figure 1. Nmr spectrum (FSO_3H) of *exo*-8-chlorohomotropylium fluorosulfonate at 20°.[8]

The spectrum corresponds well with that of the homotropylium hexachloroantimonate[2] after making allowance for the effect of the *exo*-8-chlorine. The spectrum of II ($X^- = FSO_3^-$) in fluorosulfonic acid (Figure 1) is very similar.

IA and IB exist at −15° in a mobile 46:54 equilibrium.[5] Besides $SbCl_5$ (in CH_2Cl_2 or SO_2), $SnCl_4$ (in CH_2Cl_2; II, $X^- = SnCl_5^-$)[6] or $AgSbF_6$ (in SO_2 or CD_3NO_2), respectively, also cause chloride elimination from the *exo,cis*-dichloride IA to give the *exo*-8-chloro cation II.

In contrast, fluorosulfonic acid attacks the *endo*-dichloro conformer IB. Treatment with ≥ 4 equiv of FSO_3H in SO_2 or with pure FSO_3H below 0° converted IB to the *endo*-8-chlorohomotropylium salt III ($X^- = FSO_3^-$). Also shown by the nmr spectrum of III (Figure 2[8]) is the equality of vicinal coupling constants, leading to two triplets, one for 1-H and 7-H, the other for 8-H. The τ value of *exo*-8-H is shifted by 5.69 to lower field compared with *endo*-8-H in II.

On warming a solution of III in FSO_3H to 30.4°, a first-order isomerization to the *exo*-chloro cation took

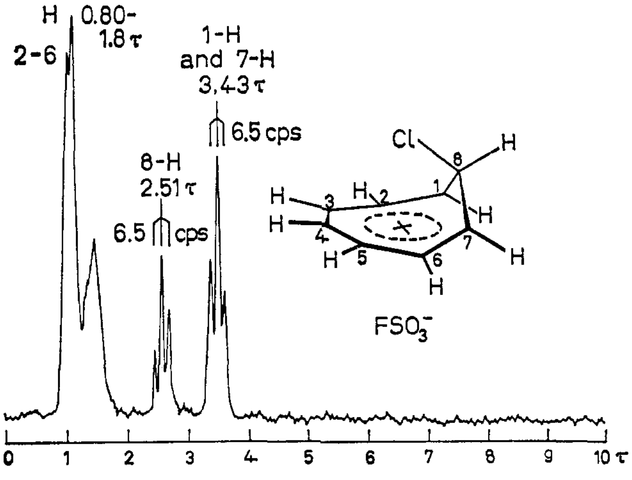


Figure 2. Nmr spectrum (FSO_3H) of *endo*-8-chlorohomotropylium fluorosulfonate at −40°.[8]

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(1) R. Huisgen, G. Boche, and H. Huber, *J. Am. Chem. Soc.*, **89**, 3345 (1967).

(2) J. L. von Rosenberg, J. E. Mahler, and R. Pettit, *ibid.*, **84**, 2842 (1962).

(3) S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *ibid.*, **87**, 3267 (1965); S. Winstein, C. G. Kreiter, and J. I. Braumann, *ibid.*, **88**, 2047 (1966).

(4) C. E. Keller and R. Pettit, *ibid.*, **88**, 604, 606 (1966).

(5) R. Huisgen, G. Boche, W. Hechtl, and H. Huber, *Angew. Chem.*, **78**, 595 (1966); *Angew. Chem. Intern. Ed. Engl.*, **5**, 585 (1966).

(6) Satisfactory carbon and hydrogen analyses were obtained.

(7) Determined on a Varian A-60 spectrometer with TMS as internal standard.

(8) TMS is destroyed by FSO_3H. Chemical shifts were corrected by using the same τ values for the two triplets as found for II ($X = SbCl_6^-$) in CD_3NO_2. For mixtures of II and III in FSO_3H, analogous corrections were applied.