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.

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

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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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