Half-Sandwich Iron(II) and Ruthenium(II) Complexes with the Dicarbollylamino Ligand System

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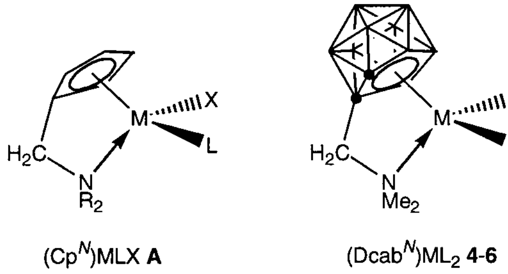
The syntheses of half-sandwich iron(II) complexes [(η^5:η^1-$C_2B_9H_{10}$-CH_2NMe_2)FeL_2] (L = CO (**4a**), CNBu^t (**4b**), PMe_3 (**4c**), 1,5-cycloctadiene (cod) (**4d**)) are reported, and the structure of **4a** has been established by an X-ray diffraction study. The complex **4a** adopts a characteristic three-legged "piano stool" structure with the iron atom η^5-coordinated on one side by a *nido o*-carboranyl group and the other by the dimethylamino group and two CO ligands. Thus, treatment of the lithium salt of DcabH^N [*nido*-7-NMe_2CH_2-7,8-$C_2B_9H_{11}$]$^{1-}$ (**2**) with $FeCl_2(THF)_n$ in THF affords solutions of the labile species [(η^5:η^1-$C_2B_9H_{10}$-CH_2NMe_2)-$Fe(THF)_2$] (**3**), which readily reacts with CO, CNBu^t, PMe_3, and cod, yielding the species **4a**−**d**. In particular, the η^4-bonding mode of the cycloctadienyl group to the metal of complex **4d** is displaced in the reaction with CNBu^t and PMe_3, yielding **4b** and **4c**, respectively. [Ru-$(CO)_3Cl_2]_2$ reacts with the lithium salt of **2** in THF to give [(η^5:η^1-$C_2B_9H_{10}$-CH_2NMe_2)Ru-$(CO)_2$] (**5**), having a molecular structure closely related to that of **4a**, as confirmed by an X-ray diffraction study. Further decarbonylation reaction of **5** with Me_3NO was carried out in acetonitrile solution to give the corresponding monosubstituted complex [(η^5:η^1-$C_2B_9H_{10}$-CH_2NMe_2)Ru(CO)(NCMe)] (**6**).

Introduction

The dicarbollide dianion *nido*-7,8-$C_2B_9H_{11}^{2-}$ and its derivatives have been used as penta-hapto ligands for transition metals,[1] forming *closo* heterocarboranes by incorporating transition metal fragments at the missing vertex of an icosahedron. Following extensive research into the chemistry of dicarbollide complexes of many transition metals bearing the unsubstituted unit, interest has now turned to substituted dicarbollides. A ligand of this kind is a heterobifunctional amino-group-linked dicarbollide DcabH^N [*nido*-7-NMe_2CH_2-7,8-$C_2B_9H_{11}$]$^-$ (**2**), whereas the dicarbollide unit is a negatively charged π-donor group and the pendent amine is an electroneutral σ-donor group. Thus, dicarbollyl derivatives with a functionalized side chain like **2** containing both a soft and a hard donor site form the well-known half-sandwich complexes (Dcab^N)ML_2 **4**−**6** (Chart 1), with metals possessing specific structures and reactivity. A functionalized side chain can also temporarily and reversibly coordinate to a metal ion, and this can stabilize a highly reactive, electronically and sterically unsaturated intermediate. As a result, a versatile catalyst design is conceivable by modifying the aminoalkyl group.

Chart 1



M = Fe, Ru; L = neutral ligand; X = anionic ligand

Similar heterobifunctional ligands include, among others, cyclopentadienylamino systems Cp^N, in which an amine functionality is directly connected to a cyclopentadienyl system. The corresponding coordination behavior of organometallic compounds containing such ligand systems has been the focus of extensive studies.[2] The design of alternate ligands to modify the molecular and electronic structure of transition metal complexes that serve as catalyst precursors remains an active area of research. With this in mind, we have attempted to modify the half-sandwich complexes (Cp^N)MLX **A** (Chart 1), by replacing the anionic cyclopentadienyl functionality with a dianionic dicarbollide group. The dicarbollide functionality behaves as a 6 π-donor, whereas the amino

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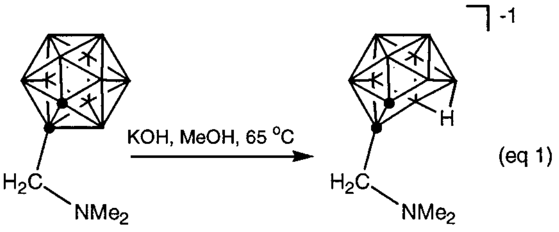
group can only function as a two-electron σ-donor. These substitutions decrease charge without perturbing significantly the molecular geometry or fontier orbitals of a half-sandwich metal complex. It is possible with these molecules to investigate how charge influences reactivity. Thus, a formal analogy between the ligating properties of the dianionic Dcab^N and the monoanionic Cp^N thus becomes apparent, leading to the expectation for the preparation of intramolecularly coordinated metallacarboranes as shown in Chart 1.

It was therefore of interest to investigate the possibility of synthesizing such intramolecularly coordinated group 8 transition metal complexes of types **4**−**6** bearing both *nido* icosahedral and amine units that might potentially stabilize the metal center. We therefore report the synthesis of the new types of bifunctional anionic carborane species DcabH^N **2** and show how the open pentagonal face of this *nido* icosahedral fragment and amine unit could function as a poly-hapto ligand toward transition metal ions. Here we report the detailed synthesis and complete characterization of the iron complexes **4a**−**d** and the ruthenium complex **5**. Particularly, compound **4d** undergoes ligand substitutions with other soft donor ligands such as CNBu^t and PMe$_3$ to give the corresponding substituted complexes **4b** and **4c**, respectively. We also report the decarbonylation reaction of **5** with trimethylamine-*N*-oxide to give the corresponding monosubstituted complex **6**. Included in our work are the X-ray diffraction structures of **4a**, **5**, and **6**.

Results and Discussion

Ligand Synthesis. The dicarbollyl ligand DcabH^N [*nido*-7-NMe$_2$CH$_2$-7,8-C$_2$B$_9$H$_{11}$]$^-$ (**2**) was prepared using a standard deborination procedure[3] involving *o*-carboranylamine CabH^N (*closo*-1-NMe$_2$CH$_2$-1,2-C$_2$B$_{10}$H$_{11}$) (**1**) (eq 1). Reaction of **1** with KOH in methanol at 65 °C leads to the formation of deborinated monoanionic system **2**. Thus, complex **1** undergoes facile degradation in methanolic KOH to selectively remove the boron atom and generate **2**.



CabH^N **1** DcabH^N **2** (eq 1)

The tetramethylammonium salt of complex **2** has been obtained from the aqueous workup. The spectroscopic characterization of this complex shows that the aminomethyl group is linked to the *nido* cage carborane. The characteristic 1:1:1:1:1:1:1:1:1 pattern in the ^{11}B-{^{1}H} NMR spectrum in the range −10 to −37 ppm and the presence of an absorption at −2.6 ppm in the ^{1}H NMR spectrum imply a B−H−B interaction on the C$_2$B$_3$ open face. Further deprotonation of this bridge hydrogen with Bu^{n}Li gives the corresponding dianionic ligand Dcab^N [*nido*-7-NMe$_2$CH$_2$-7,8-C$_2$B$_9$H$_{10}$]$^{2-}$.

Reaction of the Ligand with Fe Complex. Reaction of the lithium salt of **2** with FeCl$_2$(THF)$_2$ in THF gives a new compound, formulated as the mononuclear species [(η^5:η^1-C$_2$B$_9$H$_{10}$-CH$_2$NMe$_2$)Fe(THF)$_2$] (**3**) (Scheme 1). The precise structure of this compound is unknown due to our inability to obtain single crystals for X-ray analysis; the compound tended to dissolve out of the aromatic solvent systems employed and decomposed in chlorinated or donor solvents. Although the desired species **3** could not be isolated, spectroscopic studies on the red solutions formed in situ provided evidence of its formulation. The ^{1}H NMR spectrum of this complex displays a singlet at around δ 2.25−2.38 for the two N*Me*$_2$ groups, a broad singlet at δ 2.43 for the NC*H*$_2$ group, and a broad singlet at δ 3.45 for the *o*-carboranyl C*H* hydrogen, as well as resonances for the coordinated THF molecules. In addition, the ^{11}B chemical shifts are similar to those observed for other metal dicarbollyl complexes and support the proposed η^5-coordination.[4] As described below, THF solutions of **3** may be used for further preparative work without isolation of **3**.

The presence of the labile THF molecule in the complex **3** makes it a very versatile synthon. Therefore, it was of interest to determine whether the iron-coordinated THF molecules in **3** could be replaced by treatment of the complex with other donor molecules.

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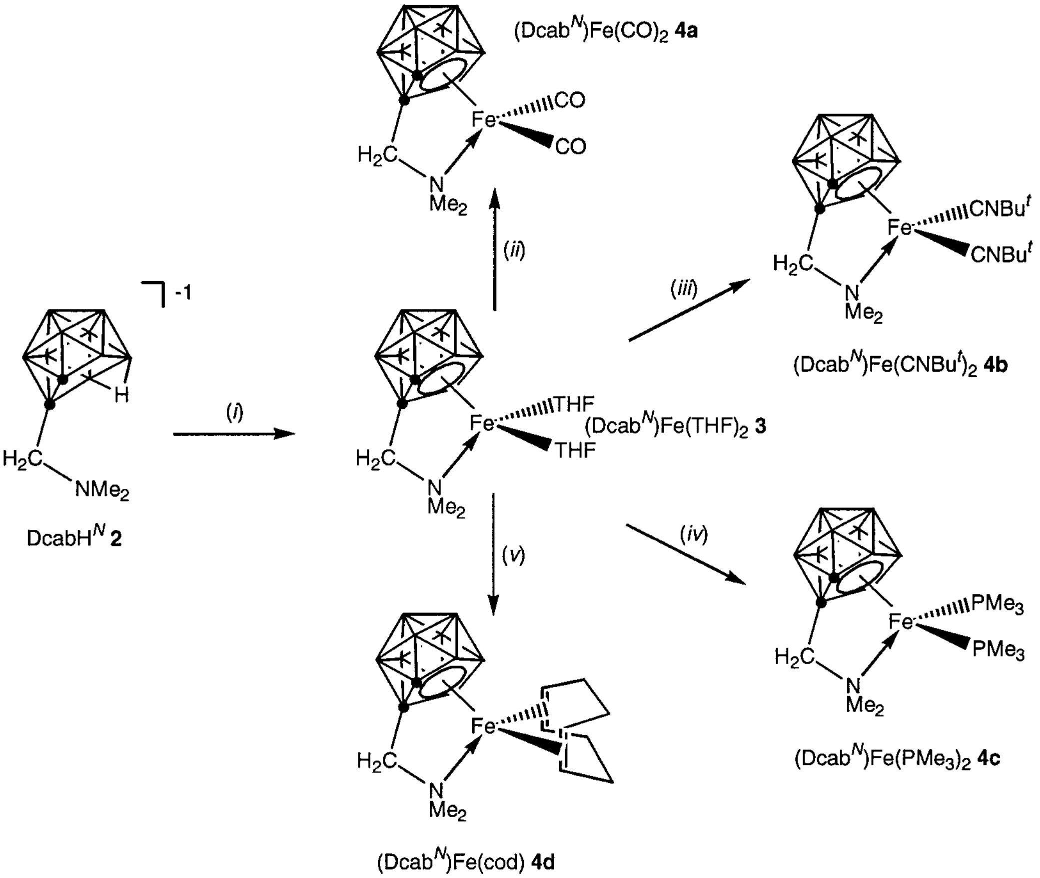
Scheme 1. Synthesis of Dicarbollyl-amino Iron(II) Complexes 4[a]



[a] Legend: (*i*) (a) LiBu^n, THF, −78 °C, (b) FeCl$_2$(THF)$_2$, THF, −78 °C; (*ii*) CO, THF, 25 °C; (*iii*) CNBu^t, THF, 65 °C; (*iv*) PMe$_3$, THF, 65 °C; (*v*) cod, THF, 65 °C.

All four of the new dicarbollylamino complexes **4** were prepared from the requisite bis(THF)-coordinated iron complex **3** and a slight excess of nucleophiles such as CO, CNBu^t, PMe$_3$, and cod in THF solutions, as shown in Scheme 1. Isolation of the pure products, which ranged from red to dark red in color, was achieved by recrystallization. Typically, the yields of **4** were on the order of 16−36%. The complexes are stable under atmospheric conditions and soluble in chlorinated solvents.

When CO gas was introduced into THF solutions of **3**, dicarbonyl complex **4a** was obtained (Scheme 1). Formation of **4a** could be easily characterized by the terminal carbonyl stretches. Two carbonyl stretches observed at 2035 and 1989 cm^{-1} for **4a** are characteristic of this type of dicarbonyl complex. Addition of *tert*-butyl isocyanide to a solution of **3** resulted in immediate coordination of isocyanide to the iron, providing **4b**. Strong bands appearing at 2139 and 2110 cm^{-1} for **4b** are characteristic of isocyanide stretches. In addition to CO and isocyanide, trimethyl phosphines also add to **3** to give the corresponding bis(phosphine) complex **4c**. Addition of PMe$_3$ to a solution of **3** resulted in an immediate color change from red to dark red. Incorporation of phosphine ligands was verified by ^{31}P chemical shifts, which appeared at δ 33.44 and 38.26 for **4c**. Similarly, the cycloctadienyl iron complex **4d** is obtained by reaction of a THF solution of **3** with cod. The IR spectrum of **4d** exhibits one stretch at 2180 cm^{-1} for the iron-coordinated C=C bond. The formation of **4d** is further provided by ^{1}H NMR data. Thus, the ^{1}H NMR spectrum of **4d** shows signals for the coordinated cod ligand at δ 2.30−2.55 (methylene protons) and at 3.97 (olefinic protons).

The NMR data for these structurally similar molecules are in accord with their formulations. In contrast to the ligand **2**, the ^{1}H NMR spectrum reveals two signals for the methyl groups at the nitrogen atom of the side chain due to the asymmetric metal center. The methylene protons of the CH_2 group in **4** are diastereotopic, each giving rise to an AB spin pattern. The most significant change in the ^{1}H NMR spectra is caused by the low-field shift of the signals for the methylene hydrogens, while for complex **2**, these signals are observed at around δ 2.3, and **4** shows values of δ 2.9−3.7. In addition, the signals for the methyl groups at the nitrogen atom are shifted downfield (δ 0.12−0.43). The corresponding downfield shifts for the methylene and methyl groups adjacent to the nitrogen atom are observed in the ^{13}C NMR spectra. This observation is consistent with similar findings for the general intramolecularly coordinated *o*-carboranyl metal complexes of the CabH^N (*closo*-1-NMe$_2$CH$_2$-1,2-C$_2$B$_{10}$H$_{11}$)[5] and CabH^P (*closo*-1-PPh$_2$CH$_2$-1,2-C$_2$B$_{10}$H$_{11}$)[6] ligand systems. The spectroscopic data for the complexes **4a**−**d** prove that the dimethyl amino group of the side chain is coordinated to the metal center in all cases. In

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Table 1. NMR Spectroscopic Data for Compounds 1−6

	NMR (δ)		
compound	^{1}H	^{13}C	^{11}B
1[a]	2.31 (s, 6H, $\mathrm{N}Me$)	46.731 ($\mathrm{N}Me$)	−13.43 (d, 4B, $J_{\mathrm{BH}} = 120$ Hz)
	2.99 (s, 2H, $\mathrm{NC}H_2$)	58.774 ($C\mathrm{HCB_{10}H_{10}}$)	−11.87 (d, 2B, $J_{\mathrm{BH}} = 110$ Hz)
	3.99 (br s, 1H, $\mathrm{C_{cab}}H$)	63.233 ($\mathrm{N}C\mathrm{H_2}$)	−9.27 (d, 2B, $J_{\mathrm{BH}} = 160$ Hz)
		75.753 ($\mathrm{CH}C\mathrm{B_{10}H_{10}}$)	−5.48 (d, 1B, $J_{\mathrm{BH}} = 150$ Hz)
			−3.33 (d, 1B, $J_{\mathrm{BH}} = 140$ Hz)
2[b]	2.11 (s, 6H, $\mathrm{N}Me_2$)	45.74 ($\mathrm{N}Me_2$)	−36.66 (d, 1B, $J_{\mathrm{BH}} = 95$ Hz)
	2.25 (br s, 1H, $\mathrm{C_{cab}}H$)	55.79 ($\mathrm{N}Me_4{}^+$)	−33.12 (d, 1B, $J_{\mathrm{BH}} = 85$ Hz)
	2.23 (d, 1H, $\mathrm{NC}H_2$, $J_{\mathrm{HH}} = 14$ Hz)	69.57 ($\mathrm{N}C\mathrm{H_2}$)	−22.31 (d, 1B, $J_{\mathrm{BH}} = 100$ Hz)
	2.42 (d, 1H, $\mathrm{NC}H_2$, $J_{\mathrm{HH}} = 14$ Hz)		−19.32 (d, 1B, $J_{\mathrm{BH}} = 100$ Hz)
	3.45 (s, 12H, $\mathrm{N}Me_4{}^+$)		−17.70 (d, 1B, $J_{\mathrm{BH}} = 80$ Hz)
			−16.71 (d, 1B, $J_{\mathrm{BH}} = 80$ Hz)
			−13.54 (d, 1B, $J_{\mathrm{BH}} = 100$ Hz)
			−10.32 (d, 1B, $J_{\mathrm{BH}} = 90$ Hz)
			−9.65 (d, 1B, $J_{\mathrm{BH}} = 90$ Hz)
3[a]	2.11 ($\mathrm{OC_4}H_8$)	26.25 ($\mathrm{O}C_4\mathrm{H_8}$)	−32.93 (d, 1B, $J_{\mathrm{BH}} = 95$ Hz)
	2.25 ($\mathrm{N}Me_2$)	44.32 ($\mathrm{N}Me_2$)	−28.19 (d, 1B, $J_{\mathrm{BH}} = 120$ Hz)
	2.38 ($\mathrm{N}Me_2$)	58.60 ($\mathrm{N}C\mathrm{H_2}$)	−16.79 (d, 3B, $J_{\mathrm{BH}} = 110$ Hz)
	2.43 ($\mathrm{NC}H_2$)	67.88 ($\mathrm{O}C_4\mathrm{H_8}$)	−10.16 (d, 1B, $J_{\mathrm{BH}} = 100$ Hz)
	3.45 (br s, 1H, $\mathrm{C_{cab}}H$)		−8.55 (d, 2B, $J_{\mathrm{BH}} = 95$ Hz)
	3.70 ($\mathrm{OC_4}H_8$)		−3.33 (d, 1B, $J_{\mathrm{BH}} = 110$ Hz)
4a[a]	2.53 (s, 3H, $\mathrm{N}Me$)	53.47 ($\mathrm{N}Me$)	−21.53 (d, 1B, $J_{\mathrm{BH}} = 115$ Hz)
	2.69 (s, 3H, $\mathrm{N}Me$)	55.99 ($\mathrm{N}Me$)	−19.97 (d, 1B, $J_{\mathrm{BH}} = 95$ Hz)
	3.56 (d, 1H, $\mathrm{NC}H_2$, $J_{\mathrm{HH}} = 14$ Hz)	75.91 ($\mathrm{N}C\mathrm{H_2}$)	−13.98 (d, 2B, $J_{\mathrm{BH}} = 100$ Hz)
	3.72 (d, 1H, $\mathrm{NC}H_2$, $J_{\mathrm{HH}} = 14$ Hz)	218.42 ($\mathrm{Fe}(C\mathrm{O})$)	−12.30 (d, 1B, $J_{\mathrm{BH}} = 95$ Hz)
	3.89 (br s, 1H, $\mathrm{C_{cab}}H$)		−7.65 (d, 1B, $J_{\mathrm{BH}} = 120$ Hz)
			−5.34 (d, 1B, $J_{\mathrm{BH}} = 160$ Hz)
			−2.94 (d, 1B, $J_{\mathrm{BH}} = 95$ Hz)
			2.01 (d, 1B, $J_{\mathrm{BH}} = 100$ Hz)
4b[a]	1.60 (s, 9H, $\mathrm{CN}Bu^t$)	31.27 ($\mathrm{CN}Bu^t$)	−24.98 (d, 2B, $J_{\mathrm{BH}} = 115$ Hz)
	1.66 (s, 9H, $\mathrm{CN}Bu^t$)	31.29 ($\mathrm{CN}Bu^t$)	−18.15 (d, 2B, $J_{\mathrm{BH}} = 95$ Hz)
	2.21 (s, 3H, $\mathrm{N}Me$)	55.52 ($\mathrm{N}Me$)	−15.98 (d, 1B, $J_{\mathrm{BH}} = 140$ Hz)
	2.38 (s, 3H, $\mathrm{N}Me$)	56.34 ($\mathrm{N}Me$)	−10.94 (d, 1B, $J_{\mathrm{BH}} = 90$ Hz)
	3.46 (d, 1H, $\mathrm{NC}H_2$, $J_{\mathrm{HH}} = 14$ Hz)	62.44 ($\mathrm{N}C\mathrm{H_2}$)	−8.97 (d, 1B, $J_{\mathrm{BH}} = 100$ Hz)
	3.63 (d, 1H, $\mathrm{NC}H_2$, $J_{\mathrm{HH}} = 14$ Hz)	134.25 ($C\mathrm{NBu}^t$)	−6.31 (d, 2B, $J_{\mathrm{BH}} = 90$ Hz)
	3.80 (br s, 1H, $\mathrm{C_{cab}}H$)	140.37 ($C\mathrm{NBu}^t$)	
4c[a]	1.76 (d, 9H, $\mathrm{P}Me_3$, $J_{\mathrm{PH}} = 11$ Hz)	33.25 ($\mathrm{P}Me_3$, $J_{\mathrm{PC}} = 32$ Hz)	−29.25 (d, 2B, $J_{\mathrm{BH}} = 120$ Hz)
	1.83 (d, 9H, $\mathrm{P}Me_3$, $J_{\mathrm{PH}} = 11$ Hz)	40.66 ($\mathrm{P}Me_3$, $J_{\mathrm{PC}} = 32$ Hz)	−21.79 (d, 2B, $J_{\mathrm{BH}} = 100$ Hz)
	2.33 (s, 3H, $\mathrm{N}Me_2$)	66.37 ($\mathrm{N}Me$)	−11.46 (d, 1B, $J_{\mathrm{BH}} = 135$ Hz)
	2.39 (s, 3H, $\mathrm{N}Me_2$)	68.13 ($\mathrm{N}Me$)	−7.06 (d, 1B, $J_{\mathrm{BH}} = 95$ Hz)
	2.86 (d, 1H, $\mathrm{NC}H_2$, $J_{\mathrm{HH}} = 14$ Hz)	78.60 ($\mathrm{N}C\mathrm{H_2}$)	−5.34 (d, 1B, $J_{\mathrm{BH}} = 100$ Hz)
	3.00 (d, 1H, $\mathrm{NC}H_2$, $J_{\mathrm{HH}} = 14$ Hz)		−2.94 (d, 2B, $J_{\mathrm{BH}} = 95$ Hz)
	3.77 (br s, 1H, $\mathrm{C_{cab}}H$)		
4d[a]	2.35 (s, 3H, $\mathrm{N}Me$)	28.17 (s, $C\mathrm{H_{2,COD}}$)	−25.66 (d, 2B, $J_{\mathrm{BH}} = 100$ Hz)
	2.48 (s, 3H, $\mathrm{N}Me$)	31.00 (s, $C\mathrm{H_{2,COD}}$)	−19.43 (d, 2B, $J_{\mathrm{BH}} = 95$ Hz)
	2.30 (br s, 4H, $\mathrm{C}H_{\mathrm{endo,COD}}$)	57.44 ($\mathrm{N}Me$)	−16.77 (d, 1B, $J_{\mathrm{BH}} = 140$ Hz)
	2.55 (br s, 4H, $\mathrm{C}H_{\mathrm{exo,COD}}$)	60.37 ($\mathrm{N}Me$)	−14.22 (d, 1B, $J_{\mathrm{BH}} = 90$ Hz)
	3.03 (d, 1H, $\mathrm{NC}H_2$, $J_{\mathrm{HH}} = 14$ Hz)	72.66 ($\mathrm{N}C\mathrm{H_2}$)	−5.87 (d, 1B, $J_{\mathrm{BH}} = 100$ Hz)
	3.23 (d, 1H, $\mathrm{NC}H_2$, $J_{\mathrm{HH}} = 14$ Hz)	95.47 (s, $=C_{\mathrm{COD}}$)	−2.64 (d, 2B, $J_{\mathrm{BH}} = 90$ Hz)
	3.88 (br s, 1H, $\mathrm{C_{cab}}H$)		
	3.97 (br s, 4H, $=\mathrm{C}H_{\mathrm{COD}}$)		
5[a]	2.81 (s, 3H, $\mathrm{N}Me$)	57.67 ($\mathrm{N}Me$)	−22.11 (d, 2B, $J_{\mathrm{BH}} = 90$ Hz)
	2.95 (s, 3H, $\mathrm{N}Me$)	58.04 ($\mathrm{N}Me$)	−16.01 (d, 1B, $J_{\mathrm{BH}} = 95$ Hz)
	3.53 (br s, 1H, $\mathrm{C_{cab}}H$)	77.46 ($\mathrm{N}C\mathrm{H_2}$)	−14.16 (d, 2B, $J_{\mathrm{BH}} = 110$ Hz)
	3.84 (d, 1H, $\mathrm{NC}H_2$, $J_{\mathrm{HH}} = 14$ Hz)	222.68 ($\mathrm{Ru}(C\mathrm{O})$)	−6.10 (d, 1B, $J_{\mathrm{BH}} = 140$ Hz)
	3.99 (d, 1H, $\mathrm{NC}H_2$, $J_{\mathrm{HH}} = 14$ Hz)		−3.41 (d, 1B, $J_{\mathrm{BH}} = 105$ Hz)
			−1.90 (d, 1B, $J_{\mathrm{BH}} = 95$ Hz)
			2.19 (d, 1B, $J_{\mathrm{BH}} = 115$ Hz)
6[a]	2.01 (s, 3H, $\mathrm{NC}Me$)	37.20 ($\mathrm{NC}Me$)	−21.55 (d, 2B, $J_{\mathrm{BH}} = 90$ Hz)
	2.81 (s, 3H, $\mathrm{N}Me$)	54.21 ($\mathrm{N}Me$)	−15.76 (d, 1B, $J_{\mathrm{BH}} = 110$ Hz)
	2.96 (s, 3H, $\mathrm{N}Me$)	58.45 ($\mathrm{N}Me$)	−14.06 (d, 2B, $J_{\mathrm{BH}} = 95$ Hz)
	3.54 (br s, 1H, $\mathrm{C_{cab}}H$)	79.77 ($\mathrm{N}C\mathrm{H_2}$)	−6.01 (d, 1B, $J_{\mathrm{BH}} = 110$ Hz)
	3.85 (d, 1H, $\mathrm{NC}H_2$, $J_{\mathrm{HH}} = 14$ Hz)	203.99 ($\mathrm{N}C\mathrm{Me}$)	−2.94 (d, 2B, $J_{\mathrm{BH}} = 130$ Hz)
	4.00 (d, 1H, $\mathrm{NC}H_2$, $J_{\mathrm{HH}} = 14$ Hz)	291.37 ($\mathrm{Ru}(C\mathrm{O})$)	3.50 (d, 1B, $J_{\mathrm{BH}} = 110$ Hz)

[a] $\mathrm{CDCl_3}$ was used as the solvent, and the chemical shifts are reported relative to the residual H of the solvent. [b] $\mathrm{CD_3(CO)CD_3}$ was used as the solvent, and the chemical shifts are reported relative to the residual H of the solvent.

addition, the ^{11}B NMR spectra (Table 1) show the expected resonances for the dicarbollyl group in the highly asymmetric environments, due to the metal complexation. Compounds **4** represent the first examples of a dicarbollyl iron(II) complex with intramolecular coordination of a donor function in the side chain.

Final proof of the intramolecular coordination of the dimethylamino group to the Fe metal in complex **4** is provided by X-ray crystal structure analysis. Suitable crystals were grown by slow diffusion of hexane into a saturated dichloromethane solution of **4a**. As shown in Figure 1, complex **4a** possesses a crystallographic

Table 2. X-ray Crystallographic Data and Processing Parameters for Compounds 4a, 5, and 6

	4a	**5**	**6**
formula	$C_7H_{18}B_9NO_2Fe$	$C_7H_{18}B_9NO_2Ru$	$C_8H_{21}B_9N_2ORu$
fw	301.36	346.58	359.63
cryst class	orthorhombic	orthorhombic	monoclinic
space group	*Pnma*	*Pnma*	$P2_1/c$
Z	8	8	4
cell constants			
a, Å	16.767(1)	16.954(1)	10.099(5)
b, Å	11.785(1)	11.9162(6)	9.157(4)
c, Å	7.1383(9)	7.2525(6)	18.059(5)
V, Å^3	1410.6(2)	1465.2(2)	1642(1)
β, deg			100.49(4)
μ, mm^{-1}	2.113	2.116	0.944
cryst size, mm	0.3 × 0.4 × 0.5	0.1 × 0.25 × 0.3	0.3 × 0.5 × 0.9
D_{calcd}, g/cm^3	2.838	3.142	1.455
$F(000)$	1232	1376	720
radiation		Mo Kα ($\lambda = 7170$ Å)	
θ range, deg	2.43−25.97	2.40−25.95	2.05−25.96
H, k, l collected	+20,+14,+8	+20,+14, +8	+12, +11, ±22
no. of rflns measd	1527	1540	3447
no. of unique reflns	1453	1503	3221
no. of reflns used in refinement ($I > 2\sigma(I)$)	1453	1503	3221
no. of params	107	107	203
data/param ratio	13.58	14.05	15.87
R_1[a]	0.0704	0.0316	0.0698
wR_2[b]	0.1501	0.0984	0.1638
GOF	0.957	0.841	1.365

[a] $R_1 = \sum|F_o| - |F_c|$ (based on reflections with $F_o^2 > 2\sigma F^2$). [b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.095P)^2]$; $P = [\max(F_o^2, 0) + 2F_c^2]/3$(also with $F_o^2 > 2\sigma F^2$).

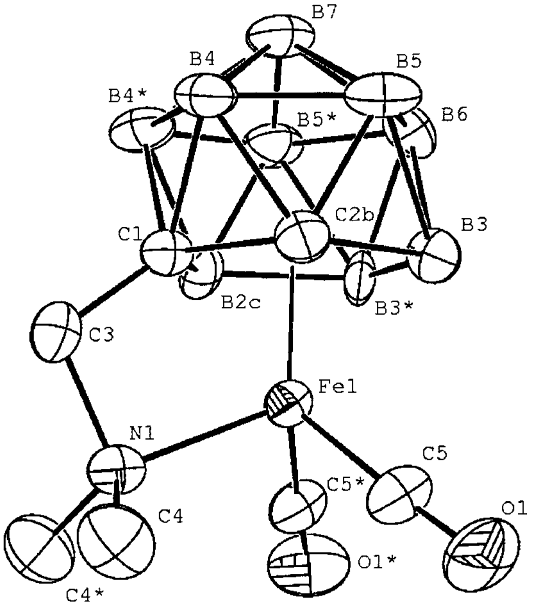

Figure 1. Molecular structure of **4a** with atom labeling; ellipsoids show 30% probability levels, and hydrogen atoms have been omitted for clarity.

disorder imposed by mirror symmetry. Thus, cage atoms Fe(1), C(1), B(6), and B(7) and the aminomethyl atoms N(1) and C(3) lie on the crystallographic mirror plane. As a consequence, the untethered carboranyl carbon atom is disordered by this plane so that the atomic positions designated by C(2b) and B(2c) are 50% occupied by C and 50% occupied by B. The molecule comprises a dicarbonyl iron(II) unit which is bonded to a penta-hapto dicarbollyl ligand. The tertiary amino fragment coordinates to the iron in the remaining basal site of the overall three-legged "piano-stool" conformation, giving a five-membered ring. The C_2B_3 bonding face in **4a** is essentially planar with no deviation from the least-squares plane by more than 0.123 Å. The iron is approximately centered over the ring, giving rise to an Fe−C_2B_3 face (centroid) distance of 1.526 Å. Selected bond lengths and angles for **4a** are listed in Tables 3 and 4. The Fe−N bond length of 2.05(1) Å closely resembles that found in $[CpFe(CO)(\kappa^2(P,N)\text{-}NH_2(CH_2)_3\text{-}PPh_2)]^+I^-$ (2.027(5) Å).[7] This value lies within the usual range for a dative bond between the iron and nitrogen atoms. The C−O distances (1.14(1) Å) are similar to those found in $[CpFe(CO)_3]PF_6$ (1.112 (av) Å),[8] $(CO)_3Fe(C_2B_3H_7)$ (1.137 (av) Å),[9] and $(CO)_3Fe(C_2B_9H_{11})$ (1.131 (av) Å).[10] As found in other ferracarboranes,[11] the Fe−B distances (2.17(1) Å) are longer than the Fe−carboranyl carbon distances (2.05(1) Å). The angle between the Fe−C_2B_3 vector and the plane defined by C(5), Fe(1), and C(5*) is close to 124.0°, and the angle C(5)−Fe(1)−N(1) is 98.4(4)°.

Ligand Substitutions. Basic ligand substitution reactions were first examined to test the reactivity of **4d** (Scheme 2). The reaction of **4d** with CNBu^t has been examined. In the presence of 2 equiv of CNBu^t in toluene at room temperature, **4d** was converted into **4b**. Similarly, **4d** reacts with PMe_3 in toluene at 65 °C. If 2 equiv of PMe_3 are used, complete conversion of **4d** into a product **4c** occurs after about 1 h. In contrast, the displacement of a cod ligand in **4d** with carbon monoxide under normal pressure is not successful. When CO is bubbled through $CDCl_3$ solutions of **4d**, no changes can

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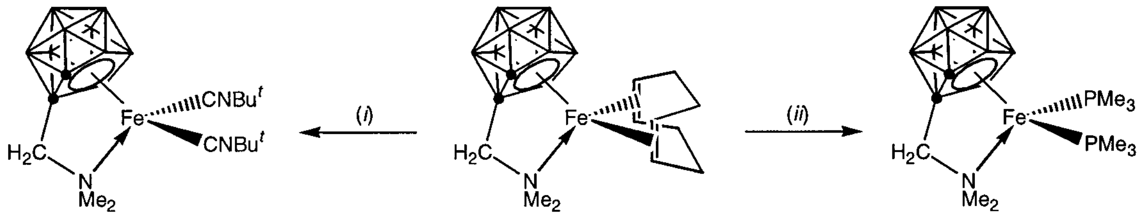
Table 3. Bond Lengths [Å] for 4a, 5, and 6

		4a			
Fe(1)−C(1)	2.05 (1)	Fe(1)−C(2b)	2.120(9)	Fe(1)−B(3)	2.17(1)
Fe(1)−N(1)	2.05(1)	Fe(1)−C(5)	1.756(9)	O(1)−C(5)	1.14(1)
		5			
Ru(1)−C(1)	2.178(8)	Ru(1)−N(1)	2.185(7)	Ru(1)−C(2b)	2.234(6)
Ru(1)−B(3)	2.240(6)	Ru(1)−C(5)	1.889(6)	O(1)−C(5)	1.132(7)
		6			
Ru(1)−C(1)	2.138(5)	Ru(1)−C(2)	2.195(5)	Ru(1)−B(3)	2.217(6)
Ru(1)−B(4)	2.243(6)	Ru(1)−B(5)	2.227(7)	C(1)−C(3)	1.517(7)
C(3)−N(1)	1.498(7)	Ru(1)−N(1)	2.225(5)	Ru(1)−C(6)	1.850(6)
Ru(1)−N(2)	2.060(5)	C(6)−O(1)	1.157(8)	N(2)−C(7)	1.139(8)
C(7)−C(8)	1.451(8)				

Table 4. Angles [deg] for 4a, 5, and 6

		4a			
C(5)−Fe(1)−N(1)	98.4(4)	O(1)−C(5)−Fe(1)	176.7(9)	C(3)−N(1)−Fe(1)	94.4(7)
C(1)−C(3)−N(1)	100.9(9)	C(4)−N(1)−C(3)	110.0(7)	C(4)−N(1)−Fe(1)	116.8(6)
		5			
C(5)−Ru(1)−N(1)	99.9(2)	O(1)−C(5)−Ru(1)	174.5(5)	C(3)−N(1)−Ru(1)	93.6(4)
C(1)−C(3)−N(1)	105.1(6)	C(4)−N(1)−C(3)	110.6(4)	C(4)−N(1)−Ru(1)	115.7(4)
		6			
C(1)−C(3)−N(1)	105.8(4)	C(3)−N(1)−Ru(1)	92.2(3)	C(6)−Ru(1)−N(2)	91.9(2)
C(6)−Ru(1)−N(1)	102.7(2)	N(2)−Ru(1)−N(1)	92.2(2)	C(3)−C(1)−Ru(1)	95.0(3)
C(1)−Ru(1)−C(2)	44.5(2)	C(2)−Ru(1)−B(3)	46.7(2)	B(3)−Ru(1)−B(4)	47.6(2)
B(4)−Ru(1)−B(5)	48.5(2)	B(5)−Ru(1)−C(1)	46.4(2)	C(3)−N(1)−C(5)	11.4(5)
C(3)−N(1)−C(4)	110.5(5)	C(5)−N(1)−Ru(1)	115.5(4)	C(4)−N(1)−Ru(1)	117.4(3)
Ru(1)−N(2)−C(7)	179.1(5)	N(2)−C(7)−C(8)	178.8(6)		

Scheme 2. Ligand Substitutions of 4d[a]

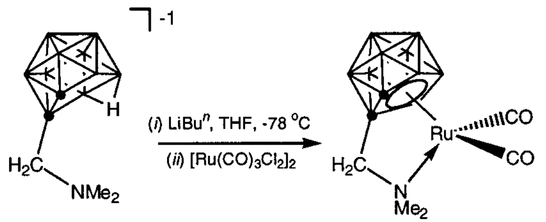


(Dcab^N)Fe(CNBu^t)$_2$ **4b** (Dcab^N)Fe(cod) **4d** (Dcab^N)Fe(PMe$_3$)$_2$ **4c**

[a]Legend: (i) CNBu^t, toluene, 25 °C; (ii) PMe$_3$, toluene, 65 °C.

be detected in the ^{1}H NMR spectra recorded immediately after the exposure to CO.

Reaction of the Ligand with Ru Complex. To extend the preceding results to ruthenium chemistry, we have used $[Ru(CO)_3Cl_2]_2$ as the starting material (eq 2). Treatment of the ruthenium dimer $[Ru(CO)_3Cl_2]_2$ with a lithium salt of **2** in THF, followed by stirring for 12 h, afforded a single product, (η^5:η^1-$C_2B_9H_{10}$-CH_2-NMe_2)Ru(CO)$_2$ (**5**), in good yields after chromatographic purification over silica gel.



(eq 2)

DcabH^N **2** (Dcab^N)Ru(CO)$_2$ **5**

This complex, obtained as a yellow powder, was recrystallized in a methylene chloride and hexane mixture, affording mostly stable crystals, further identified by elemental analysis. The IR spectrum of **5** exhibits peaks at 2043 and 1990 cm^{-1}, as expected for CO ligands attached to Ru(II). Complex **5** has been further identified by its ^{1}H and ^{13}C NMR spectra, displaying features nearly identical to those of **4a**. The presence of a stable intramolecular coordination, involving the dimethylaminomethyl unit, is indicated in the ^{1}H NMR spectra by a downfield shift of the methylene protons of the side chain. Furthermore, the multiplicity of the spin system of the NCH_2 moiety changes from a singlet of the free side chain to an AB spin system upon coordination to the metal atom, because of the restricted conformational freedom.

The molecular structure of **5**, determined by an X-ray diffraction study, is shown in Figure 2. The structure has a strong resemblance to that of **4a**. As expected, complex **5** possesses a crystallographic disorder imposed by mirror symmetry. Cage atoms Ru(1), C(1), B(6), and B(7) and the aminomethyl atoms N(1) and C(3) lie on the crystallographic mirror plane. As a consequence, the untethered carboranyl carbon atom is disordered by this plane such that the atomic positions designated by C(2b) and B(2c) are 50% occupied by C and 50% occupied by B. The structural analysis of **5** shows that the dimethylamino group is intramolecularly coordinated to the ruthenium atom. Therefore, the complex adopts an essentially "piano-stool" structure with the ruthenium atom η^5-coordinated on one side by a *nido* *o*-carboranyl

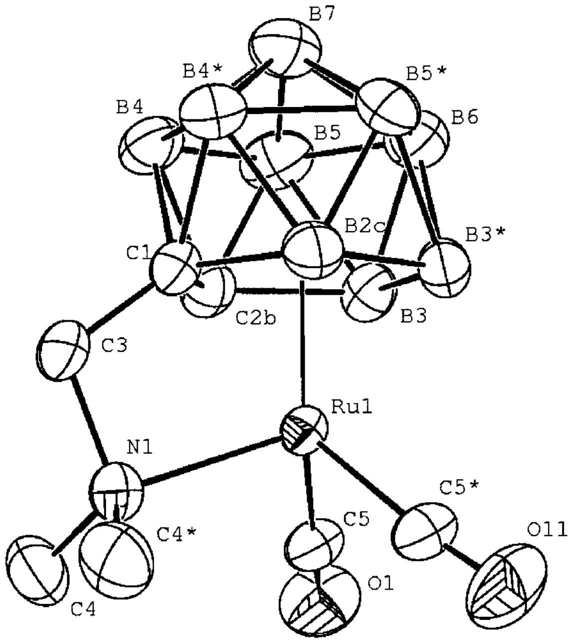


Figure 2. Molecular structure of **5** with atom labeling; ellipsoids show 30% probability levels, and hydrogen atoms have been omitted for clarity.

group and the other by the dimethylamino group and two CO ligands. The C_2B_3 bonding face in **5** is planar (maximum deviation of 0.037 Å) with the ruthenium approximately centered over the ring at a distance of 1.652 Å. Selected bond lengths and angles for **5** are listed in Tables 3 and 4. The Ru(1)−N(1) distance (2.185(7) Å) is shorter than that found in the complexes $[(\eta^5:\eta^1\text{-}C_5H_4(CH_2)_3NMe_2)Ru(dppm)]^+$ (2.238(3) Å),[2f] Cp* Ru(κ^2(*P*,*N*)-$Ph_2PCH_2CH_2NMe_2$)Cl (2.260(2) Å),[12] Cp*Ru-(κ^2(*P*,*N*)-$Ph_2PCH_2CH_2NMe_2$)(η^1-OSO_2CF_3) (2.256(2) Å),[12] and [Cp*Ru(κ^2(*P*,*N*)-$Ph_2PCH_2CH_2NMe_2$)(C=C=CHPh)]$^+$ (2.22(1) Å).[12] This value lies within the usual range for a dative bond between ruthenium and nitrogen atoms. Using accepted radii for both atoms, a value of 2.185 Å is estimated for a single bond. The C−O distances (1.132(7) Å) are similar to those found in $[(\eta^5\text{-}C_2B_9H_{11})RuCl(CO)_2]^-$ (1.156 (av) Å),[13a] $[(\eta^2:\eta^5\text{-}C(H){=}C(H)\text{-}Bu^t\text{-}C_2B_9H_{10})Ru(CO)_2]$ (1.147 (av) Å),[13b] $[(\mu\text{-}\eta^5\text{-}Me_2\text{-}NMe_2\text{-}CH_2{-}C_2B_9H_8)Ru_2(CO)_5]$ (1.157 (av) Å),[13c] and $(\eta^2:\eta^5\text{-}C(H){=}C(H)Ph\text{-}C_2B_9H_{10})Ru(CO)(PPh_3)]$ (1.157 (av) Å).[13d]

Decarbonylation of Ruthenium(II) Carbonyl Complex. The carbonyl groups of complex **5** are tightly bonded to the metal and are not displaced by isocyanides and trimethylphosphine at ambient temperature through a dissociation−association mechanism. It has been known that amine oxide can effectively remove coordinated carbon monoxide to generate coordinatively unsaturated organometallic complexes in metal carbonyls.[14] Thus, extrusion of a carbonyl ligand using *N*-oxide was therefore investigated. Complex **5** reacted with trimethylamine-*N*-oxide in acetonitrile solution at room temperature to yield the corresponding monosubstituted acetonitrile complex **6** (eq 3). In general, slightly more than a stoichiometric amount of trimethylamine-*N*-oxide was required. After separation, complex **6** was obtained as yellow crystals.

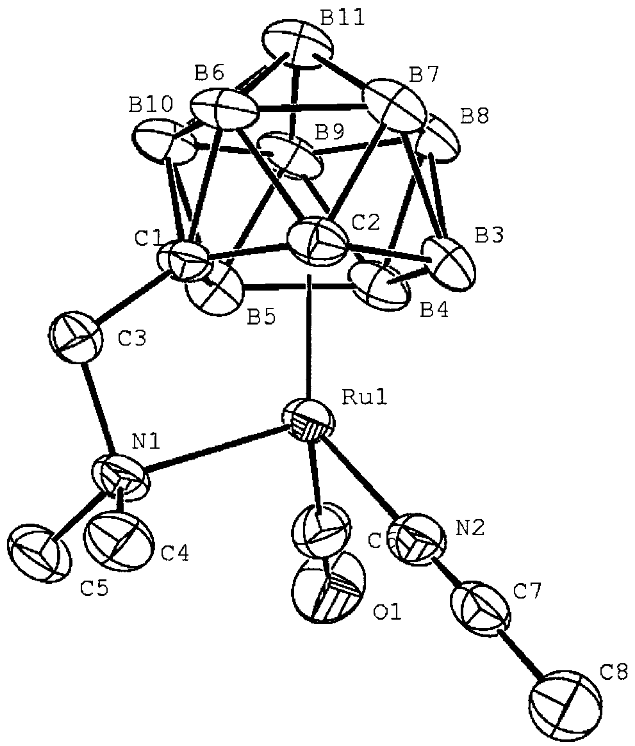
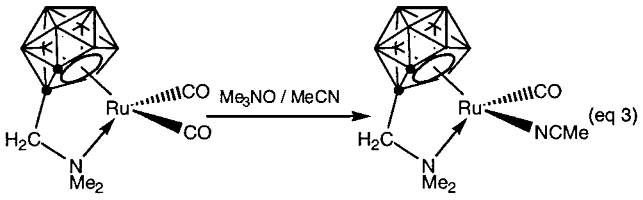


Figure 3. Molecular structure of **6** with atom labeling; ellipsoids show 30% probability levels, and hydrogen atoms have been omitted for clarity.

The reaction was monitored by IR spectroscopy by following the disappearance of the ν(CO) band due to complex **5**. In the carbonyl stretching region of the IR spectrum only one absorption at 1961 cm^{-1} was observed, indicating a terminal CO ligand. In addition, the terminal nitrile stretching of complex **6** appeared at 2350 cm^{-1}, suggesting that the acetonitrile is coordinated in a σ^1 fashion.[15] Therefore, the new complex has an IR spectrum of ν(CO) quite unlike that of **5** but is related to that of a monosubstituted metal complex for which structure **6** has been established. The ^{1}H NMR spectrum shows the signal at δ 2.01, which may be assigned to *Me*CN of the coordinated acetonitrile ligand.



(eq 3)

(Dcab^N)Ru(CO)$_2$ **5** (Dcab^N)Ru(CO)(NCMe) **6**

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Definitive structural characterization of **6** was carried out by a single-crystal X-ray analysis. Figure 3 shows that the acetonitrile molecule binds to the ruthenium in an η^1 fashion with *exo* orientation. The overall geometry may be described as hexacoordinate, using the same formalism as in complexes **4a** and **5**. Compound **6** has similar Ru−N bond lengths of Ru(1)−N(1) 2.225(5) Å, in good agreement with the existing values in the literature for typical Ru−N dative bonds.[2f,12] The distance for the Ru(1)−C(6) carbonyl bond of 1.850(6) Å and the nearly linear Ru(1)−C(6)−O(1) bond angle of 176.9(14)° in **6** agree well with the analogous lengths and angles reported for other ruthenium carbonyl complexes.[13] The carbonyl resides at the less hindered site, and the acetonitrile moiety is situated just below the pentagonal face of the C_2B_3 moiety. Therefore, the higher field shift of the acetonitrile methyl proton of **6** may be ascribed to the shielding effect of the aromatic ring current of the carboranyl group.

Conclusion

We have demonstrated that a series of half-sandwich iron and ruthenium complexes could easily be prepared when the amino group was tethered to the dicarbollyl ligand. Thus, we have synthesized and fully characterized the novel 18-electron iron and ruthenium complex with heterobifunctional ligand system **2**. Having an intramolecular coordination by **2** at the metal center, complex **3** is found to undergo ligand substitution toward nucleophiles such as CO, CNBu^t, PMe_3, and cod. Included are the first organometallic iron and ruthenium complexes possessing an amine-tethered dicarbollyl ligand. The resulting complexes **4** and **5** provide further opportunity for studying the reactivity of half-sandwich metal complexes, such as ligand exchanges and decarbonylation reactions. Further study on the utilization of complexes **4** and **5** for the synthesis of new types of organometallic complexes is actively under investigation.

Experimental Section

General Procedures. All manipulations were performed under a dry, oxygen-free, nitrogen or argon atmosphere using standard Schlenk techniques or in a Vacuum Atmosphere HE-493 drybox. THF was freshly distilled over potassium benzophenone. Toluene was dried and distilled from sodium benzophenone. Dichloromethane and hexane were dried and distilled over CaH_2. ^{11}B, ^{13}C, ^{1}H, and ^{31}P NMR spectra were recorded on a Varian Gemini 2000 spectrometer operating at 64.2, 50.3, 200.1, and 80.0 MHz, respectively. All boron-11 chemical shifts were referenced to $BF_3{\cdot}O(C_2H_5)_2$ (0.0 ppm) with a negative sign, indicating an upfield shift. All proton and carbon chemical shifts were measured relative to internal residual benzene from the lock solvent (99.5% C_6D_6) and then referenced to Me_4Si (0.00 ppm). The ^{31}P NMR spectra were recorded with 85% H_3PO_4 as an external standard. IR spectra were recorded on a Biorad FTS-165 spectrophotometer. Elemental analyses were performed with a Carlo Erba Instruments CHNS-O EA1108 analyzer. All melting points were uncorrected. Decaborane and *N*,*N*-(dimethylamino)-2-propyne were purchased from the Katechem and Aldrich, respectively, and used without purification. CabH^N **1**[16] was prepared by the literature methods. The starting materials $FeCl_2$ and $[Ru(CO)_3Cl_2]_2$ were purchased from Strem Chemical and used as received.

DcabH^N [*nido*-7-NMe$_2$CH$_2$-7,8-C$_2$B$_9$H$_{11}$]$^{2-}$ (2). Compound **1** (0.60 g, 3.0 mmol) was dissolved in degassed MeOH (20 mL), KOH (0.22 g, 4.0 mmol) was added, and the reaction mixture was heated to reflux for 12 h. CO_2 was bubbled through the cooled solution, and the resulting precipitate of K_2CO_3 was filtered off to afford a clear yellow solution. The methanol was removed in vacuo, the residue was dissolved in H_2O (40 mL), and an aqueous solution of NMe_4Cl (0.35 g, 3.2 mmol) was added, which resulted in the formation of a white sticky precipitate. The solution was extracted three times with acetone (3 × 30 mL), and the combined extract dried over $MgSO_4$ to afford 0.74 g (2.8 mmol, 93%) of **2**. Recrystallization from an acetone/THF mixture gave colorless crystalline solids. Data for **2**: Anal. Found for $C_9B_9H_{31}N_2$: C 40.89, H 11.92, N 10.54. Calcd: C 40.85, H 11.81, N 10.59. Mp: 130 °C (dec). IR spectrum (KBr pellet, cm^{-1}): ν(C−H) 3033, ν(B−H) 2537.

General Procedure for the Preparation of (Dcab^N)Fe(THF)$_2$ (3). To a stirred solution of the potassium salt of **2** (0.69 g, 3.0 mmol) in THF (20 mL) was added 2.4 mL of 1.5 M Bu^{n}Li (1.2 equiv). The mixture was stirred for 3 h at room temperature. The resulting clear yellow supernant was decanted via syringe. Removal of the solvent in vacuo and washing with light petroleum afford a yellow-tinted powder of the lithium salt of **2** (0.64 g, 2.7 mmol, 90%). Over a period of 30 min, a 20 mL THF solution of $FeCl_2(THF)_2$ (0.87 g, 3.2 mmol) was added to a stirred solution of the lithium salt of **2** in THF (20 mL) at −78 °C. After addition was complete, the cold bath was removed and the solution was stirred at room temperature for 20−30 min. Solvent was removed in vacuo and the residue purified by recrystallization with a THF/hexane mixture. The resulting red precipitate indicated the formation of **3** and was ready for further reactions.

(η^5:η^1-C$_2$B$_9$H$_{10}$-CH$_2$NMe$_2$)Fe(CO)$_2$ (4a). CO was allowed to bubble through the red solution of **3** in THF (40 mL) using a stainless needle for 2 h. The resulting dark red solution was filtered through 3 g of silica gel. The dark residue after the removal of the solvent was flash-chromatographed on silica gel using 10% EtOAc in hexane to remove some organics, followed by 50% EtOAc in hexane. The red band was collected and concentrated to provide 0.28 g (0.93 mmol, 31%) of **4a** as dark red solids. Anal. Found: C 28.04, H 6.11, N 4.73. Calcd: C 27.9, H 6.02, N 4.65. R_f = 0.07 (TLC silica gel ethyl acetate/hexane, 5:5). Mp: 160 °C (dec). IR spectrum (KBr pellet, cm^{-1}): ν(C−H) 2985, ν(B−H) 2546, ν(C=O) 2035, 1989.

(η^5:η^1-C$_2$B$_9$H$_{10}$-CH$_2$NMe$_2$)Fe(CNBu^t)$_2$ (4b). A 0.68 mL (6.0 mmol) amount of CNBu^t was added to the red solution of **3** in THF (40 mL), and the mixture was heated to reflux for 3 h. The resulting deep red solution was concentrated under reduced pressure. The residue was dissolved with CH_2Cl_2 (2 mL) and then chromatographed on silica gel upon elution with 10% EtOAc in hexane. The red band was collected and concentrated to provide the desired product **4b** (0.21 g, 0.51 mmol) with a 17% yield. Anal. Found: C 43.85, H 8.93, N 10.33. Calcd: C 43.77, H 8.82, N 10.21. R_f = 0.25 (TLC silica gel benzene). Mp: 170 °C (dec). IR spectrum (KBr pellet, cm^{-1}): ν(C−H) 2981, 2933, ν(B−H) 2574, 2548, 2521, ν(N=C) 2139, 2110.

(η^5:η^1-C$_2$B$_9$H$_{10}$-CH$_2$NMe$_2$)Fe(PMe$_3$)$_2$ (4c). A 0.61 mL (6.0 mmol) amount of PMe_3 was added to the red solution of **3** in THF (40 mL), and the mixture was heated to reflux for 3 h. The resulting deep red solution was concentrated under reduced pressure. The residue was dissolved with CH_2Cl_2 (2 mL) and then chromatographed on silica gel upon elution with 10% EtOAc in hexane. The red band was collected and concentrated to provide the desired product **4c** (0.19 g, 0.48 mmol) with a 16% yield. Anal. Found: C 33.33, H 9.20, N 3.58. Calcd: C 33.24, H 9.13, N 3.52. R_f = 0.04 (TLC silica gel EtOAc/hexane, 5:5). Mp: 138 °C (dec). $^{31}P\{^1H\}$ NMR (80.0

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MHz, δ, $CDCl_3$): 33.44 (d, *P*Me, $J_{PC} = 32$ Hz), 38.26 (d, *P*Me, $J_{PC} = 32$ Hz). IR spectrum (KBr pellet, cm^{-1}): ν(C−H) 2924, 2854, ν(B−H) 2539, ν(P−C) 1458.

(η^5:η^1-$C_2B_9H_{10}$-CH_2NMe_2)Fe(cod) (4d). A 0.37 mL (3.0 mmol) amount of cod was added to the red solution of **3** in THF (40 mL), and the mixture was heated to reflux for 3 h. The resulting dark red solution was filtered through 3 g of silica gel. The dark residue after removal of solvents was flash-chromatographed on silica gel using 10% EtOAc in hexane to remove some of the unreacted ligand, followed by 50% EtOAc in hexane. The red band was collected and concentrated to provide 0.38 g (1.1 mmol, 36%) of **4d** as dark red solids. Anal. Found: C 44.23, H 8.63, N 3.90. Calcd: C 44.17, H 8.55, N 3.96. $R_f = 0.09$ (TLC silica gel ethyl acetate/hexane, 5:5). Mp: 162 °C (dec). IR spectrum (KBr pellet, cm^{-1}): ν(C−H) 3046, 2955, ν(B−H) 2580, 2551, ν(C═C, COD) 2180.

Reaction of 4d with $CNBu^t$. A 0.18 g amount of **4d** (0.50 mmol) was dissolved in 10 mL of dry toluene and cooled to −10 °C. A 0.14 mL amount of solution of $CNBu^t$ (1.2 mmol) was added with stirring over 30 min, and the solution was allowed to warm to room temperature. The red solution turned dark red as the solution warmed. The solution was filtered in air, and the solvent was removed under reduced pressure. The remaining solid was passed through a short column of silica gel with CH_2Cl_2 as the eluent. A 0.16 g amount of **4b** was obtained after removal of the solvent (0.39 mmol, 78% yield).

Reaction of 4d with PMe_3. Under inert atmosphere, 0.18 g of **4d** (0.50 mmol) was dissolved in 10 mL of dry toluene. A 0.12 mL amount of PMe_3 (1.2 mmol) in about 2 mL of dry toluene was slowly added to the Fe solution using a cannula for 10 min at room temperature. The mixture was heated at 65 °C, and the reaction was monitored by ^1H and ^{31}P NMR spectroscopy. Clean and quantitative conversion to **4c** was observed after about 2 h. The solution was filtered in air, and the solvent was removed under reduced pressure. The remaining solid was passed through a short column of silica gel with CH_2Cl_2 as the eluent. A 0.12 g amount of **4c** was obtained after removal of solvent (0.30 mmol, 60% yield).

(η^5:η^1-$C_2B_9H_{10}$-CH_2NMe_2)Ru$(CO)_2$ (5). A 0.69 g amount of **2** (3.0 mmol) was dissolved in 15 mL of dry THF and cooled to −78 °C. A 2.7 mL amount of a 1.5 M solution of Bu^nLi (4.0 mmol) was added with stirring over 30 min, and the solution was allowed to warm to room temperature. The mixture was stirred for 1 h, and the solids were allowed to settle. The resulting clear yellow supernant was decanted via a cannula and added to a THF (10 mL) solution of $[Ru(CO)_3Cl_2]_2$ (0.77 g, 1.5 mmol), and the solution was stirred overnight. The solution was filtered in air, and the solvent was removed under reduced pressure. The remaining solid was passed through a short column of silica gel with CH_2Cl_2 as the eluent. The orange band was collected and concentrated to provide 0.76 g (2.2 mmol, 73%) of **5** as orange-colored solids. Anal. Found: C 24.33, H 5.32, N 4.10. Calcd: C 24.26, H 5.23, N 4.04. $R_f = 0.34$ (TLC silica gel benzene). Mp: 176 °C (dec). IR spectrum (KBr pellet, cm^{-1}): ν(C−H) 3046, ν(B−H) 2579, 2542, ν(C═O) 2043, 1990.

(η^5:η^1-$C_2B_9H_{10}$-CH_2NMe_2)Ru(CO)(NCMe) (6). Compound **5** (0.35 g, 1.0 mmol) was dissolved in CH_2Cl_2 (15 mL) containing CH_3CN (3 mL). A solution of Me_3NO (0.09 g, 1.2 mmol) in methanol (50 mL) was added carefully until the peaks in the IR spectrum due to **5** had just disappeared. The solvent was removed under vacuum and the residue recrystallized from a minimum volume of CH_2Cl_2 to give the bright yellow microcrystalline products **6** (0.09 g, 0.25 mmol, 25%). Anal. Found: C 26.82, H 5.98, N 7.88. Calcd: C 26.72, H 5.89, N 7.79. $R_f = 0.24$ (TLC silica gel methylenechloride/benzene). Mp: 138−142 °C (dec). IR spectrum (KBr pellet, cm^{-1}): ν(C−H) 3046, ν(B−H) 2520, ν(C═N, acetonitrile) 2350, ν(C═O) 1961.

X-ray Crystallography. Suitable crystals of **4a**, **5**, and **6** were obtained by slow diffusion of hexane into a methylene chloride solution of the complexes at room temperature and were mounted on a glass fiber. Crystal data and experimental details are given in Table 2. The data sets for **4a**, **5**, and **6** were collected on an Enraf CAD4 automated diffractometer. Mo Kα radiation (λ = 0.7107 Å) was used for all structures. Each structure was solved by the application of direct methods using the SHELXS-96 program[17a] and least-squares refinement using SHELXL-97.[17b] All non-hydrogen atoms in compounds **4a**, **5**, and **6** were refined anisotropically. All other hydrogen atoms were included in calculated positions.

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Supporting Information Available: Crystallographic data (excluding structure factors) for the structures (**4a**, **5**, and **6**) reported in this paper. This material is available free of charge via the Internet at http://pubs.acs.org. These data have also been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-163056 (**4a**), -163057 (**5**), and -163058 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44) 1223-336-033; e-mail, deposit@ccdc.cam. ac.uk).

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