

## Syntheses of Charge-Compensated Dicarbollide Ligand Precursors and Their Use in the Preparation of Novel Metallacarboranes

Han Chyul Kang, Sharon S. Lee, Carolyn B. Knobler, and M. Frederick Hawthorne\*

Received July 18, 1990

A series of charge-compensated, boron-substituted carborane cage derivatives, [*nido*-9-L-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>] or [*nido*-10-L-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>] (L = nitrogen-containing ligand), were prepared by the ferric chloride-promoted oxidative coupling reaction of K[*nido*-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>] with the Lewis base, L. Another series of neutral boron-substituted carborane cage derivatives, [*nido*-10-L-7,9-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>], were synthesized directly from the reaction of [closo-1,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>] with the nitrogen-containing ligand, L. When Na[*nido*-10-N-(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] (Na-2), Na[*nido*-9-(4-(C<sub>5</sub>H<sub>4</sub>N)CO<sub>2</sub>CH<sub>3</sub>)-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] (Na-3), or Na[*nido*-10-C<sub>5</sub>H<sub>5</sub>N-7,9-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] (Na-4) were reacted with anhydrous ferrous chloride in THF at 298 K, the three corresponding ferrocene-like neutral *commo*-ferracarboranes were obtained. The complex [*commo*-3,3'-Fe{8-N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>-3,1,2-FeC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>}<sub>2</sub>] (5) was characterized both by spectroscopic methods and by a single-crystal X-ray diffraction study. The well-known unsubstituted iron sandwich [*commo*-3,3'-Fe{3,1,2-FeC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>}<sub>2</sub>][N(CH<sub>3</sub>)<sub>4</sub>]<sub>2</sub> (6) was also characterized crystallographically for the first time. Complexes 5 and 6 each crystallized in the monoclinic space group P2<sub>1</sub>/c, with *a* = 9.017 (3) Å, *b* = 11.341 (3) Å, *c* = 32.941 (11) Å, β = 91.84 (1)°, *V* = 3409 Å<sup>3</sup>, and *Z* = 4 for 5 and *a* = 7.278 (2) Å, *b* = 15.830 (4) Å, *c* = 11.994 (3) Å, β = 91.80 (2)°, *V* = 1381 Å<sup>3</sup>, and *Z* = 2 for 6. The sandwich species [*commo*-3,3'-Fe{4-(4-(C<sub>5</sub>H<sub>4</sub>N)CO<sub>2</sub>CH<sub>3</sub>)-3,1,2-FeC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>}<sub>2</sub>] (7) and [*commo*-2,2'-Fe{11-C<sub>5</sub>H<sub>5</sub>N-2,1,7-FeC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>}<sub>2</sub>] (8) were characterized by spectroscopic means. A novel cationic cobaltacarborane sandwich analogous to the cobalticenium ion, [*commo*-3,3'-Co{4-(4-(C<sub>5</sub>H<sub>4</sub>N)CO<sub>2</sub>CH<sub>3</sub>)-3,1,2-CoC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>}<sub>2</sub>][Cl] (9-Cl) was isolated and characterized. This is the first example of a cationic metallacarborane that incorporates the dicarbollide ligand.

### Introduction

The dicarbollide dianions<sup>1</sup> [*nido*-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]<sup>2-</sup> (1) and [*nido*-7,9-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]<sup>2-</sup>, by virtue of their similarities<sup>2</sup> with the formally isolobal cyclopentadienide ion, [C<sub>5</sub>H<sub>5</sub>]<sup>-</sup>, demonstrate a strong propensity for the formation of metallocene-type sandwich complexes.<sup>1b,3</sup> Although the variety of now known metallacarborane sandwich complexes is very extensive, the presence of two negative charges on each of the dicarbollide ions leads to anionic species in those cases that employ low-valent metals.<sup>3a,b</sup> It is to be expected that reduction of the charge by one unit on each of the dicarbollide moieties through the incorporation of charge-compensating substituents would result in the formation of neutral,<sup>4</sup> cationic,<sup>5</sup> or clustered metallacarborane complexes<sup>6</sup> with metals in accessible low oxidation states. Further, a judicious choice of the charge-compensating substituents could provide a route to important metallacarboranes that serve as components of metallacarborane polymers. Such anchored-metal polymeric supports might find useful applications including the generation of polymer-bound catalysts.<sup>7</sup>

Some metallacarborane complexes reported in the literature, which contain charge-compensated carborane ligands, have been prepared by various methods including ligand rearrangement from the metal site to the carborane cage,<sup>8</sup> reduction of a metalla-

Table I. Yield and Characterization Data for [*nido*-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>L] Species

L	isomer	yield, %	Mp, °C	calcd, % found, %			
				C	H	B	N
4-(C <sub>5</sub> H <sub>4</sub> N)- CO <sub>2</sub> CH <sub>3</sub>	asym	91	140–142	40.10	6.73	36.10	5.20
				40.14	6.78	35.55	5.20
N(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	sym	3.9	158–159	41.13	11.22	41.65	6.00
				41.92	11.04	40.96	6.07
C <sub>6</sub> H <sub>5</sub> N(CH <sub>3</sub> ) <sub>2</sub>	sym	15	141–142	47.36	8.74	38.37	5.52
				48.18	8.65	37.80	5.21
	asym	19	169–170	47.36	8.74	38.37	5.52
				47.42	8.67	38.29	5.39
HCON(CH <sub>3</sub> ) <sub>2</sub>	asym	43	120–121	29.22	8.83	47.35	6.82
				29.88	8.59	46.27	6.52
CH <sub>3</sub> CON- (CH <sub>3</sub> ) <sub>2</sub>	asym	43	171–173	32.83	9.18	44.32	6.38
				32.49	9.36	43.09	6.04

carborane complex by a Lewis base,<sup>5,9</sup> addition of dialkyl sulfide to a protonated metallocene-type sandwich complex,<sup>4b</sup> and metalation of a pyridine-substituted carborane ligand.<sup>10</sup> In order to develop a more general methodology for the synthesis of novel metallacarborane complexes of this type, we have investigated the synthesis of neutral charge-compensated carborane cage derivatives for use as precursors to monoanionic substituted dicarbollide ligands and the use of the latter in the preparation of metallacarborane complexes.<sup>6</sup>

Reported herein are the detailed accounts of the synthesis of four new *commo*-metallacarboranes, each of which contains a monoanionic charge-compensated ligand. To confirm the close sandwich geometry and to establish general structural parameters for this new class of dicarbollide ligands, the molecular structure of 5 was determined by X-ray diffraction. As a complementary comparison, the molecular structure of the well-known iron sandwich complex<sup>1b</sup> containing the parent dicarbollide ion, 6, was also crystallographically elucidated.

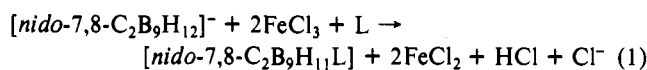
### Results and Discussion

**Synthesis of Charge-Compensated Boron-Substituted *nido*-C<sub>2</sub>B<sub>9</sub> Cages.** Two general methods have been developed for the synthesis

- (1) (a) Hawthorne, M. F.; Young, D. C.; Garrett, P. M.; Owen, D. A.; Schwerin, S. G.; Tebbe, F. N.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 862. (b) Hawthorne, M. F.; Young, D. C.; Andrews, T. M.; Howe, D. V.; Pilling, R. L.; Pitts, A. D.; Reintjes, M.; Warren, L. F., Jr.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 879.
- (2) (a) Brown, D. A.; Fanning, M. O.; Fitzpatrick, N. J. *Inorg. Chem.* **1978**, *17*, 1620. (b) Hanusa, T. P. *Polyhedron* **1982**, *1*, 663.
- (3) (a) Warren, L. F., Jr.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1968**, *90*, 4823. (b) Warren, L. F., Jr.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1970**, *92*, 1157. (c) Hawthorne, M. F.; Callahan, K. P. *Adv. Organomet. Chem.* **1976**, *14*, 145. (d) Rees, W. S., Jr.; Schubert, D. M.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1986**, *108*, 5349.
- (4) (a) Churchill, M. R.; Gold, K.; Francis, J. N.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1969**, *91*, 1222. (b) Hawthorne, M. F.; Warren, L. F., Jr.; Callahan, K. P.; Travers, N. F. *J. Am. Chem. Soc.* **1971**, *93*, 2407.
- (5) Jones, C. J.; Francis, J. N.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1973**, *95*, 7633.
- (6) (a) Kang, H. C.; Do, Y.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1987**, *109*, 6530. (b) Kang, H. C.; Do, Y.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1988**, *27*, 1716.
- (7) Sosinsky, B. A.; Kalb, W. C.; Grey, R. A.; Uski, V. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1977**, *99*, 6768.
- (8) (a) Miller, S. B.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1976**, 787. (b) King, R. E., III; Miller, S. B.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1983**, *22*, 3548.

- (9) (a) Churchill, M. R.; Gold, K. *Inorg. Chem.* **1973**, *12*, 1157. (b) Plešek, J.; Stibr, B.; Hermanek, S. *Collect. Czech. Chem. Commun.* **1984**, *49*, 1492.
- (10) (a) Teller, R. G.; Wilczynski, J. J.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1979**, 472. (b) Colquhoun, H. M.; Greenhough, T. J.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton Trans.* **1979**, 619.

of neutral boron-substituted *nido*-C<sub>2</sub>B<sub>9</sub> cages. The first method may be termed "oxidative substitution" wherein the formal substitution of a terminal hydride ion by a neutral electron donor ligand occurs via the ferric chloride-driven oxidative coupling reaction of [*nido*-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>]<sup>-</sup> with the electron pair donor.<sup>11</sup> When a benzene solution of either the potassium or trimethylammonium salt of [*nido*-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>]<sup>-</sup> and ferric chloride is heated in the presence of a nitrogen-containing donor, L, such as triethylamine, methyl isonicotinate, *N,N*-dimethylacetamide, *N,N*-dimethylformamide, or *N,N*-dimethylaniline, a series of neutral charge-compensated species are produced according to the reaction scheme in eq 1. Since substitution takes place on



one of the three boron atoms of the open pentagonal C<sub>2</sub>B<sub>3</sub> ring of the carborane anion, the resulting [*nido*-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>L] species can be either of two possible isomers, designated as symmetric [*nido*-10-L-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>] and asymmetric [*nido*-9-L-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]. While the symmetric product carries the attached ligand on the unique middle boron atom (B(10)), the asymmetric isomer is substituted on one of the equivalent boron atoms (B(09), B(11)) of the open face and adjacent to a carbon atom. The experimental results are summarized in Table I. The isolated yield and the structure of the resulting [*nido*-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>L] species is dependent upon the nature of the ligand, L. Varying the nitrogen-containing base in this reaction from triethylamine to the less basic aniline, amide, or isonicotinate, results in increasing yields, and this suggests that the weaker bases are more effective in the formation of the substitution product.<sup>11</sup>

The basicity of triethylamine is apparently sufficient to deprotonate the starting [*nido*-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>]<sup>-</sup> ion to form dicarbolide ion 1, which functions as a ligand in the formation of the well-known sandwich complex [*closo*-3,3'-Fe{3,1,2-FeC<sub>2</sub>B<sub>9</sub>H<sub>11</sub>}]<sub>2</sub>-[N(CH<sub>3</sub>)<sub>4</sub>]<sub>2</sub> (6), observed as a major product,<sup>1b</sup> and the (η<sup>6</sup>-arene)ferracarborane complex, found as a minor product when the reaction is carried out in toluene or xylene.<sup>12</sup> The triethylamine-substituted *nido*-C<sub>2</sub>B<sub>9</sub> cage, obtained in the above reaction as a minor product, proved to be the symmetric isomer. This species was isolated from the reaction mixture by liquid-phase chromatography on neutral alumina, using benzene as the eluting solvent. The 200-MHz <sup>1</sup>H FTNMR spectrum at 298 K in CD<sub>2</sub>Cl<sub>2</sub> exhibits one broad singlet at 2.0 ppm in the region of the carboranyl CH resonance. The 160-MHz <sup>11</sup>B{<sup>1</sup>H} FTNMR spectrum at 298 K in THF consists of five resonances (2:3:1:2:1). Both spectra are in agreement with those reported for the symmetrically substituted *nido*-C<sub>2</sub>B<sub>9</sub> cage.<sup>13</sup> Thus, the compound was designated as the symmetrically substituted [*nido*-10-N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>], which contains a plane of molecular symmetry.

The methyl isonicotinate derivative was obtained in essentially quantitative yield as a single isomer. The 200-MHz <sup>1</sup>H FTNMR spectrum at 298 K exhibits two broad singlets in the carboranyl CH region, indicating that this compound is an asymmetrically substituted isomer, [*nido*-9-(4-(C<sub>3</sub>H<sub>4</sub>N)CO<sub>2</sub>CH<sub>3</sub>)-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]. This fact is further substantiated by the 160-MHz <sup>11</sup>B{<sup>1</sup>H} FTNMR spectrum, which shows nine unique resonances. The methyl isonicotinate-substituted *nido*-C<sub>2</sub>B<sub>9</sub> cage is a yellow crystalline solid.

When *N,N*-dimethylaniline was used in this reaction, a mixture of isomers that are white crystalline solids was obtained in a moderate yield. Separation of the mixture by liquid-phase chromatography with benzene as the eluting solvent afforded two compounds. The first compound eluted has one carboranyl CH resonance in the 200-MHz <sup>1</sup>H FTNMR spectrum in CD<sub>2</sub>Cl<sub>2</sub> solution at 298 K and six resonances in a 2:1:2:1:2:1 ratio in its 160-MHz <sup>11</sup>B{<sup>1</sup>H} FTNMR spectrum at 298 K, similar to those

**Table II.** Yield and Characterization Data for [*nido*-10-L-7,9-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>] Species

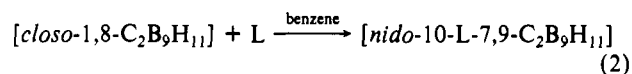
L	yield, %	Mp, °C	calcd, % found, %			
			C	H	B	N
N(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	98	138–140	41.13	11.22	41.65	6.00
			41.01	11.10	41.43	5.99
{(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> NH}	95	157–158	41.13	11.22	41.65	6.00
			41.22	11.16	41.28	5.97
C <sub>3</sub> H <sub>5</sub> N	93	171–173	39.75	7.63	46.00	6.62
			39.60	7.55	45.26	6.73

of the symmetric [*nido*-10-N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]. Therefore, this compound was determined to be the symmetrically substituted isomer, [*nido*-10-C<sub>6</sub>H<sub>5</sub>N(CH<sub>3</sub>)<sub>2</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>].

The <sup>1</sup>H and <sup>11</sup>B{<sup>1</sup>H} FTNMR spectra of the more slowly eluted product clearly indicated that this was the asymmetric isomer, [*nido*-9-C<sub>6</sub>H<sub>5</sub>N(CH<sub>3</sub>)<sub>2</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]. The two methyl groups in this isomer are distinguishable in the 200-MHz <sup>1</sup>H FTNMR spectrum at 298 K, due to the chirality in the asymmetrically substituted *nido*-C<sub>2</sub>B<sub>9</sub> cage.

The analogous reactions carried out with the amides-*N,N*-dimethylformamide and *N,N*-dimethylacetamide afforded two amide-substituted carborane derivatives both of which were isolated in 43% yield. The presence of a strong carbonyl stretching band in the infrared spectra of these compounds at 1691 and 1641 cm<sup>-1</sup>, respectively, suggests that nitrogen rather than oxygen in the amide attacks the C<sub>2</sub>B<sub>9</sub> cage and forms a boron–nitrogen bond. The usual NMR studies indicate that both compounds are asymmetrically substituted carborane derivatives, [*nido*-9-L-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>] (L = HCON(CH<sub>3</sub>)<sub>2</sub>, CH<sub>3</sub>CON(CH<sub>3</sub>)<sub>2</sub>).

The second general route to neutral substituted *nido*-C<sub>2</sub>B<sub>9</sub> derivatives is the reductive addition of a nucleophile, L, to [*closo*-1,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]<sup>-</sup>.<sup>14</sup> Reaction of the 11-vertex *closo* carborane and a nitrogen-containing base such as triethylamine, diisopropylamine, or pyridine for 1 day at ambient temperature in benzene solution produced the corresponding substituted *nido*-C<sub>2</sub>B<sub>9</sub> carborane derivative in quantitative yield (eq 2). The *closo*-C<sub>2</sub>B<sub>9</sub>



cage, in which the two nonadjacent carbon atoms are in the 1- and 8-positions, is opened upon nucleophilic attack by a Lewis base, L.<sup>14</sup> The resulting ligand adduct is [*nido*-10-L-7,9-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]<sup>-</sup>. Isolated yields and characterization data are summarized in Table II. The 160-MHz <sup>11</sup>B FTNMR spectra of each of the three products shows a similar pattern, which includes eight terminal proton-coupled resonances (*J* = 128–158 Hz) in the region between –2 and –37 ppm and one bridging proton-coupled peak (*J* = 43 Hz in the diisopropylamine derivative) near –10 ppm due to the nitrogen-substituted boron. Such a pattern is characteristic of a substituted-boron atom located at the open pentagonal face of the *nido* cage and occupying either of the equivalent B(10) or B(11) positions. In the 200-MHz <sup>1</sup>H FTNMR spectra of CD<sub>2</sub>Cl<sub>2</sub> solutions of each product at 298 K, two different carboranyl CH resonances with equal intensity around 2 ppm were observed. In addition, the diisopropylamine-substituted *nido*-C<sub>2</sub>B<sub>9</sub> cage displays four different doublets in the methyl proton region as a consequence of both the chirality in the substituted [*nido*-7,9-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]<sup>-</sup> cage and the barrier to rotation around the B–N and C–N bonds. The NMR studies described above indicate that, as expected, only an asymmetrically substituted isomer was produced through the "reductive-addition" method as previously observed.<sup>14b,c</sup>

**Preparation and Characterization of Neutral and Cationic Metallocarboranes Containing Charge-Compensated Dicarbolide Ligands.** The boron-substituted *nido*-C<sub>2</sub>B<sub>9</sub> cages that were pro-

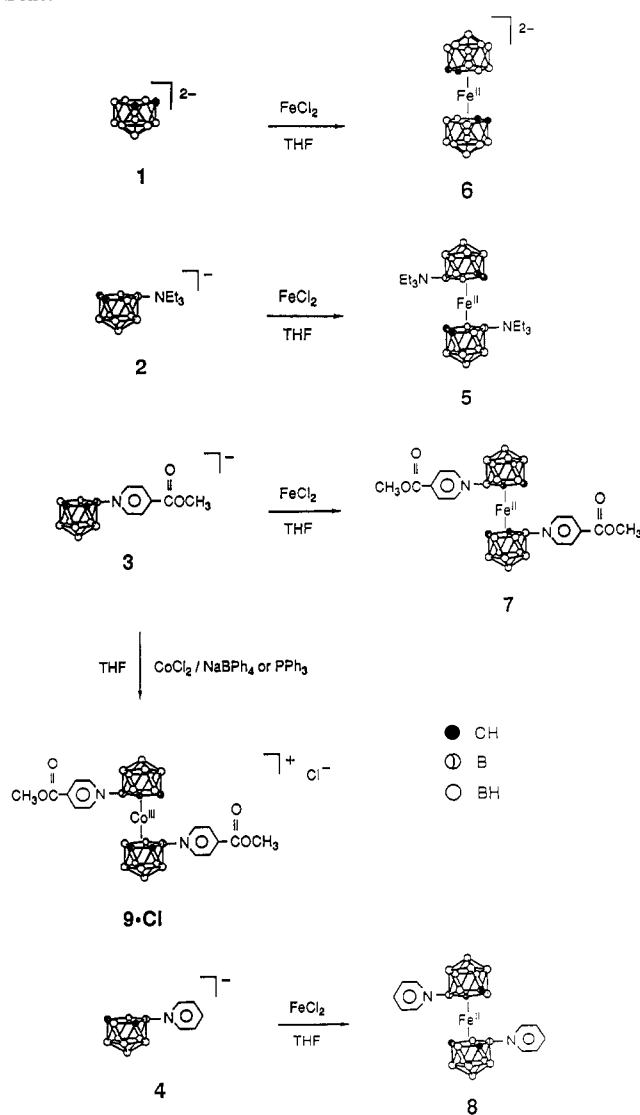
(11) Young, D. C.; Howe, D. V.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1969**, *91*, 859.

(12) Kang, H. C.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1987**, *26*, 3409.

(13) Young, D. C. Ph.D. Thesis, University of California, Riverside, 1966.

(14) (a) Tebbe, F. N.; Garrett, P. M.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1968**, *90*, 869. (b) Owen, D. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1969**, *91*, 6002. (c) Chowdhry, V.; Pretzer, W. R.; Rai, D. N.; Rudolph, R. W. *J. Am. Chem. Soc.* **1973**, *95*, 4560.

Scheme I



duced by using the two methods described above consist of a cationic donor atom at the substitution site and an anionic *nido*-C<sub>2</sub>B<sub>9</sub> cage, forming the neutral charge-compensated species. Since this species has one bridging hydrogen on the open face of the *nido* cage, deprotonation using NaH will generate a monoanionic substituted dicarbollide ion, as in the case of the parent ion, which is formally isolobal and isoelectronic with the cyclopentadienide ion, [C<sub>5</sub>H<sub>5</sub>]<sup>-</sup>. We have recently reported the synthesis and structure of the mononuclear cupracarborane [*closo*-3-(PPh<sub>3</sub>)-4-(4-(C<sub>5</sub>H<sub>4</sub>N)CO<sub>2</sub>CH<sub>3</sub>)-3,1,2-CuC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] and the trinuclear clustered cluster [Cu<sub>3</sub>(μ-H)<sub>3</sub>(C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>(4-(C<sub>5</sub>H<sub>4</sub>N)CO<sub>2</sub>CH<sub>3</sub>))<sub>3</sub>] containing the methyl isonicotinate-substituted dicarbollide ligand.<sup>6</sup> Among the charge-compensated ligands prepared in the work reported here are two *nido*-7,8-carborane monoanions, Na[*nido*-10-N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] (Na·2) and Na[*nido*-9-(4-(C<sub>5</sub>H<sub>4</sub>N)CO<sub>2</sub>CH<sub>3</sub>)-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] (Na·3), and a *nido*-7,9-carborane anion, Na[*nido*-10-C<sub>5</sub>H<sub>5</sub>N-7,9-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] (Na·4). These dicarbollide derivatives display superior ligand properties in the formation of neutral ferrocene-like sandwich complexes. Synthetic routes to metallocarboranes derived from 1,<sup>1b</sup> 2, 3, and 4 are summarized in Scheme I.

Reaction of Na·2 and anhydrous ferrous chloride in THF solution at ambient temperature proceeded to form a neutral ferrocene-like sandwich complex, [*commo*-3,3'-Fe{8-N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>-3,1,2-FeC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>}<sub>2</sub>] (5), which was isolated as purple crystals after recrystallization and characterized by X-ray diffraction and other means. The 160-MHz <sup>11</sup>B{<sup>1</sup>H} FTNMR spectrum of a THF solution of this compound at 298 K exhibits six resonances with area ratios of 1:2:1:2:1:2, which demonstrates that, as expected,

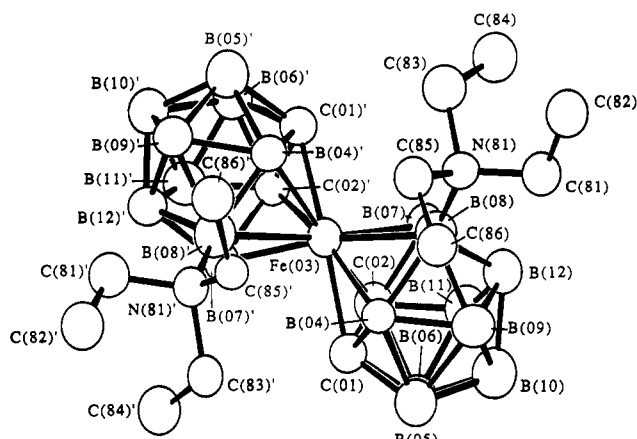
the symmetrically substituted C<sub>2</sub>B<sub>9</sub> cage ligands freely rotate at this temperature in solution.

The reaction of a THF solution of Na·3 with a slurry of anhydrous ferrous chloride in THF at ambient temperature formed another neutral sandwich complex, [*commo*-3,3'-Fe{4-(4-(C<sub>5</sub>H<sub>4</sub>N)CO<sub>2</sub>CH<sub>3</sub>)-3,1,2-FeC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>}<sub>2</sub>] (7) in a yield of 27%. Compound 7 was obtained as analytically pure black crystals after recrystallization. No single crystal suitable for an X-ray diffraction study was obtained. The 200-MHz <sup>1</sup>H and 160-MHz <sup>11</sup>B{<sup>1</sup>H} FTNMR spectra indicate the presence of the methyl isonicotinate group and the asymmetrically substituted C<sub>2</sub>B<sub>9</sub> cage. The mass spectrum exhibited a peak with maximum intensity at *m/e* 593, consistent with that calculated for [<sup>12</sup>C<sub>18</sub><sup>1</sup>H<sub>34</sub><sup>11</sup>B<sub>15</sub><sup>10</sup>B<sub>3</sub><sup>14</sup>N<sub>2</sub><sup>16</sup>O<sub>4</sub><sup>56</sup>Fe]<sup>+</sup>, and the results of the elemental analysis are in agreement with characterization of these black crystals as a *commo*-ferracarborane complex.

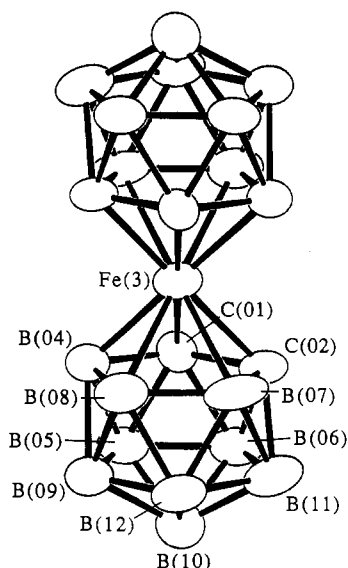
The reaction of a deep purple THF solution of Na·4 with anhydrous ferrous chloride at ambient temperature led to the formation of [*commo*-2,2'-Fe{11-C<sub>5</sub>H<sub>5</sub>N-2,1,7-FeC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>}<sub>2</sub>] (8) in a yield of 46%. Red microcrystals of complex 8 obtained by recrystallization from the mixture of THF and heptane were characterized spectroscopically. The 200-MHz <sup>1</sup>H FTNMR spectrum of 8 consisted of resonances attributable to the pyridine substituent and to the carbon-bound protons in the carborane cage. The 160-MHz <sup>11</sup>B FTNMR spectrum displayed a pattern characteristic of the asymmetrically substituted *nido*-7,9-C<sub>2</sub>B<sub>9</sub> cage. The observation of the peak with maximum intensity at *m/e* 477 in the mass spectrum agrees with the expected molecular ion, [<sup>12</sup>C<sub>14</sub><sup>1</sup>H<sub>30</sub><sup>11</sup>B<sub>15</sub><sup>10</sup>B<sub>3</sub><sup>14</sup>N<sub>2</sub><sup>56</sup>Fe]<sup>+</sup>. Elemental analyses confirmed this formulation. From the foregoing data it can be concluded that the product is a diamagnetic Fe(II) sandwich complex. Although cobalt and nickel *commo* complexes containing the unsubstituted [*nido*-7,9-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]<sup>2-</sup> ligands have previously been reported,<sup>1b</sup> complex 8 provides an interesting example of a charge-compensated analogue.

An equimolar reaction of Na·3 with anhydrous cobalt(II) chloride in THF at ambient temperature in the presence of sodium tetraphenylborate, which served as an anion source, resulted in the formation of an unstable diamagnetic Co(III) cationic complex, [*commo*-3,3'-Co{4-(4-(C<sub>5</sub>H<sub>4</sub>N)CO<sub>2</sub>CH<sub>3</sub>)-3,1,2-CoC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>}<sub>2</sub>]Cl (9-Cl) in a yield of ca. 13%. As observed in the synthesis of the parent cobalticenium ion analogue,<sup>1b</sup> a black residue of the reduced cobalt metal was obtained in the reaction mixture, indicating the disproportionation of Co(II) to Co(III) and cobalt metal. Compound 9-Cl was isolated as green crystals from a solvent mixture of CH<sub>3</sub>CN and (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O and characterized by spectroscopic methods including mass spectroscopy. In the 200-MHz <sup>1</sup>H FTNMR spectrum (CD<sub>3</sub>CN solvent) at 298 K, all of the resonances attributable to the methyl isonicotinate group along with two broad peaks assigned to the carboranyl CH in the downfield region (5–6 ppm) were observed. The 160-MHz <sup>11</sup>B FTNMR spectrum at 298 K showed seven of the nine distinct boron environments expected for the asymmetrically substituted carborane cage and one unique uncoupled peak at 6.4 ppm. Although the reaction was performed in the presence of sodium tetraphenylborate, no peak due to the tetraphenylborate ion was detected in this spectrum. The mass spectrum, obtained by using the fast atom bombardment technique, showed a peak with maximum intensity at *m/e* 596, which corresponds to the mass calculated for [<sup>12</sup>C<sub>18</sub><sup>1</sup>H<sub>34</sub><sup>11</sup>B<sub>15</sub><sup>10</sup>B<sub>3</sub><sup>14</sup>N<sub>2</sub><sup>16</sup>O<sub>4</sub><sup>59</sup>Co]<sup>+</sup>, the cationic portion 9 of the ion pair.

The same reaction carried out in the absence of sodium tetraphenylborate afforded a brown solution followed by the precipitation of brown solids. The addition of triphenylphosphine to this reaction mixture resulted in the formation of green crystals that proved to be 9-Cl. The roles played by tetraphenylborate and triphenylphosphine are not clear at this time. Attempts to exchange the chloride ion for a larger anion, such as tetraphenylborate or hexafluorophosphate, failed to give crystalline products but instead gave unidentified brown solids that resulted from the continuous decomposition of the reaction mixture. However, in the presence of the monoanion [*nido*-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>]<sup>-</sup>,



**Figure 1.** Structure of [commo-3,3'-Fe{8-(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>-3,1,2-FeC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>}<sub>2</sub>] (5), showing the atom-labeling scheme. All hydrogen atoms have been omitted for clarity.



**Figure 2.** Structure of [commo-3,3'-Fe{3,1,2-FeC<sub>2</sub>B<sub>9</sub>H<sub>12</sub>}[N(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>] (6), showing the atom-labeling scheme. All hydrogen atoms have been omitted for clarity.

yellow crystals that grew slowly from the green solution were obtained. These proved to be 9-[nido-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>] from spectroscopic data including NMR, IR, and mass spectra.<sup>15</sup>

As in the case of the parent dicarbollide ligand 1, the d<sup>6</sup> Co(III) attains a stable electronic configuration via donation of six electrons from each of the substituted dicarbollide ligands. However, in the case of 9, by means of a pair of charge-compensating substituents the parent anionic metallocarborane has been transformed into a cationic complex. We believe this to be the first reported example of a cationic metallocarborane. The instability of 9 most certainly arises from the presence of a net positive charge.

**Structural Analysis of 5 and 6.** Although the unsubstituted iron sandwich anion is well-known,<sup>1b</sup> it had not been structurally characterized. A comparison of the structures of the salt 6 and the neutral compound 5 is presented here. Although the presence of a disordered solvent molecule in the crystal causes difficulties in the final solution and refinement of the structure, the resulting molecular structure of 5, as illustrated in Figure 1, demonstrates that the iron atom is sandwiched between the two planar pen-

**Table III.** Selected Interatomic Distances and Angles for 5

Distances (Å)			
Fe(03)-C(02)	2.03 (3)	Fe(03)-C(01)	2.04 (3)
Fe(03)-B(07)	2.12 (4)	Fe(03)-B(04)	2.14 (3)
Fe(03)-B(08)	2.27 (4)	N(81)-C(83)	1.52 (3)
N(81)-C(85)	1.56 (3)	N(81)-C(81)	1.56 (3)
N(81)-B(08)	1.63 (4)	C(02)-C(01)	1.65 (4)
C(02)-B(07)	1.74 (5)	C(02)-B(11)	1.75 (5)
C(02)-B(06)	1.78 (4)	B(04)-C(01)	1.69 (4)
B(04)-B(09)	1.79 (5)	B(04)-B(05)	1.79 (5)
B(04)-B(08)	1.83 (5)	C(01)-B(05)	1.70 (4)
C(01)-B(06)	1.84 (5)	C(83)-C(84)	1.58 (4)
B(07)-B(11)	1.80 (5)	B(07)-B(12)	1.83 (5)
B(07)-B(08)	1.87 (5)	B(09)-B(12)	1.70 (5)
B(09)-B(08)	1.75 (5)	B(09)-B(05)	1.76 (5)
B(09)-B(10)	1.76 (5)	C(82)-C(81)	1.51 (4)
C(85)-C(86)	1.54 (4)	B(11)-B(06)	1.80 (5)
B(11)-B(12)	1.81 (5)	B(11)-B(10)	1.85 (5)
B(10)-B(06)	1.70 (5)	B(10)-B(12)	1.79 (5)
B(10)-B(05)	1.83 (6)	B(12)-B(08)	1.73 (5)
B(06)-B(05)	1.85 (5)		

Angles (deg)			
C(02)-Fe(03)-C(01)	48 (1)	C(02)-Fe(03)-C(02)'	86 (1)
C(02)-Fe(03)-C(01)'	117 (1)	C(02)-Fe(03)-B(07)	49 (1)
C(02)-Fe(03)-B(04)'	167 (1)	C(02)-Fe(03)-B(04)	83 (1)
C(02)-Fe(03)-B(07)'	91 (1)	C(02)-Fe(03)-B(08)	83 (1)
C(02)-Fe(03)-B(08)'	135 (1)	C(01)-Fe(03)-C(02)'	118 (1)
C(01)-Fe(03)-C(01)'	162 (1)	C(01)-Fe(03)-B(07)	84 (1)
C(01)-Fe(03)-B(04)'	143 (1)	C(01)-Fe(03)-B(04)	47 (1)
C(01)-Fe(03)-B(07)'	90 (1)	C(01)-Fe(03)-B(08)	82 (1)
C(01)-Fe(03)-B(08)'	104 (1)	C(02)''-Fe(03)-C(01)'	45 (1)
C(02)''-Fe(03)-B(07)	93 (1)	C(02)''-Fe(03)-B(04)'	82 (1)
C(02)''-Fe(03)-B(04)	166 (1)	C(02)''-Fe(03)-B(07)'	47 (1)
C(02)''-Fe(03)-B(08)	138 (1)	C(02)''-Fe(03)-B(08)'	80 (1)
C(01)''-Fe(03)-B(07)	90 (1)	C(01)''-Fe(03)-B(04)'	51 (1)
C(01)''-Fe(03)-B(04)	149 (1)	C(01)''-Fe(03)-B(07)'	81 (1)
C(01)''-Fe(03)-B(08)	107 (1)	C(01)''-Fe(03)-B(08)'	81 (1)
B(07)-Fe(03)-B(04)'	127 (1)	B(07)-Fe(03)-B(04)	87 (1)
B(07)-Fe(03)-B(07)'	128 (1)	B(07)-Fe(03)-B(08)	50 (1)
B(07)-Fe(03)-B(08)'	171 (1)	B(04)''-Fe(03)-B(04)	109 (1)
B(04)''-Fe(03)-B(07)'	84 (1)	B(04)''-Fe(03)-B(08)	103 (1)
B(04)''-Fe(03)-B(08)'	47 (1)	B(04)''-Fe(03)-B(07)'	124 (1)
B(04)''-Fe(03)-B(08)	49 (1)	B(04)''-Fe(03)-B(08)'	101 (1)
B(07)''-Fe(03)-B(08)	171 (1)	B(07)''-Fe(03)-B(08)'	50 (1)
B(08)-Fe(03)-B(08)'	133 (1)	C(83)-N(81)-C(85)	103 (2)
C(83)-N(81)-C(81)	108 (2)	C(83)-N(81)-B(08)	110 (2)
C(85)-N(81)-C(81)	112 (2)	C(85)-N(81)-B(08)	109 (2)
C(81)-N(81)-B(08)	114 (2)		

tagonal faces of the substituted dicarbollide ligands. Unlike 5, which possesses two unique cages, complex 6, shown in Figure 2, exhibits one distinct dicarbollide ligand, which is related to the other via an inversion center at the iron atom. The bonding faces in 6 are staggered, and the carbon atoms of one bonding face are at maximum distance from carbon atoms of the other bonding face. The bonding faces in 5 are also mutually staggered with triethylamine groups in the gauche conformation, but only one of the two carbon atoms (C(01), C(01)') is at maximum separation. The average Fe-C(C<sub>2</sub>B<sub>3</sub> face) bond lengths in 5 and 6 are 2.05 and 2.03 Å, respectively. The average Fe-B(C<sub>2</sub>B<sub>3</sub> face) bond length of 2.20 Å in 5 is somewhat longer than that of 2.03 Å found in 6. All interatomic distances of the icosahedral cage, metal-carbon, and metal-boron bonds are within the normal range found in *cis*-MC<sub>2</sub>B<sub>9</sub> complexes.<sup>16</sup> In 5, the iron atom is located between the somewhat distorted C<sub>2</sub>B<sub>3</sub> bonding faces of each C<sub>2</sub>B<sub>9</sub> cage,<sup>17</sup> with distances of 1.50 and 1.56 Å from the least-squares

(15) Spectroscopic data for 9-[nido-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>] are as follows. IR spectrum (Nujol): ν(BH) = 2573, 2538, 2507 cm<sup>-1</sup>; ν(CO) = 1730 cm<sup>-1</sup>. <sup>1</sup>H FTNMR (200.133 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 1.9, 4.3, 5.1 (br, s, carborane CH), 4.1 (s, -CH<sub>3</sub>), 8.4 (d, -C<sub>2</sub>H<sub>4</sub>N-), 8.9 (br, s, -C<sub>2</sub>H<sub>4</sub>N-) ppm. <sup>11</sup>B{<sup>1</sup>H} FTNMR (160.463 MHz, THF): 5.9, 2.3, -5.0 (br), -11.3, -17.4, -22.5, -33.6, -38.3 ppm. Mass spectrum (xenon-FAB): *m/e* 596 (peak with maximum intensity), [<sup>12</sup>C<sub>18</sub><sup>1</sup>H<sub>34</sub><sup>11</sup>B<sub>15</sub><sup>10</sup>B<sub>3</sub><sup>14</sup>N<sub>2</sub><sup>16</sup>O<sub>4</sub><sup>39</sup>Co]<sup>+</sup>.

(16) Grimes, R. N. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 1, Chapter 5 and references therein.

(17) The extent of this facial distortion can be described in terms of the fold parameters θ and φ. This complex shows the values of θ + φ, 1.5° + 5.5° = 7.0° and 4.6° + 3.6° = 8.2°, in each cage, respectively. These parameters describe the "folding" of bonding pentagonal faces as defined in: (a) Mingos, D. M. P.; Forsyth, M. I.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* 1977, 605. (b) Mingos, D. M. P.; Forsyth, M. I.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* 1978, 1363.

Table IV. Selected Interatomic Distances and Angles for 6

		Distances (Å)					
Fe(3)-C(01)	2.015 (8)	Fe(3)-C(02)	2.047 (8)	B(05)-B(09)	1.740 (2)	B(05)-B(10)	1.768 (16)
Fe(3)-B(04)	2.073 (10)	Fe(3)-B(07)	2.112 (10)	B(06)-B(10)	1.760 (15)	B(06)-B(11)	1.770 (16)
Fe(3)-B(08)	2.144 (10)	C(01)-C(02)	1.616 (12)	B(07)-B(08)	1.792 (15)	B(07)-B(11)	1.822 (14)
C(01)-B(04)	1.671 (13)	C(01)-B(05)	1.716 (13)	B(07)-B(12)	1.817 (15)	B(08)-B(09)	1.856 (15)
C(01)-B(06)	1.755 (12)	C(02)-B(06)	1.734 (13)	B(08)-B(12)	1.813 (14)	B(09)-B(10)	1.758 (16)
C(02)-B(07)	1.720 (14)	C(02)-B(11)	1.759 (13)	B(09)-B(12)	1.740 (2)	B(10)-B(11)	1.780 (2)
B(04)-B(05)	1.803 (14)	B(04)-B(08)	1.808 (15)	B(10)-B(12)	1.747 (16)	B(11)-B(12)	1.771 (15)
B(04)-B(09)	1.817 (14)	B(05)-B(06)	1.779 (16)				
		Angles (deg)					
C(01)-Fe(3)-C(02)	46.9 (3)	C(01)-Fe(3)-B(04)	48.2 (4)	Fe(3)-B(07)-C(02)	63.6 (4)	Fe(3)-B(07)-B(08)	66.0 (5)
C(01)-Fe(3)-B(07)	82.9 (4)	C(01)-Fe(3)-B(08)	83.7 (4)	Fe(3)-B(07)-B(11)	118.2 (6)	Fe(3)-B(07)-B(12)	117.5 (6)
C(02)-Fe(3)-B(04)	83.4 (4)	C(02)-Fe(3)-B(07)	48.8 (4)	C(02)-B(07)-B(08)	106.0 (7)	C(02)-B(07)-B(11)	59.5 (6)
C(02)-Fe(3)-B(08)	84.0 (4)	B(04)-Fe(3)-B(07)	86.2 (4)	C(02)-B(07)-B(12)	102.9 (7)	B(08)-B(07)-B(11)	108.9 (7)
B(04)-Fe(3)-B(08)	50.7 (4)	B(07)-Fe(3)-B(08)	49.8 (4)	B(08)-B(07)-B(12)	60.3 (6)	B(11)-B(07)-B(12)	58.2 (6)
Fe(3)-C(01)-C(02)	67.6 (4)	Fe(3)-C(01)-B(04)	67.7 (4)	Fe(3)-B(08)-B(04)	62.6 (4)	Fe(3)-B(08)-B(07)	64.2 (5)
Fe(3)-C(01)-B(05)	126.5 (6)	Fe(3)-C(01)-B(06)	125.6 (5)	Fe(3)-B(08)-B(09)	114.8 (6)	Fe(3)-B(08)-B(12)	116.1 (6)
C(02)-C(01)-B(04)	113.0 (6)	C(02)-C(01)-B(05)	111.7 (7)	B(04)-B(08)-B(07)	105.2 (7)	B(04)-B(08)-B(09)	59.5 (6)
C(02)-C(01)-B(06)	61.8 (5)	B(04)-C(01)-B(05)	64.3 (6)	B(04)-B(08)-B(12)	104.1 (7)	B(07)-B(08)-B(09)	105.2 (7)
B(04)-C(01)-B(06)	115.5 (7)	B(05)-C(01)-B(06)	61.6 (6)	B(07)-B(08)-B(12)	60.5 (6)	B(09)-B(08)-B(12)	56.6 (6)
Fe(3)-C(02)-C(01)	65.5 (4)	Fe(3)-C(02)-B(06)	124.9 (6)	B(04)-B(09)-B(05)	60.9 (6)	B(04)-B(09)-B(08)	59.0 (6)
Fe(3)-C(02)-B(07)	67.6 (4)	Fe(3)-C(02)-B(11)	125.1 (6)	B(04)-B(09)-B(10)	109.0 (7)	B(04)-B(09)-B(12)	106.8 (7)
C(01)-C(02)-B(06)	63.1 (5)	C(01)-C(02)-B(07)	110.0 (6)	B(05)-B(09)-B(08)	108.9 (7)	B(05)-B(09)-B(10)	60.7 (6)
C(01)-C(02)-B(11)	110.7 (6)	B(06)-C(02)-B(07)	113.6 (7)	B(05)-B(09)-B(12)	108.0 (8)	B(08)-B(09)-B(10)	109.5 (7)
B(06)-C(02)-B(11)	60.9 (6)	B(07)-C(02)-B(11)	63.2 (6)	B(08)-B(09)-B(12)	60.5 (6)	B(10)-B(09)-B(12)	59.9 (6)
Fe(3)-B(04)-C(01)	64.0 (4)	Fe(3)-B(04)-B(05)	118.5 (6)	B(05)-B(10)-B(06)	60.5 (6)	B(05)-B(10)-B(09)	59.1 (6)
Fe(3)-B(04)-B(08)	66.6 (5)	Fe(3)-B(04)-B(09)	120.0 (6)	B(05)-B(10)-B(11)	108.1 (8)	B(05)-B(10)-B(12)	106.4 (8)
C(01)-B(04)-B(05)	59.1 (6)	C(01)-B(04)-B(08)	105.8 (7)	B(06)-B(10)-B(09)	108.1 (8)	B(06)-B(10)-B(11)	60.0 (6)
C(01)-B(04)-B(09)	103.1 (7)	B(05)-B(04)-B(08)	108.2 (7)	B(06)-B(10)-B(12)	107.6 (8)	B(09)-B(10)-B(11)	108.4 (8)
B(05)-B(04)-B(09)	57.4 (6)	B(08)-B(04)-B(09)	61.6 (6)	B(09)-B(10)-B(12)	59.5 (6)	B(11)-B(10)-B(12)	60.3 (6)
C(01)-B(05)-B(04)	56.6 (5)	C(01)-B(05)-B(06)	60.3 (6)	C(02)-B(11)-B(06)	58.9 (5)	C(02)-B(11)-B(07)	57.4 (5)
C(01)-B(05)-B(09)	104.6 (7)	C(01)-B(05)-B(10)	105.3 (7)	C(02)-B(11)-B(10)	104.0 (7)	C(02)-B(11)-B(12)	103.2 (7)
B(04)-B(05)-B(06)	108.0 (7)	B(04)-B(05)-B(09)	61.7 (6)	B(06)-B(11)-B(07)	107.2 (7)	B(06)-B(11)-B(10)	59.4 (6)
B(04)-B(05)-B(10)	109.2 (8)	B(06)-B(05)-B(09)	108.1 (8)	B(06)-B(11)-B(12)	106.1 (7)	B(07)-B(11)-B(10)	107.9 (8)
B(06)-B(05)-B(10)	59.5 (6)	B(09)-B(05)-B(10)	60.2 (6)	B(07)-B(11)-B(12)	60.7 (6)	B(10)-B(11)-B(12)	58.9 (6)
C(01)-B(06)-C(02)	55.2 (5)	C(01)-B(06)-B(05)	58.1 (5)	B(07)-B(12)-B(08)	59.2 (6)	B(07)-B(12)-B(09)	109.1 (7)
C(01)-B(06)-B(10)	104.0 (7)	C(01)-B(06)-B(11)	104.0 (7)	B(07)-B(12)-B(10)	109.7 (7)	B(07)-B(12)-B(11)	61.0 (6)
C(02)-B(06)-B(05)	103.5 (7)	C(02)-B(06)-B(10)	106.0 (7)	B(08)-B(12)-B(09)	62.9 (6)	B(08)-B(12)-B(10)	112.0 (8)
C(02)-B(06)-B(11)	60.3 (6)	B(05)-B(06)-B(10)	60.0 (6)	B(08)-B(12)-B(11)	110.2 (7)	B(09)-B(12)-B(10)	60.6 (6)
B(05)-B(06)-B(11)	108.1 (7)	B(10)-B(06)-B(11)	60.6 (6)	B(09)-B(12)-B(11)	109.7 (8)	B(10)-B(12)-B(11)	60.8 (6)

planes of each face, respectively.<sup>18</sup> In the case of the parent dicarbollide ligand, the  $C_2B_3$  face of **6** is nearly planar (maximum deviation of 0.012 Å) with a Fe- $C_2B_3$  face (centroid) distance of 1.48 Å. The shorter distances of Fe-C( $C_2B_3$  face), Fe-B( $C_2B_3$  face), and the Fe- $C_2B_3$  face (centroid) found in **6**, with respect to **5**, are expected and can be explained by using simple electrostatic arguments. The unsubstituted carborane cage in **6** is a dianion, in contrast to the charge-compensated carboranyl ligand in **5**, which is a monoanion. Hence, a stronger metal-ligand interaction is invoked. Since the triethylamine substituent of **5** apparently affects the geometry of the molecule, the bonding faces are not parallel to each other, as found in **6**, showing a dihedral angle of 14.0°. Selected interatomic distances and angles for **5** and **6** are summarized in Tables III and IV, respectively.

### Experimental Section

All operations were conducted under an inert atmosphere of dinitrogen or argon with Schlenk techniques or in a Vacuum Atmospheres glovebox unless otherwise indicated.

- (18) Fe- $C_2B_3$  plane distances in *closo*-ferracarboranes are as follows. (a) 1.49 Å in  $[(C_2H_5)_2FeC_2B_9H_{11}]$ . Zalkin, A.; Templeton, D. H.; Hopkins, T. E. *J. Am. Chem. Soc.* **1965**, *87*, 3988. (b) 1.58 Å in  $Cs_2[(C_2B_9H_{11})_2Fe_2(CO)_4] \cdot (CH_3)_2CO \cdot H_2O$ . Greene, P. T.; Briyan, R. F. *Inorg. Chem.* **1970**, *9*, 1464. (c) 1.48 Å in  $[(C_6(CH_3)_3H_3)FeC_2B_9H_{11}]$ . Haanusa, T. P.; Huffman, J. C.; Todd, L. J. *Polyhedron* **1982**, *1*, 77. (d) 1.494 Å (toluene) and 1.480 Å (xylene) in  $[(\eta^6\text{-arene})FeC_2B_9H_{11}]$ .<sup>12</sup> (e) 1.487 Å in  $[(\eta^6\text{-}C_6H_6)FeC_2B_9H_{11}]$ . Lee, S. S.; Knobler, C. B.; Hawthorne, M. F. *J. Organomet. Chem.* **1990**, *394*, 29. (f) 1.574 Å in  $[(CO)_2PPh_3FeC_2B_9H_{11}]$ , 1.545 Å in  $[(CO)PPh_3(MeCN)FeC_2B_9H_{11}]$ , 1.570 Å in  $[(CO)P(OMe)_3]_2FeC_2B_9H_{11}]$ , and 1.562 Å in  $[(CO)_2FeC_2B_9H_{11}]$ . Lee, S. S.; Knobler, C. B.; Hawthorne, M. F. *Organometallics*, in press. (g) 1.557 Å in  $[(CO)_2SnPh_3FeC_2B_9H_{11}][N(C_2H_5)_4]$ , 1.530 and 1.514 Å in  $[(CO)(\eta^6\text{-}C_6H_6)FeC_2B_9H_{11}][PPN]$ , and 1.572 Å in  $[(CO)(COCH_3)(PMe_3)FeC_2B_9H_{11}][PPN]$ . Lee, S. S.; Knobler, C. B.; Hawthorne, M. F. *Organometallics*, in press.

**Physical Measurements.** The  $^1H$  (200.133 MHz) and  $^{11}B$  (160.463 MHz) FTNMR spectra were recorded on Bruker WP-200 and Bruker AM-500 spectrometers, respectively. Proton chemical shifts were referenced to residual protons in the solvent ( $CD_2Cl_2$ , 5.32 ppm;  $CD_3CN$ , 1.93 ppm vs  $(CH_3)_4Si$ ). Boron chemical shifts were referenced to external  $BF_3 \cdot O(C_2H_5)_2$  with downfield shifts taken as positive. Infrared spectra were recorded as KBr pellets on a Beckman FT-1100 spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN, and melting points were determined on a Thomas-Hoover capillary apparatus and were uncorrected. The mass spectra were recorded on an Associated Electrical Industries MS-9 spectrometer fitted with a fast atom bombardment attachment.

**Materials.** All solvents were reagent grade and when necessary were distilled from appropriate drying agents.<sup>19</sup> NMR solvents were obtained from commercial sources and dried and degassed prior to use. Anhydrous iron(II, III) chlorides (Cerac), anhydrous cobalt(II) chloride (Aldrich), sodium hydride (Aldrich), methyl isonicotinate (Aldrich), *N,N*-dimethylformamide (Aldrich), *N,N*-dimethylacetamide (Aldrich), and *N,N*-dimethylaniline were purchased and used as received. Triethylamine, diisopropylamine, and pyridine were freshly distilled before use.  $K[nido\text{-}7,8\text{-}C_2B_9H_{12}]$ ,<sup>1a</sup>  $[com\text{-}3,3'\text{-}Fe\{3,1,2\text{-}FeC_2B_9H_{11}\}_2][N(CH_3)_4]_2$  (**6**),<sup>1b</sup> and  $[closo\text{-}1,8\text{-}C_2B_9H_{11}]^{14a}$  were prepared according to the literature methods.

**[nido-9-(4-( $C_3H_4N$ ) $CO_2CH_3$ )-7,8- $C_2B_9H_{11}]$ . General Procedure.** To a refluxing solution of 4.2 g (0.022 mol) of  $Me_3NH[nido\text{-}7,8\text{-}C_2B_9H_{12}]$  and 20 mL (0.15 mol) of 4-( $C_3H_4N$ ) $CO_2CH_3$  in 100 mL of benzene was added a slurry of 7.0 g (0.043 mol) of ferric chloride in 400 mL of benzene dropwise over a period of 1 h. Reflux of the resulting amber solution for 4 h was followed by the removal of the precipitates formed via filtration over a Celite pad. The yellow filtrates were washed 4 times with 200-mL portions of distilled water. The washed benzene solution was dried over anhydrous magnesium sulfate, evaporated in vacuo at 40

(19) Gordon, A. J.; Ford, R. A. *The Chemist Companion*; Wiley: New York, 1972.

°C to a volume of 100 mL, and treated with 200 mL of heptane. A yellow crystalline solid (5.0 g) separated and was collected by filtration. Upon further concentration of the mother liquor, an additional 0.30 g of product was obtained. Only asymmetric isomer was produced. Total yield: 5.3 g, 91%. IR spectrum: 3116 (w), 2561 (s), 2529 (s), 1731 (s), 1434 (s), 1325 (w), 1288 (s), 1244 (w), 1118 (m), 1026 (w), 959 (w), 868 (w), 766 (w), 687 (w)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 9.0 (d,  $-\text{C}_5\text{H}_4\text{N}-$ ), 8.2 (d,  $-\text{C}_5\text{H}_4\text{N}-$ ), 4.1 (s,  $-\text{CH}_3$ ), 2.9 (br, s, carborane CH), 2.2 (br, s, carborane CH) ppm.  $^{11}\text{B}\{^1\text{H}\}$  NMR (THF): 1.3, -5.6, -16.6, -17.7, -20.2, -22.0, -27.7, -30.5, -37.7 ppm.

[*nido*-10- $\text{N}(\text{C}_2\text{H}_5)_3$ -7,8- $\text{C}_2\text{B}_9\text{H}_{11}$ ]. From the procedure described above, a dark red oily mixture, which was found to include the Fe(III) sandwich complex and the symmetrically substituted [*nido*-10- $\text{N}(\text{C}_2\text{H}_5)_3$ -7,8- $\text{C}_2\text{B}_9\text{H}_{11}$ ], was obtained and characterized spectroscopically. The mixture was dissolved in 10 mL of benzene, and the solution applied to a liquid phase chromatographic column packed with neutral alumina and eluted with benzene. The symmetric [*nido*-10- $\text{N}(\text{C}_2\text{H}_5)_3$ -7,8- $\text{C}_2\text{B}_9\text{H}_{11}$ ] was eluted first as a yellow band. The volume of the yellow solution was reduced to 10 mL and heptane was added, forming a colorless crystalline solid. Recrystallization from benzene/heptane afforded analytically pure symmetric product in a yield of 3.9%. IR spectrum: 2987 (m), 2591 (s), 2550 (s), 1460 (m), 1397 (m), 1183 (w), 1164 (w), 1094 (w), 1027 (m), 1010 (m), 917 (m), 822 (w), 789 (w)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 3.1 (qr,  $-\text{CH}_2-$ ), 2.0 (br, s, carborane CH), 1.3 (t,  $-\text{CH}_3$ ) ppm.  $^{11}\text{B}\{^1\text{H}\}$  NMR (THF): -10.5, -15.6, -17.7, -20.3, -36.5 ppm (2:3:1:2:1).

[*nido*-7,8- $\text{C}_2\text{B}_9\text{H}_{11}[\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2]$ ] Isomers. From the general procedure described above, a 35% yield of the mixed isomers of [*nido*-7,8- $\text{C}_2\text{B}_9\text{H}_{11}[\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2]$ ] was obtained. Chromatographic separation of 0.60 g of the mixed isomers on neutral alumina using benzene eluent yielded 0.26 g of the symmetric isomer (15% yield) and 0.32 g of the asymmetric isomer (19% yield). These compounds were readily recrystallized from benzene/heptane solutions.

(a) [*nido*-10- $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$ -7,8- $\text{C}_2\text{B}_9\text{H}_{11}$ ]. IR spectrum: 2970 (w), 2586 (s), 2529 (s), 1597 (w), 1498 (m), 1482 (s), 1460 (m), 1439 (m), 1406 (w), 1093 (w), 1032 (w), 1005 (w), 986 (m), 926 (s), 901 (m), 873 (m), 788 (w), 768 (m), 688 (m)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 7.4-7.6 (envelope,  $-\text{C}_6\text{H}_5$ ), 3.3 (s,  $-\text{CH}_3$ ), 1.9 (br, s, carborane CH) ppm.  $^{11}\text{B}\{^1\text{H}\}$  NMR (THF): -11.5, -14.1, -17.5, -21.0, -23.2, -39.1 ppm (2:1:2:1:2:1).

(b) [*nido*-9- $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$ -7,8- $\text{C}_2\text{B}_9\text{H}_{11}$ ]. IR spectrum: 3031 (w), 2577 (s), 2546 (s), 2527 (s), 1596 (w), 1481 (s), 1460 (m), 1445 (m), 1434 (m), 1404 (w), 1272 (w), 1151 (w), 1030 (m), 1001 (m), 976 (m), 935 (m), 865 (w), 767 (m), 686 (m)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 7.4-7.6 (envelope,  $-\text{C}_6\text{H}_5$ ), 3.6 (s,  $-\text{CH}_3$ ), 3.4 (s,  $-\text{CH}_3$ ), 2.3 (br, s, carborane CH), 1.9 (br, s, carborane CH) ppm.  $^{11}\text{B}\{^1\text{H}\}$  NMR (THF): 7.2, -5.0, -16.6, -17.5, -19.1, -24.3, -27.5, -31.6, -38.4 ppm.

[*nido*-9-HCON( $\text{CH}_3$ ) $_2$ -7,8- $\text{C}_2\text{B}_9\text{H}_{11}$ ]. Employing the general procedure produced a 43% yield of white crystalline asymmetric [*nido*-9-HCON( $\text{CH}_3$ ) $_2$ -7,8- $\text{C}_2\text{B}_9\text{H}_{11}$ ]. The symmetric isomer was not detected by spectroscopic methods. IR spectrum: 2539 (s), 1691 (s), 1427 (m), 1343 (s), 1264 (w), 1251 (w), 1104 (m), 1064 (w), 1003 (m), 960 (w), 860 (w)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 8.3 (s,  $-\text{OCH}$ ), 3.3 (s,  $-\text{CH}_3$ ), 3.2 (s,  $-\text{CH}_3$ ), 2.6 (br, s, carborane CH), 1.8 (br, s, carborane CH) ppm.  $^{11}\text{B}\{^1\text{H}\}$  NMR (THF): 7.8, -9.6, -18.4, -20.6, -22.3, -24.7, -28.9, -35.2, -40.8 ppm.

[*nido*-9- $\text{CH}_3\text{CON}(\text{CH}_3)_2$ -7,8- $\text{C}_2\text{B}_9\text{H}_{11}$ ]. With the same procedure, a 43% yield of white, crystalline asymmetric [*nido*-9- $\text{CH}_3\text{CON}(\text{CH}_3)_2$ -7,8- $\text{C}_2\text{B}_9\text{H}_{11}$ ] was obtained. IR spectrum: 2947 (w), 2568 (s), 2512 (s), 1641 (s), 1470 (s), 1403 (s), 1267 (s), 1183 (m), 1111 (m), 1068 (m), 1011 (s), 957 (m), 922 (m), 874 (m), 756 (w), 586 (w)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 3.3 (s,  $-\text{CH}_3$ ), 3.2 (s,  $-\text{CH}_3$ ), 2.7 (s,  $\text{CH}_3\text{CO}-$ ), 2.5 (br, s, carborane CH), 1.8 (br, s, carborane CH) ppm.  $^{11}\text{B}\{^1\text{H}\}$  NMR (THF): 6.2, -8.3, -18.9, -20.5, -21.8, -24.1, -28.0, -33.8, -40.6 ppm.

[*nido*-10- $\text{N}(\text{C}_2\text{H}_5)_3$ -7,9- $\text{C}_2\text{B}_9\text{H}_{11}$ ]. General Procedure. To a solution of 0.45 g (3.4 mmol) of [*closo*-1,8- $\text{C}_2\text{B}_9\text{H}_{11}$ ] in 100 mL of benzene was slowly added 2.0 mL (14 mmol) of triethylamine. After the solution was allowed to stir for 5 h, the benzene and excess triethylamine were evaporated at low pressure and the resulting solid was crystallized from benzene/heptane. A 0.78-g amount of the white crystalline adduct was obtained (98% yield). IR spectrum: 2990 (m), 2563 (s), 2530 (s), 1478 (m), 1443 (m), 1388 (m), 1349 (w), 1148 (m), 1106 (m), 1032 (m), 969 (w), 938 (m), 827 (w)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 3.1 (qr,  $-\text{CH}_2-$ ), 1.5 (br, s, carborane CH), 1.3 (t,  $-\text{CH}_3$ ) ppm.  $^{11}\text{B}\{^1\text{H}\}$  NMR (THF): -4.4, -6.0, -7.5, -20.9, -24.2, -25.1, -34.0, -36.5 ppm.

[*nido*-10- $\{(\text{CH}_3)_2\text{CH}_2\text{NH}-7,9-\text{C}_2\text{B}_9\text{H}_{11}\}$ ]. With the procedure described above, a 95% yield of the asymmetrically substituted product was obtained. Recrystallization from dichloromethane/petroleum ether afforded analytically pure product. IR spectrum (Nujol mull): 3221 (m), 2552 (s), 2527 (s), 1262 (m), 1120 (m), 1099 (m), 972 (w), 952 (m), 937 (w), 616 (w)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 3.9 (m,  $-\text{CH}$ ), 3.7 (m,  $-\text{CH}$ ),

1.7 (br, s, carborane CH), 1.6 (br, s, carborane CH), 1.57 (d,  $-\text{CH}_3$ ), 1.44 (d,  $-\text{CH}_3$ ), 1.35 (d,  $-\text{CH}_3$ ), 1.27 (d,  $-\text{CH}_3$ ) ppm.  $^{11}\text{B}\{^1\text{H}\}$  NMR ( $\text{CH}_2\text{Cl}_2$ ): -2.8, -3.7, -5.0, -13.0, -20.0, -21.1, -23.8, -34.4, -35.6 ppm.

[*nido*-10- $\text{C}_6\text{H}_5\text{N}-7,9-\text{C}_2\text{B}_9\text{H}_{11}$ ]. With the same procedure, a 93% yield of the asymmetrically substituted adduct was obtained. This reaction product was recrystallized from dichloromethane/heptane to afford an analytically pure sample. IR spectrum: 3119 (m), 2527 (s), 2510 (s), 1630 (m), 1496 (w), 1462 (s), 1191 (m), 1160 (m), 1111 (m), 1092 (m), 1026 (m), 983 (m), 946 (w), 930 (w), 771 (m), 681 (m)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 8.7 (m,  $-\text{NC}_5\text{H}_5$ ), 8.3 (m,  $-\text{NC}_5\text{H}_5$ ), 7.8 (t,  $-\text{NC}_5\text{H}_5$ ), 2.0 (br, s, carborane CH), 1.8 (br, s, carborane CH) ppm.  $^{11}\text{B}\{^1\text{H}\}$  NMR (THF): -2.4, -4.1, -5.0, -8.6, -19.8, -23.8, -24.2, -32.8, -33.6 ppm.

[*commo*-3,3'-Fe[8- $\text{N}(\text{C}_2\text{H}_5)_3$ -3,1,2- $\text{FeC}_2\text{B}_9\text{H}_{10}$ ] $_2$ ] (5). To a slurry of 0.032 g (0.25 mmol) of anhydrous  $\text{FeCl}_2$  in 20 mL of THF was added a solution of Na-2, which was generated by refluxing a slurry of 0.11 g (0.47 mmol) of [*nido*-10- $\text{N}(\text{C}_2\text{H}_5)_3$ -7,8- $\text{C}_2\text{B}_9\text{H}_{11}$ ] and 0.020 g of NaH in 40 mL of THF for 3 h. Stirring the reaction mixture for 5 h at 298 K resulted in the appearance of a purple color as well as the formation of white solids, which were removed by filtration. The volume of the purple filtrate was reduced to 10 mL under reduced pressure at 298 K and heptane was added, forming a purple crystalline solid. A 0.030-g amount of pure crystals was obtained (24% yield) by recrystallizing the purple solid from dichloromethane/heptane. IR spectrum: 2965 (w), 2945 (w), 2565 (s), 2517 (s), 1460 (m), 1387 (m), 1176 (m), 1147 (m), 1107 (m), 1091 (m), 1070 (m), 1034 (m), 1012 (m), 997 (m), 803 (w)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 3.6 (envelope,  $-\text{CH}_2-$ ), 1.3 (t,  $-\text{CH}_3$ ) ppm.  $^{11}\text{B}\{^1\text{H}\}$  NMR (THF): 9.1, -11.7, -14.9, -16.1, -24.8, -28.4 ppm (1:2:1:2:1:2). Mass spectrum:  $m/e$  521 (peak with maximum intensity in the mass region for the parent ion), [ $^{12}\text{C}_{16}^{1}\text{H}_{30}^{11}\text{B}_{15}^{10}\text{B}_3^{14}\text{N}_2^{56}\text{Fe}$ ] $^+$ .

[*commo*-3,3'-Fe[4-(4-( $\text{C}_5\text{H}_4\text{N})\text{CO}_2\text{CH}_3$ )-3,1,2- $\text{FeC}_2\text{B}_9\text{H}_{10}$ ] $_2$ ] (7). To a slurry of 0.070 g of (0.55 mmol) anhydrous  $\text{FeCl}_2$  in 50 mL of THF was added a deep purple solution of Na-3 generated by refluxing a slurry of 0.27 g (1.0 mmol) of [*nido*-9-(4-( $\text{C}_5\text{H}_4\text{N})\text{CO}_2\text{CH}_3$ )-7,8- $\text{C}_2\text{B}_9\text{H}_{11}$ ] and 0.10 g of NaH in 100 mL of THF for 3 h, resulting in a slow color change to dark red as well as the formation of white solids. The reaction mixture was stirred for 24 h at 298 K and filtered through Celite. The dark red filtrate was reduced in volume, and heptane was added. The resulting black crystals were collected and washed with diethylether, dried in vacuo, and recrystallized from dichloromethane/diethyl ether, affording analytically pure product in a yield of 27% (0.081 g). Anal. Calcd for  $\text{C}_{18}\text{H}_{34}\text{B}_9\text{N}_2\text{O}_4\text{Fe}$ : C, 36.46; H, 5.78; B, 32.82; N, 4.72; Fe, 9.42. Found: C, 36.51; H, 5.97; B, 32.36; N, 4.77; Fe, 9.62. IR spectrum: 2950 (w), 2555 (s), 1739 (s), 1435 (s), 1325 (w), 1297 (s), 1243 (w), 1195 (m), 1120 (m), 986 (w), 827 (w), 766 (m)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 8.7 (m,  $-\text{C}_5\text{H}_4\text{N}-$ ), 8.1 (d,  $-\text{C}_5\text{H}_4\text{N}-$ ), 4.0 (s,  $-\text{CH}_3$ ), 3.0 (br, s, carborane CH) ppm.  $^{11}\text{B}\{^1\text{H}\}$  NMR (THF): 2.2, -3.3, -8.9, -10.7, -11.7, -20.2, -25.7, -27.3 ppm. Mass spectrum:  $m/e$  593 (peak with maximum intensity in the mass region for the parent ion), [ $^{12}\text{C}_{18}^{1}\text{H}_{34}^{11}\text{B}_9^{10}\text{B}_3^{14}\text{N}_2^{16}\text{O}_4^{56}\text{Fe}$ ] $^+$ .

[*commo*-2,2'-Fe[11- $\text{C}_5\text{H}_5\text{N}-2,1,7-\text{FeC}_2\text{B}_9\text{H}_{10}$ ] $_2$ ] (8). A deep purple solution of Na-4, which was produced by refluxing a slurry of 0.80 g (3.8 mmol) of [*nido*-10- $\text{C}_5\text{H}_5\text{N}-7,9-\text{C}_2\text{B}_9\text{H}_{11}$ ] and 0.30 g of NaH in 150 mL of THF for 3 h, was added to the slurry of 0.36 g (2.8 mmol) of anhydrous  $\text{FeCl}_2$  in 50 mL of THF, resulting in the immediate color change to dark red. Stirring of the resulting red slurry for 20 h at 298 K was followed by removal of brown solids. Addition of heptane to the filtrate led to the formation of red microcrystalline solids. Recrystallization from THF/heptane afforded the pure product in a yield of 46% (0.41 g). Anal. Calcd for  $\text{C}_{14}\text{H}_{30}\text{B}_9\text{N}_2\text{Fe}$ : C, 35.26; H, 6.34; B, 40.81; N, 5.87; Fe, 11.71. Found: C, 35.90; H, 5.89; B, 38.88; N, 5.70; Fe, 11.35. IR spectrum: 2553 (s), 1626 (m), 1491 (w), 1460 (m), 1172 (w), 1038 (w), 997 (w), 861 (w), 762 (m), 738 (w), 688 (m)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $(\text{CD}_2)_2\text{CO}$ ): 8.8 (envelope,  $-\text{NC}_5\text{H}_5$ ), 8.4 (m,  $-\text{NC}_5\text{H}_5$ ), 7.9 (br, s,  $-\text{NC}_5\text{H}_5$ ), 2.7 (s, carborane CH) ppm.  $^{11}\text{B}\{^1\text{H}\}$  NMR (THF): 2.3, -9.8, -11.9, -14.2, -17.4, -18.4, -23.9, -24.9 ppm. Mass spectrum:  $m/e$  477 (peak with maximum intensity in the mass region for the parent ion), [ $^{12}\text{C}_{14}^{1}\text{H}_{30}^{11}\text{B}_9^{10}\text{B}_3^{14}\text{N}_2^{56}\text{Fe}$ ] $^+$ .

[*commo*-3,3'-Co[ $\text{C}_5\text{H}_4\text{N}$ ] $\text{CO}_2\text{CH}_3$ ]-3,1,2- $\text{CoC}_2\text{B}_9\text{H}_{10}$ ] $_2$ ]Cl (9-Cl). A deep purple solution of Na-3, which was produced by using the method described above, was slowly added to a slurry of 0.13 g (1 mmol) of anhydrous  $\text{CoCl}_2$  in 50 mL of THF. A sudden color change of the reaction mixture to greenish yellow was observed, and 0.21 g (0.6 mmol) of  $\text{NaB}(\text{C}_6\text{H}_5)_4$  was added. After the mixture was stirred for 20 h at 298 K, the black solids formed were removed by filtration through Celite. The volume of a resulting filtrate was reduced to 30 mL, and diethyl ether was added. Green crystalline solids, which were collected and recrystallized from acetonitrile/diethyl ether, were formed as well as white solids. A 0.040-g amount of green crystals was obtained (13% yield). IR spectrum: 3164 (m), 3013 (m), 2978 (w), 2573 (s), 1740 (s), 1434 (s), 1401 (m), 1296 (s), 1117 (m), 1052 (w), 825 (w), 771 (w)  $\text{cm}^{-1}$ .

**Table V.** Details of the Crystallographic Data Collection for **5** and **6**

compd	<b>5</b>	<b>6</b>
temp/°C	25	25
chem formula	C <sub>16</sub> H <sub>50</sub> FeB <sub>18</sub> N	C <sub>12</sub> H <sub>46</sub> FeB <sub>18</sub> N <sub>2</sub>
fw	520.4	468.4
radiation (graphite monochromator)	Mo K $\alpha$	Mo K $\alpha$
wavelength/Å	0.7107	0.7107
space group	P2 <sub>1</sub> /c	P2 <sub>1</sub> /c
a/Å	9.017 (3)	7.278 (2)
b/Å	11.341 (3)	15.830 (4)
c/Å	32.941 (11)	11.994 (3)
$\beta$ /deg	91.84 (1)	91.80 (20)
V/Å <sup>3</sup>	3409	1381
Z	4	2
$\rho$ (calcd)/g cm <sup>-3</sup>	a	1.13
$\mu$ /cm <sup>-1</sup>	a	5.5
range of transm factors		0.97–0.91
av transm factor		0.96
no. of params refined	149	171
R, R <sub>w</sub> , GOF	0.126, 0.169, 3.37	0.094, 0.104, 2.37

<sup>a</sup> Because of the poorly characterized solvent contents, neither the density nor the absorption coefficient can be calculated for **5**.

<sup>1</sup>H NMR (CD<sub>3</sub>CN): 9.1 (br, s, -C<sub>3</sub>H<sub>4</sub>N-), 8.4 (br, s, -C<sub>3</sub>H<sub>4</sub>N-), 5.9 (br, s, carborane CH), 5.1 (br, s, carborane CH), 4.0 (s, -CH<sub>3</sub>) ppm. <sup>11</sup>B{<sup>1</sup>H} NMR (CH<sub>3</sub>CN): 6.4, 2.8, -2.9, -4.9, -11.8, -18.1, -21.5 ppm. Mass spectrum (xenon-FAB): *m/e* 596 (base peak), [<sup>12</sup>C<sub>18</sub><sup>1</sup>H<sub>34</sub><sup>11</sup>B<sub>15</sub><sup>10</sup>B<sub>3</sub><sup>14</sup>N<sub>2</sub><sup>16</sup>O<sub>4</sub><sup>59</sup>Co]<sup>+</sup>. Crystals were very small and were unstable when removed from the solvent, even when placed in a sealed capillary containing some solvent.

**Collection and Reduction of X-ray Data for [commo-3,3'-Fe]8-N-(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>-3,1,2-FeC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]<sub>2</sub>Cl (**5**).** A purple crystalline platelet, obtained from dichloromethane/heptane solution, was mounted on a thin glass fiber on a diffractometer constructed by Professor C. E. Strouse of this department. Systematic absences were found for reflections 0*k*0, *k* = 2*n* + 1, and for *h*0*l*, *l* = 2*n* + 1. Unit cell parameters were determined from a least-squares fit of 19 accurately centered reflections (8.1 < 2 $\theta$  < 17.8°). These dimensions and other parameters, including conditions of data collection, are summarized in Table V. Data were collected in the  $\theta$ -2 $\theta$  scan mode to a limit in 2 $\theta$  of 45°. Three reflections of medium intensity (200), (016), and (123) were monitored every 97 reflections to check stability. Intensities of the reflections decreased by 7% over 81.8 h of exposure. Of the 4408 reflections measured, 1339 were considered observed (*I* > 3 $\sigma$ (*I*)) and were used in the subsequent structure analysis. Data were corrected for Lorentz and polarization effects but not for absorption. Programs used in this work include locally modified versions of the programs listed in the reference section.<sup>20</sup>

**Solution and Refinement of the Structure of [commo-3,3'-Fe]8-N-(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>-3,1,2-FeC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]<sub>2</sub> (**5**).** Atoms were located by use of the heavy-atom method. All calculations were performed on the VAX 11/750 computer of the J. D. McCullough Laboratory for Crystallography. No anisotropic thermal parameters were refined. Scattering factors for hydrogen were obtained from Stewart et al.<sup>21</sup> and for the other atoms were taken from ref 22. Anomalous dispersion terms were applied to the scattering of Fe. A disordered poorly characterized solvent with partial occupancy is present in the crystal. Only 12 hydrogen atoms were located. These parameters were not refined but were included in the structure factor calculations. Hydrogen atoms have been assigned isotropic thermal parameters, *B* = 7.0 Å<sup>2</sup>. An attempt to cool this crystal to 128 K in order to obtain better data failed because the crystal cracked. Final positional and thermal parameters for non-hydrogen atoms are given in Table VI.

**Collection and Reduction of X-ray Data for [commo-3,3'-Fe]3,1,2-FeC<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]<sub>2</sub>[N(CH<sub>3</sub>)<sub>4</sub>]<sub>2</sub> (**6**).** A red air-stable crystal, obtained from a CH<sub>3</sub>CN/(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O solution,<sup>1b</sup> was mounted on a thin glass fiber on a diffractometer constructed by Professor C. E. Strouse of this department. Systematic absences were found for 0*k*0 reflections for which *k* = 2*n* and

**Table VI.** Positional and Equivalent Isotropic Temperature Parameters for **5**<sup>a</sup>

atom	<i>x</i>	<i>y</i>	<i>z</i>	$\langle U_{eq} \times 10^4 \rangle, \text{Å}^2$
Fe(03)	0.0921 (5)	0.203 (4)	0.1366 (1)	43 (1)
N(81)	0.212 (2)	0.186 (2)	0.2370 (6)	46 (7)
N(81)'	0.258 (2)	-0.034 (2)	0.0901 (7)	47 (7)
C(01)	0.252 (3)	0.305 (3)	0.1122 (8)	48 (8)
C(02)	0.098 (3)	0.377 (3)	0.1227 (9)	60 (11)
C(81)	0.280 (3)	0.253 (3)	0.2747 (9)	59 (10)
C(82)	0.283 (3)	0.183 (3)	0.3137 (9)	66 (10)
C(83)	0.058 (3)	0.146 (3)	0.2475 (10)	63 (10)
C(84)	-0.046 (4)	0.245 (3)	0.2643 (10)	75 (12)
C(85)	0.295 (3)	0.068 (3)	0.2293 (9)	60 (10)
C(86)	0.464 (3)	0.081 (3)	0.2305 (9)	55 (10)
C(01)'	-0.112 (3)	0.133 (3)	0.1511 (9)	47 (9)
C(02)'	-0.117 (3)	0.204 (3)	0.1099 (8)	43 (8)
C(81)'	0.231 (3)	-0.150 (3)	0.0622 (9)	60 (10)
C(82)'	0.370 (3)	-0.208 (3)	0.0488 (9)	68 (10)
C(83)'	0.364 (3)	0.054 (3)	0.0667 (9)	49 (9)
C(84)'	0.309 (3)	0.089 (3)	0.0249 (10)	66 (11)
C(85)'	0.345 (3)	-0.071 (2)	0.1258 (8)	40 (8)
C(86)'	0.298 (3)	-0.183 (3)	0.1473 (9)	66 (10)
B(04)	0.322 (3)	0.229 (3)	0.1523 (10)	41 (10)
B(05)	0.405 (4)	0.364 (4)	0.1357 (12)	67 (13)
B(06)	0.258 (4)	0.467 (3)	0.1179 (11)	47 (11)
B(07)	0.049 (4)	0.353 (3)	0.1727 (11)	46 (11)
B(08)	0.205 (4)	0.264 (3)	0.1953 (11)	63 (13)
B(09)	0.368 (4)	0.345 (3)	0.1874 (12)	58 (12)
B(10)	0.330 (4)	0.484 (4)	0.1656 (13)	73 (14)
B(11)	0.127 (4)	0.492 (4)	0.1573 (12)	65 (13)
B(12)	0.209 (4)	0.416 (3)	0.2006 (12)	59 (12)
B(04)'	0.035 (4)	0.025 (3)	0.1494 (11)	44 (10)
B(05)'	-0.168 (4)	-0.011 (4)	0.1428 (12)	65 (13)
B(06)'	-0.265 (4)	0.113 (3)	0.1177 (11)	56 (12)
B(07)'	0.004 (4)	0.161 (3)	0.0743 (11)	49 (11)
B(08)'	0.101 (4)	0.032 (4)	0.1001 (13)	65 (13)
B(09)'	-0.043 (4)	-0.081 (3)	0.1122 (11)	49 (11)
B(10)'	-0.219 (4)	-0.019 (4)	0.0886 (12)	63 (12)
B(11)'	-0.183 (4)	0.125 (3)	0.0703 (12)	59 (12)
B(12)'	-0.053 (4)	0.010 (3)	0.0663 (11)	50 (11)

<sup>a</sup>  $U_{eq} = [1/(6\pi^2)] \sum \sum \beta_{ij} a_i a_j$ . The complete temperature factor is  $\exp[-8\pi^2 U(\sin^2 \theta)/\lambda^2]$  or  $\exp[-B(\sin^2 \theta)/\lambda^2]$ , where  $B = 8\pi^2 U$ .

**Table VII.** Positional and Equivalent Isotropic Thermal Parameters for **6**<sup>a</sup>

atom	<i>x</i>	<i>y</i>	<i>z</i>	$\langle U^2 \rangle, \text{Å}^2$
Fe(3)	1.0000	0.5000	1.0000	0.053
C(01)	1.1283 (12)	0.5530 (5)	0.8710 (6)	0.049
C(02)	1.0917 (11)	0.4532 (6)	0.8527 (6)	0.050
B(04)	0.9394 (14)	0.6061 (6)	0.9044 (8)	0.056
B(05)	1.0280 (17)	0.6122 (7)	0.7659 (8)	0.070
B(06)	1.1292 (13)	0.5131 (7)	0.7345 (8)	0.057
B(07)	0.8638 (15)	0.4304 (7)	0.8719 (8)	0.064
B(08)	0.7559 (14)	0.5291 (7)	0.9029 (9)	0.061
B(09)	0.7931 (15)	0.5969 (7)	0.7794 (8)	0.065
B(10)	0.9099 (16)	0.5389 (7)	0.6785 (9)	0.069
B(11)	0.9535 (15)	0.4357 (8)	0.7319 (8)	0.067
B(12)	0.7474 (13)	0.4898 (8)	0.7608 (8)	0.065
C(03)	1.5565 (16)	0.7698 (6)	0.5550 (8)	0.090
C(04)	1.3662 (14)	0.7424 (7)	0.3881 (8)	0.088
C(05)	1.6562 (13)	0.6716 (7)	0.4161 (9)	0.087
C(06)	1.4018 (16)	0.6337 (7)	0.5288 (8)	0.093
N(02)	1.4984 (10)	0.7040 (4)	0.4736 (5)	0.057

<sup>a</sup> Units of each esd, in parentheses, are those of the least significant digit of the corresponding parameter. Isotropic values are [ $1/8\pi^2$ ] times the "equivalent *B* value" as defined by Hamilton.<sup>23</sup>

for *h*0*l* reflections for which *l* = 2*n*. Unit cell parameters were determined from a least-squares fit of 17 accurately centered reflections (7.6° < 2 $\theta$  < 18.2°). These dimensions and other parameters, including conditions of data collection, are summarized in Table V. Data were collected at 25 °C in the  $\theta$ -2 $\theta$  scan mode. Three reflections of medium intensity (033), (120), and (202) were monitored every 97 reflections to check stability. Intensities of these reflections fluctuated ca.  $\pm 5\%$  during the course of the experiment (48.8 h). Of the 2431 unique reflections measured, 1118 were considered observed (*I* > 3 $\sigma$ (*I*)) and were used in

(20) CARESS (Broach, Coppens, Becker, and Blessing), peak profile analysis, Lorentz and polarization corrections; ORFLS (Busing, Martin, and Levy), structure factor calculation and full-matrix least-squares refinement; ABSORB (Coppens, Edwards, and Hamilton), absorption correction calculation; ORTEP (Johnson), figure plotting; SHELX76 (Sheldrick), structure analysis package.

(21) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(22) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

the subsequent structure analysis. Data were corrected for Lorentz, polarization, and absorption effects. Programs used in this work include locally modified versions of the programs listed in the reference section.<sup>20</sup>

**Solution and Refinement of the Structure of [*com*-3,3'-Fe(3,1,2-FeC<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>][N(CH<sub>3</sub>)<sub>4</sub>]<sub>2</sub> (6).** Atoms were located by use of direct methods. All calculations were performed on the VAX 11/750 computer of the J. D. McCullough Laboratory for Crystallography. All H atoms on the anion were kept in located positions with an assigned value of  $U = 0.08 \text{ \AA}^2$ . All methyl H were included in calculated positions in structure factor calculations with an assigned  $U$  value of  $0.10 \text{ \AA}^2$ . No hydrogen parameters were refined. Scattering factors for H were obtained from Stewart et al.<sup>21</sup> and for other atoms were taken from ref 22. Anomalous dispersion terms were applied to the scattering of Fe. The largest peak on a final difference electron density map was  $0.8 \text{ e/\AA}^{-3}$ . Final positional and thermal parameters for non-hydrogen atoms are given in Table VII.

(23) Hamilton, W. C. *Acta Crystallogr.* 1959, 12, 609.

**Acknowledgment.** We gratefully acknowledge financial support provided by the Office of Naval Research.

**Registry No.** 5, 132232-99-6; 6, 12304-96-0; 7, 132233-00-2; 8, 132259-25-7; 9-Cl, 132233-01-3; K[*nido*-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>], 12304-72-2; [*nido*-9-(4-C<sub>2</sub>H<sub>4</sub>N)CO<sub>2</sub>CH<sub>3</sub>]-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>], 110433-08-4; [*nido*-10-N-(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>], 132205-46-0; [*nido*-10-C<sub>6</sub>H<sub>5</sub>N(CH<sub>3</sub>)<sub>2</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>], 132205-47-1; [*nido*-9-C<sub>6</sub>H<sub>5</sub>N(CH<sub>3</sub>)<sub>2</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>], 132205-48-2; [*nido*-9-HCON(CH<sub>3</sub>)<sub>2</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>], 132205-49-3; [*nido*-9-CH<sub>3</sub>CON(CH<sub>3</sub>)<sub>2</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>], 132205-50-6; [*nido*-10-N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>-7,9-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>], 132205-51-7; [*closo*-1,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>], 52952-24-6; [*nido*-10-[(CH<sub>3</sub>)<sub>2</sub>CH]<sub>2</sub>NH-7,9-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>], 132205-52-8; [*nido*-10-C<sub>6</sub>H<sub>5</sub>N-7,9-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>], 73066-29-2; 4-(C<sub>2</sub>H<sub>4</sub>N)CO<sub>2</sub>CH<sub>3</sub>, 2459-09-8; Me<sub>3</sub>NH[*nido*-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>], 12543-22-5.

**Supplementary Material Available:** For 5 and 6, tables of crystallographic parameters, positional and thermal parameters, and interatomic distances and angles (14 pages); listings of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, Syracuse University, New York 13244, and Pharmaceuticals Research, Johnson Matthey, 1401 King Road, West Chester, Pennsylvania 19380

## Investigations of the Technetium–Hydrazido Core. Synthesis and Structural Characterization of [(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N][Tc<sub>2</sub>(NNPh<sub>2</sub>)<sub>2</sub>(C<sub>6</sub>Cl<sub>4</sub>O<sub>2</sub>)<sub>4</sub>]-CH<sub>2</sub>Cl<sub>2</sub>·2CH<sub>3</sub>OH, a Tc(V)/Tc(VI) Catecholate Complex with the Hydrazido Ligands Adopting the Unusual $\eta^1$ Bridging Mode

Michael J. Abrams,\*<sup>†</sup> Scott K. Larsen,<sup>†</sup> and Jon Zubietta\*<sup>‡</sup>

Received December 4, 1990

Reaction of the oxo-bis(tetrachlorocatecholate) Tc(V) complex [(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N][TcO(C<sub>6</sub>Cl<sub>4</sub>O<sub>2</sub>)<sub>2</sub>] (1) with *N,N*-diphenylhydrazine in CH<sub>2</sub>Cl<sub>2</sub> yields the binuclear paramagnetic Tc(V)/Tc(VI) mixed-valence complex [(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N][Tc<sub>2</sub>(NNPh<sub>2</sub>)<sub>2</sub>(C<sub>6</sub>Cl<sub>4</sub>O<sub>2</sub>)<sub>4</sub>]-CH<sub>2</sub>Cl<sub>2</sub>·2CH<sub>3</sub>OH (2). The structure of the molecular anion of 2 consists of two distorted octahedral Tc centers bridged by two hydrazido(2-) groups bonding in the  $\eta^1$  mode, an unusual bonding motif for this ligand, having been previously described only for cyclopentadienyl-metal species. Complex 2 is also a unique example of a Tc(V)/Tc(VI) mixed-valence species; the Tc–Tc distance of 2.612 (2) Å is consistent with direct metal–metal interaction. Crystal data for 1:  $P\bar{1}$ ,  $a = 9.579$  (2) Å,  $b = 11.705$  (3) Å,  $c = 16.391$  (4) Å,  $\alpha = 83.95$  (2)°,  $\beta = 88.63$  (2)°,  $\gamma = 74.51$  (2)°,  $V = 1761.3$  (7) Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calc}} = 1.60 \text{ g cm}^{-3}$ ; 3637 reflections,  $R = 0.046$ . Crystal data for 2:  $P\bar{1}$ ,  $a = 14.210$  (3) Å,  $b = 16.663$  (4) Å,  $c = 19.644$  (4) Å,  $\alpha = 76.82$  (2)°,  $\beta = 80.52$  (2)°,  $\gamma = 66.79$  (2)°,  $V = 4151.8$  (15) Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calc}} = 1.55 \text{ g cm}^{-3}$ ; 6999 reflections,  $R = 0.075$ .

### Introduction

The intense contemporary interest in the fundamental coordination chemistry of the synthetic radioactive element technetium is a consequence of its expanding application in diagnostic nuclear medicine.<sup>1–3</sup> Technetium-99 remains the radionuclide of choice for numerous applications by virtue of its reasonable cost, ready availability, and optimal nuclear properties ( $\gamma = 140 \text{ keV}$  with no particulate emissions,  $t_{1/2} = 6 \text{ h}$ ), which allow images of high resolution to be obtained with a low radiation dose to the patient. In order to be clinically useful, a technetium-containing complex must be easily prepared in a radiochemically pure form, must exhibit stability under biological conditions, and must possess useful biodistribution properties. Although a variety of technetium coordination complexes that locate in a particular organ have been described,<sup>4–7</sup> a more general approach exploits the binding of <sup>99m</sup>Tc to tumor-localizing monoclonal and polyclonal antibodies.<sup>8–10</sup>

Methods employed in the conjugation of <sup>99m</sup>Tc to proteins include the use of diethylenetriaminepentaacetic acid<sup>11</sup> and of N<sub>2</sub>S<sub>2</sub> and N<sub>3</sub>S<sup>12–18</sup> functionalized ligands and direct reduction<sup>19</sup> of the protein disulfide bonds to form free sulfhydryl groups. Difficulties encountered with these technologies include protein denaturation, nonspecific binding of technetium, and slow kinetics of Tc-labeling.

We have recently described a simple, efficient, and general method for labeling proteins with <sup>99m</sup>Tc based on bifunctional

- (1) Nicolini, M.; Bandoli, G.; Mazzi, U., Eds. *Technetium in Chemistry and Nuclear Medicine*; Raven: New York, 1986.
- (2) Deutsch, E.; Libson, K. *Comments Inorg. Chem.* 1984, 3, 83.
- (3) Deutsch, E.; Libson, K.; Vanderheyden, J.-L.; Ketring, A. R.; Maxon, H. R. *Nucl. Med. Biol.* 1986, 13, 465 and references therein.
- (4) Deutsch, E.; Libson, K.; Jurisson, S.; Lindoy, L. F. *Prog. Inorg. Chem.* 1983, 30, 70.
- (5) Clarke, M. J.; Podbielski, L. *Coord. Chem. Rev.* 1987, 78, 253.
- (6) Eakins, J. D.; Humphreys, D. G.; Mellish, C. E. *J. Chem. Soc.* 1963, 6012.
- (7) Radnovich, L. J.; Hoard, J. L. *J. Phys. Chem.* 1984, 88, 6713.
- (8) Franz, J.; Freeman, G. M.; Barefield, E. K.; Volkert, W. A.; Ehrhardt, G. J.; Holmes, R. A. *Nucl. Med. Biol.* 1987, 14, 479.
- (9) Meares, C. F.; Wensel, T. G. *Acc. Chem. Res.* 1984, 17, 202.
- (10) Huber, G. J.; Alberto, R. A.; Bläuenstein, P.; Andereg, G. *J. Chem. Soc., Chem. Commun.* 1989, 879.
- (11) Hnatowich, D. J.; Layne, W. W.; Childs, R. L.; Lanteigne, D.; Davis, M. A.; Griffin, T. W.; Doherty, P. W. *Science (Washington, DC)* 1983, 220, 613.
- (12) Rao, T. N.; Adhikesavalu, D.; Camerman, A.; Fritzberg, A. R. *J. Am. Chem. Soc.* 1990, 112, 5798.
- (13) Fritzberg, A. R.; Kasina, S.; Vanderheyden, J. L.; Srinivasan, A. *Eur. Pat. Appl.* EP 284071, 1988.
- (14) Lanteigne, D.; Hnatowich, D. J. *Int. J. Appl. Radiat. Isot.* 1984, 35, 617.
- (15) Arano, Y.; Yokoyama, A.; Furukawa, T.; Horiuchi, K.; Yahata, T.; Saji, H.; Sakahara, H.; Nakashima, T.; Koizumi, M.; Endo, K.; Torizuka, K. *J. Nucl. Chem.* 1987, 28, 1027.

\* To whom correspondence should be addressed.

<sup>†</sup> Johnson Matthey.

<sup>‡</sup> Syracuse University.