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Reversible $\eta^6-\eta^4$ Coordination in the Association−Dissociation Reactions of Metallatricarbadecaboranyl Complexes: An Analogue of the $\eta^5-\eta^3$ Cyclopentadienyl Ring-Slippage Process

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We have previously shown that the 6-R-*nido*-5,6,9-$C_3B_7H_9^-$ anion is a versatile monoanionic ligand similar to the cyclopentadienide anion, which can function as either an η^6, 6-electron or an η^4, 4-electron donor to transition metals (Figure 1).[1] We report here synthetic and crystallographic studies of the first reversible cage slippage between the $\eta^6-\eta^4$ coordination modes of the tricarbadecaboranyl group that occurs upon the association−dissociation reactions of ferra- and ruthenatricarbadecaboranyl complexes with *tert*-butyl isocyanide. This reversible $\eta^6-\eta^4$ coordination is analogous to the $\eta^5-\eta^3$ ring slippage process that is proposed to occur in related reactions of cyclopentadienyl metal complexes.[2]

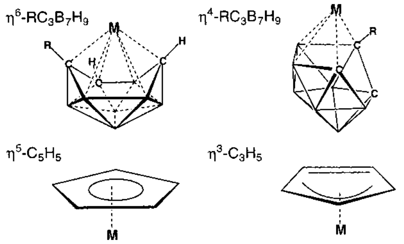

Figure 1. Comparison of structures and bonding modes of the tricarbadecaborane and cyclopentadienide monoanions.

The syntheses of ruthenatricarbadecaboranyl analogues of ruthenocene, *closo*-1-(η^5-C_5Me_5)Ru(η^6-[2-R-2,3,4-$C_3B_7H_9$]) [R = Me (**1**), Ph (**2**)], were accomplished in 75% and 66% isolated yields by the reaction of 6-R-*nido*-5,6,9-$C_3B_7H_9^-$ with $[Cp^*RuCl_2]_x$. The synthesis of the isoelectronic ferrocene analogue, *closo*-1-(η^5-C_5H_5)Fe(η^6-[2-Ph-2,3,4-$C_3B_7H_9$]) (**3**) was achieved in 49% yield by the reaction of the anion with (η^5-C_5H_5)Fe(CO)$_2$I. Crystallographic determinations of **2**[3] and **3** established the structures shown in the ORTEP diagrams in Figure 2. As in ruthenocene and ferrocene, the metals in **2** and **3** are sandwiched between two 6-electron donating monoanionic ligands with the metals having a formal +2 oxidation state. In both cases, the metals show η^6-coordination to the tricarbadecaboranyl cage and are approximately centered over the puckered six-membered open face. The closest metal cage interactions are with the two carbons, C2 and C3, that are puckered out of the ring. Longer and approximately equivalent bond lengths are observed between the metals and the remaining four atoms (C4, B5, B6, and B7) on the tricarbadecaboranyl bonding face.

As shown in eqs 1 and 2, addition of excess *tert*-butyl isocyanide to glyme solutions of either *closo*-1-(η^5-C_5Me_5)Ru(η^6-[2-Me-2,3,4-$C_3B_7H_9$]) (**1**) (reddish-orange) or *closo*-1-(η^5-C_5H_5)-Fe(η^6-[2-Ph-2,3,4-$C_3B_7H_9$]) (**3**, blue) resulted in an immediate color change characteristic of the formation of the *nido*-8-(η^5-C_5Me_5)Ru(CNBu^t)(η^4-[9-Me-7,9,10-$C_3B_7H_9$]) (**4**, yellow) and *nido*-8-(η^5-C_5H_5)Fe(CNBu^t)(η^4-[9-Ph-7,9,10-$C_3B_7H_9$]) (**5**, brownish-red) products, respectively. Crystallization from the reaction solutions gave 97% and 62% isolated yields, respectively, of pure materials. Elemental analyses are consistent with the indicated compositions resulting from the association of 1 equiv of the *tert*-butyl isocyanide.

$$\textit{closo}\text{-1-}(\eta^5\text{-}C_5Me_5)Ru(\eta^6\text{-[2-Me-2,3,4-}C_3B_7H_9])\ (\mathbf{1}) + CNBu^t \rightleftharpoons \textit{nido}\text{-8-}[(\eta^5\text{-}C_5Me_5)Ru(CNBu^t)](\eta^4\text{-[9-Me-7,9,10-}C_3B_7H_9])\ (\mathbf{4}) \tag{1}$$

$$\textit{closo}\text{-1-}(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-[2-Ph-2,3,4-}C_3B_7H_9])\ (\mathbf{3}) + CNBu^t \rightleftharpoons \textit{nido}\text{-8-}[(\eta^5\text{-}C_5H_5)Fe(CNBu^t)](\eta^4\text{-[9-Ph-7,9,10-}C_3B_7H_9])\ (\mathbf{5}) \tag{2}$$

Reactions 1 and 2 are reversible. Heating a toluene solution of **4** at reflux under flowing N_2 for 20 min resulted in the quantitative formation of **1**, while simply dissolving pure **5** in glyme resulted in the formation of an equilibrium mixture of **3** and **5**. Heating the solution to reflux under flowing N_2 resulted in complete conversion to **3**.

The metals in **1**, **2**, and **3**, as in ruthenocene and ferrocene, have formal 18-electron counts. Thus, unless there is a change in the donor properties of either the cyclopentadienyl or tricarbadecaboranyl ligands, the metal-coordination of a 2-electron isocyanide ligand would result in the formation of a 20-electron complex. As shown in the ORTEP drawings in Figures 3 and 4, crystallographic studies of **4** and **5** demonstrated that upon isocyanide addition, the cyclopentadienyl rings remain symmetrically bonded to the metals with only a slight increase in the metal to ring-centroid distances in **4** (1.871 Å) and **5** (1.736 Å) relative to their values in **2** (1.829 Å) and **3** (1.695 Å), respectively. However, the coordination mode of the tricarbadecaboranyl ligand in **4** and **5** has changed from η^6 to η^4. Thus, in **4** and **5**, the ruthenium and iron atoms are no longer centered over the six-membered face, but instead, the metals have slipped to one side of the cage. The metals are now centered above the C7−B3−B4−C9 face with the bond lengths between the metal and the four facial atoms being similar. Nonbonding distances (>3.0 Å) are found between the metals and the C10 and B11 cage atoms. In **2** and **3**, the M−C2−B8−B9−C3 atoms were coplanar, but in **4** and **5** the metals lie significantly out of the plane of the other four atoms, so that the dihedral angles between the C7−M−C9 and C7−B2−B5−C9 planes in **4** and **5** are 36.8(1)° and 36.3(3)°, respectively.

As we have previously discussed,[1e,4] the change from the η^6- to η^4-coordination mode corresponds to a conversion of the tricarbadecaboranyl ligand from a 6- to a 4-electron donor. An

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(1) (a) Plumb, C. A.; Carroll, P. J.; Sneddon, L. G. *Organometallics* **1992**, *11*, 1665−1671. (b) Plumb, C. A.; Carroll, P. J.; Sneddon, L. G. *Organometallics* **1992**, *11*, 1672−1680. (c) Weinmann, W.; Wolf, A.; Pritzkow, H.; Siebert, W.; Barnum, B. A.; Carroll, P. J.; Sneddon, L. G. *Organometallics* **1995**, *14*, 1911−1919. (d) Barnum, B. A.; Carroll, P. J.; Sneddon, L. G. *Organometallics* **1996**, *15*, 645−654. (e) Barnum, B. A.; Carroll, P. J.; Sneddon, L. G. *Inorg. Chem.* **1997**, *36*, 1327−1337. (f) Wasczcak, M. D.; Hall, I. H.; Carroll, P. J.; Sneddon, L. G. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2227−2228.

(2) For some examples see: (a) Basolo, F. *New J. Chem.* **1994**, *18*, 19−24 and references therein. (b) Basolo, F. *Polyhedron* **1990**, *9*, 1503−1535 and references therein. (c) O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307−318 and references therein. (d) Schuster-Woldan, H. G.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 1657−1663. (e) Rerek, M. E.; Basalo, F. *J. Am. Chem. Soc.* **1984**, *106*, 5908−5912. (f) Simanko, W.; Tesch, W.; Sapunov, V. N.; Mereiter, K.; Schmid, R.; Kirchner, K; Coddington, J.; Wherland, S. *Organometallics* **1998**, *17*, 5674−5688. (g) Calhorda, M. J.; Gamelas, C. A.; Romão, C. C.; Veiros, L. F. *Eur. J. Inorg. Chem.* **2000**, 331−340.

(3) Only one of the two independent molecules found in the asymmetric unit of the structural determination of **2** is shown. There were no significant differences in the values of the bond distances and angles between the two structures.

(4) Weinmann, W.; Pritzkow, H.; Siebert, W.; Sneddon, L. G. *Chem. Ber. Recl.* **1997**, *130*, 329−333.

10.1021/ja0022876 CCC: \$19.00

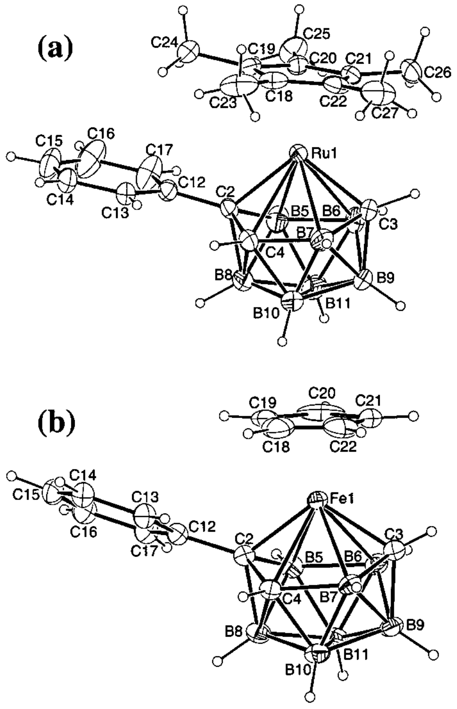


Figure 2. ORTEP drawings of the structures of (a) *closo*-1-(η^5-C_5Me_5)-Ru(η^6-[2-Ph-2,3,4-$C_3B_7H_9$]) (**2**) and (b) *closo*-1-(η^5-C_5H_5)Fe(η^6-[2-Ph-2,3,4-$C_3B_7H_9$]) (**3**). Selected bond lengths (Å): **2**, Ru−C2 2.111(3), Ru−C3 2.073(4), Ru−C4 2.355(4), Ru−B7 2.358(4), Ru−B5 2.339(5), Ru−B6 2.352(5); **3**, Fe−C2 1.982(3), Fe−C3 1.955(3), Fe−C4 2.258(3), Fe−B7 2.275(3), Fe−B5 2.239(3), Fe−B6 2.253(3).

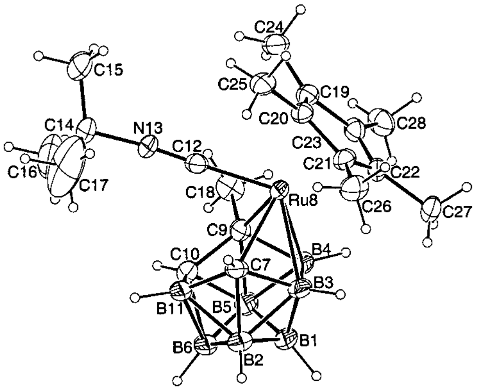


Figure 3. ORTEP drawing of the structure of *nido*-8-(η^5-C_5Me_5)Ru-(CNBu^t)(η^4-[9-Me-7,9,10-$C_3B_7H_9$]) (**4**). Selected bond lengths (Å): Ru−C7 2.218(5), Ru−C9 2.204(6), Ru−B3 2.273(6), Ru−B4 2.246(5), Ru−C12 1.954(6), C12−N13 1.163(7).

η^4-tricarbadecaboranyl ligand could therefore be considered the electronic analogue of a metal-coordinated η^3-$C_3H_5{}^{1-}$ allyl or a "slipped" η^3-$C_5H_5{}^{1-}$ ligand. Thus, the net result of the addition of the 2-electron isocyanide ligand to complexes **1** and **3** is to convert the tricarbadecaboranyl ligands to their η^4-coordination modes reducing their electron donation to the metals to only 4 electrons and thereby preserving the metal's favorable 18-electron count.[5] From a skeletal-electron counting point of view (Wade's rules[6]), this process simply corresponds to a cage-opening of the metallatricarbadecaboranyl fragment brought about by the addition of 2 electrons to the *closo*-M(R)$C_3B_7H_9$ cage (24 skeletal electrons) frameworks of **1** and **3** to form the *nido*-M(R)$C_3B_7H_9$ cage (26 skeletal electrons) structures of **4** and **5**.

Although not observed for ferrocene and ruthenocene, reversible ring slippage from η^5 to η^3 has been proposed, as shown in the well-studied example[2d,e] below, to be a key step in the substitution reactions of numerous cyclopentadienyl complexes[2] and some dicarbaboranyl complexes.[7]

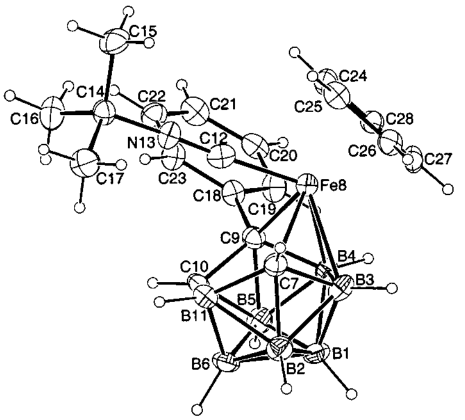
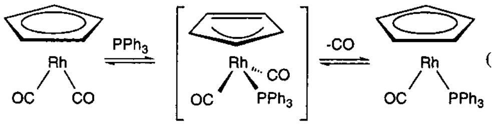


Figure 4. ORTEP drawing of the structure of *nido*-8-(η^5-C_5H_5)Fe-(CNBu^t)(η^4-[9-Ph-7,9,10-$C_3B_7H_9$]) (**5**). Selected bond lengths (Å): Fe−C7 2.114(8), Fe−C9 2.102(8), Fe−B3 2.191(9), Fe−B4 2.175(9), Fe−C12 1.854(8), C12−N13 1.170(10).



(3)

As discussed above for the tricarbadecaboranyl complexes, cyclopentadienyl η^5 to η^3 ring slippage both provides an open coordination site for the incoming ligand and avoids the formation of an unfavorable 20-electron intermediate, thus providing a low-energy pathway for the substitution reaction. Similar cyclopentadienyl ring-slippages are thought to be critical steps in many other important stoichiometric and catalytic organometallic reactions.[2] The η^6 to η^4 cage-slippage reaction reported herein not only further illustrates the similarities of the cyclopentadienyl and tricarbadecaboranyl ligands, but also demonstrates that tricarbadecaboranyl cage-slippage is preferred over η^5 to η^3 cyclopentadienyl ring-slippage in these complexes. The facile nature of the tricarbadecaboranyl rearrangement further suggests that metallatricarbadecaboranyl complexes may exhibit even greater reactivities than their cyclopentadienyl counterparts for many transformations requiring the generation of a coordinatively unsaturated metal center. Such reactivity studies are in progress and will be reported in future publications.

Acknowledgment. We thank the National Science Foundation for support of this research.

Supporting Information Available: Descriptions of the synthetic methods and characterization data for compounds **1**−**5** and tables listing refined positional and thermal parameters, bond distances, and bond angles for compounds **2**, **3**, and **4** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(5) Siebert has also shown that the diborolyl rings in the formal 16-electron complexes, (η^5-C_5Me_5)Ru($R_3{}'C_3B_2R_2$) and (η^5-C_5H_5)Fe($R_3{}'C_3B_2R_2$), reversibly change their degree of folding upon the association/dissociation reactions of the complexes with *tert*-butyl isocyanide to form the 18-electron (η^5-C_5Me_5)-Ru(CNBu^t)($R_3{}'C_3B_2R_2$) and (η^5-C_5H_5)Fe(CNBu^t)($R_3{}'C_3B_2R_2$) complexes. See: (a) Hettrich, R.; Kaschke, M.; Wadepohl, H.; Weinmann, W.; Stephan, M.; Pritzkow, H.; Siebert, W.; Hyla-Kryspin, I.; Gleiter, R. *Chem. Eur. J.* **1996**, *2*, 487−494. (b) Müller, T.; Kaschke, M.; Strauch, M.; Ginsberg, A.; Pritzkow, H.; Siebert, W. *Eur. J. Inorg. Chem.* **1999**, 1685−1692.

(6) (a) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1−66. (b) Williams, R. E. *Chem. Rev.* **1992**, *92*, 177−207 and references therein.

(7) See, for example: Shen, J. K.; Zhang, S.; Basolo, F.; Johnson, S. E.; Hawthorne, M. F. *Inorg. Chim. Acta* **1995**, *235*, 89−97.