

THF as solvent and allows for rapid reaction with the alkyl halides under homogeneous conditions. A possible explanation for the success of the current procedure is found in the report by Ephritikine and Baudry that Cp_2ReCH_3 reacts with methyl halides to afford the cationic dimethyl complex $[\text{Cp}_2\text{Re}(\text{CH}_3)_2]^+$.⁷ We have found that this complex can act as a proton donor to Cp_2ReLi to afford 1. The nature of the other rhenium-containing products has not been determined, but it is clear that in the preparation of the rhenocene alkyl complexes, where an excess of alkyl halide has typically been employed, the formation of the dialkyl complexes should be avoided. The heterogeneous conditions employed by previous workers may have accentuated this problem, since the alkyls are freely soluble in hexane, while the lithiated intermediates have very limited solubility.

Reaction of Rhenocene Alkyls with Acids. We have previously reported¹⁰ that Cp_2ReCH_3 reacts with protic acids (HCl or $\text{HBF}_4 \cdot \text{Et}_2\text{O}$) to afford the thermally unstable methyl hydride complex $[\text{Cp}_2\text{Re}(\text{H})\text{CH}_3]^+$. Reductive elimination of methane from this complex is facile in solution and in the solid state at room temperature, but the cation can be isolated by protonation in diethyl ether at low temperature. Careful removal of the supernatant solution by syringe followed by vacuum drying at temperatures $\leq 0^\circ\text{C}$ affords the product as a colorless powder. The proton NMR spectrum obtained at low temperatures in CD_2Cl_2 exhibits a Cp resonance, a methyl signal, and a

resonance for the hydride proton at $\delta -12.10$. Reductive elimination of methane from the chloride salt leads to clean formation of Cp_2ReCl .

Similar protonation reactions have been carried out with the ethyl, *n*-propyl, and benzyl complexes. The products were identified as alkyl hydride complexes by their low-temperature ^1H NMR spectra (see Experimental Section). Reductive elimination of the corresponding alkane was observed under conditions similar to those noted above for the methyl case. The qualitative trend in rates of reductive elimination observed was *n*-propyl > ethyl > methyl \approx benzyl. In the case of the (trimethylsilyl)methyl derivative, protonation led to very rapid formation of TMS, and the presumed alkyl hydride intermediate could not be observed directly.

These observations establish that the rhenocene alkyls act as bases toward protic acids, as noted in the initial reports on the reactivity of the parent hydride.² In contrast to the thermal stability² of the dihydride cation $[\text{Cp}_2\text{Re}(\text{H})_2]^+$ with respect to reductive elimination of hydrogen, the corresponding alkyl hydrides eliminate readily to afford alkanes and the rhenocene cation.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Support for this investigation was also provided by the National Science Foundation (Grant CHE-8814191).

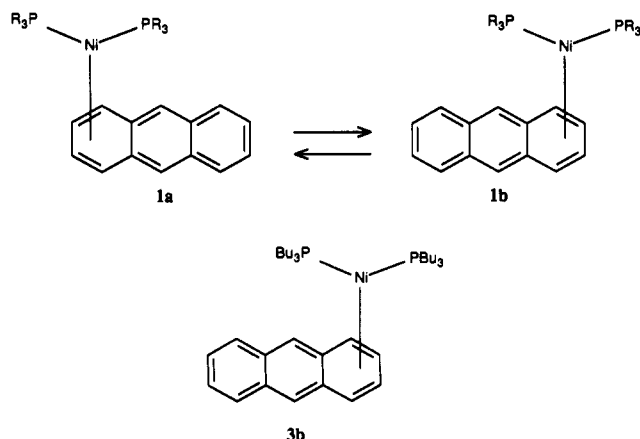
Is the Haptotropic Rearrangement in Bis(tributylphosphine)(anthracene)nickel Inter- or Intramolecular? Determination of the Molecularity by a Spin Saturation Transfer Approach¹

Amnon Stanger

Department of Chemistry, Technion—Israel Institute of Technology, Haifa 32000, Israel

Received December 21, 1990

Summary: A simple, fast, and inexpensive method for the determination of the molecularity of a reaction is presented. The method is based on spin saturation transfer technique coupled with VTNMR spectroscopy. A sample containing the complex under study and the ligand, with which a possible exchange might take place, is brought to a temperature at which saturation transfer can be observed. Which of the nuclei in the mixture is coupled to a saturated nucleus is then determined by magnetization transfer. The rearrangement $1\text{a} \rightleftharpoons 1\text{b}$ was studied as a test case. A mixture of **3b** and free anthracene was cooled to -70°C , and H_2 and H_3 were saturated. No change in the other resonances was observed. The experiment was repeated at -50°C , where the diminishing of H_5 and H_6 was clearly observed, but the free anthracene's resonances stayed unchanged. It is thus concluded that the rearrangement $1\text{a} \rightleftharpoons 1\text{b}$ is intramolecular. The advantages and disadvantages of the method as compared to crossover methodology and 2D EXSY experiments are discussed.

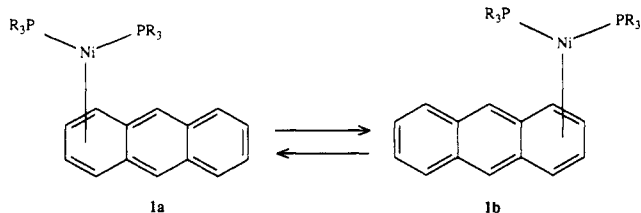


The investigation of mechanisms in organometallic chemistry is a complex task. In many cases, several competing reaction paths of similar activation energies might take place simultaneously, creating multichannel processes that are difficult to study. One of the most important

criteria for a reaction mechanism is the reaction's molecularity. Kinetic studies do not always give full information about it, since they manifest only changes occurring at the rate-determining step. It is thus possible that first-order kinetics are observed (i.e., the rate-determining step is unimolecular) although fast bimolecular steps occur before or after the highest energy-transition state. These potential problems become critical to the understanding of the reactions when homotopic type processes (i.e., the starting material and the product are chemically identical) are involved and product study is uninformative. Thus, all the usual kinetic criteria (such as the concentration dependence of the rate constant, ΔS^\ddagger etc.)² are not always sufficient for the determination of the molecularity of a reaction. Moreover, in some cases, similar organometallic systems undergo similar haptotropic rearrangements but via different mechanisms.³ The problem of inter- vs intramolecular reaction had been overlooked in some cases, and numerous mechanistic studies have assumed that the studied rearrangements are intramolecular without proving it.⁴

One of the more frequently used solutions to these difficulties is a crossover type experiment. Unfortunately, these experiments are time consuming (the syntheses of labeled compounds are required) and expensive (the labeling is usually isotopic in order to use compounds with maximum similarity), and the detection method is usually mass spectroscopy, under which conditions many of the organometallic compounds are unstable. In favorable cases, NMR spectroscopy can be used, but if the crossover products are similar enough, this method cannot distinguish between them. Thus, a noninvasive method, which is fast and inexpensive is desirable.

In the course of our studies of the bis(trialkylphosphine)(anthracene)nickel complexes (1),⁵ we needed to know whether the haptotropic rearrangement $1a \rightleftharpoons 1b$ is inter- or intramolecular. Kinetically, the rearrangement



is concentration independent and unaffected by free anthracene and tris(trialkylphosphine)nickel.⁵ The rates of

(1) Presented in part at the 10th IUPAC conference on Physical Organic Chemistry, Technion, Haifa, Israel, Aug 5-10, 1990.

(2) For example see: (a) Moore, W. J. *Physical Chemistry*, 5th ed.; Prentice-Hall: Englewood Cliffs, NJ, 1972; pp 329-339, 405-408. (b) Lowry, T. H.; Richardson, K. S. *Mechanisms and Theory in Organic Chemistry*, 3rd ed.; Harper & Row publishers: New York, 1987; pp 190-229.

(3) $(CO)_3Cr$ -naphthalene undergoes a dissociative haptotropic rearrangement in coordinative solvents (Albright, T. A.; Hofmann, P.; Hoffmann, R.; Lillya, P. C.; Dobosh, P. A. *J. Am. Chem. Soc.* 1983, 105, 3396 and ref 11 therein). However, the Ni-anthracene complex presented here undergoes an intramolecular rearrangement (see text). For related systems see also: Benn, R.; Mynott, R.; Topalović, I.; Scott, F. *Organometallics* 1989, 8, 2299.

(4) There are numerous examples of mechanistic NMR studies of haptotropic rearrangements, and although it is likely that these rearrangements involve intramolecular pathways, it is not unambiguously proved. For example, see the following references regarding $L_nM(COT)$ complexes: (a) Gracey, B. P.; Mann, B. E.; Spencer, C. M. *J. Organomet. Chem.* 1985, 297, 375. (b) Cotton, F. A.; Hunter, D. L.; Lahuerta, P. *J. Am. Chem. Soc.* 1974, 96, 7926. (c) Grassi, M.; Mann, B. E.; Spencer, C. M. *J. Chem. Soc., Chem. Commun.* 1985, 1169.

(5) (a) Stanger, A.; Vollhardt, K. P. C. Haptotropic Rearrangements in L_nNi -Anthracene Complexes. Kinetics and Mechanisms. Presented at the 4th International Conference on The Chemistry of the Platinum Group Metals, University of Cambridge, Cambridge, U.K., July 9-13, 1990. (b) Stanger, A.; Vollhardt, K. P. C. Submitted for publication.

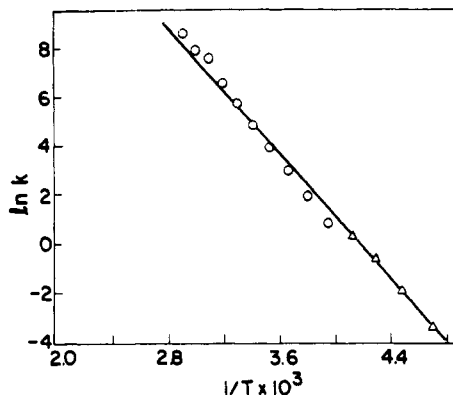
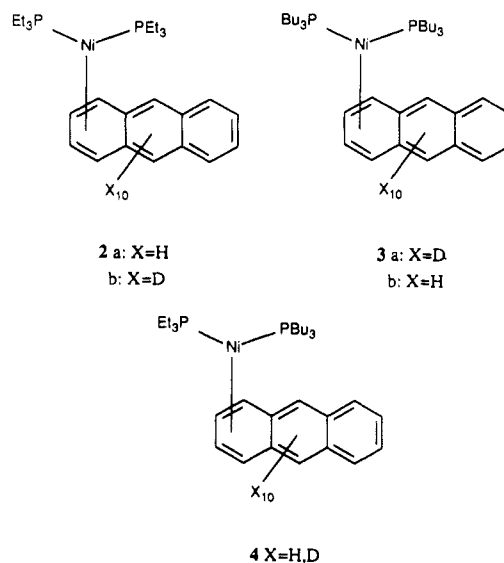


Figure 1. Plot of $\ln k$ as a function of $1/T$ for the haptotropic rearrangement rates of bis(triethylphosphine)(anthracene)nickel: (Δ) spin saturation transfer data; (O) line shape analysis data.

the rearrangement have been measured over a temperature range -70 to $+86$ °C⁶ (Figure 1), and it was found that ΔH^\ddagger is ~ 15 kcal mol⁻¹ (ca. 50% of the Ni-anthracene bond energy) and ΔS^\ddagger is small. Therefore, a first-order reaction was postulated. However, it is feasible that the rate-determining step involves a coordination number change, for example, followed by fast dissociation-recombination or associative type steps. A crossover experiment between **2a** and **3a** which could distinguish between an intramo-



lecular rearrangement (by finding the starting materials only) and an intermolecular rearrangement (by finding also **2b**, **3b**, and/or **4**), could not be carried out since the compounds are unstable under chromatography and mass spectrometer conditions and the possible crossover products (i.e. **2a** and **3a** vs **2b** and **3b** or **4**) are indistinguishable by NMR spectroscopy.

Line shape analysis could be principally used for the determination of the molecularity of the reaction. Thus,

(6) The rates were determined by using spin saturation transfer techniques over the temperature range -70 to -20 °C. H_2 and H_3 were saturated, and the magnetization transfer was measured to H_6 and H_7 . From -30 to $+86$ °C the rates were determined by using line shape analysis for the ^{31}P spectra, which changes from an AB pattern at the low-temperature limit to a singlet at the high-temperature limit. For spin saturation transfer see: (a) Forsen, F.; Hoffman, R. A. *J. Chem. Phys.* 1961, 39, 2892. (b) Campbell, I. P.; Dobson, C. M.; Ratcliffe, R. G.; Williams, R. J. P. *J. Magn. Reson.* 1978, 29, 297. (c) Martin, M. L.; Delpuech, J. J.; Martin, G. L. *Practical NMR spectroscopy*; Heyden: Chichester, U.K., 1980; pp 315-321. For spectral simulations, we used the program DYNAMAR, written by P. Meakin and modified by S. T. McKenna, Department of Chemistry, University of California, Berkeley, CA 94720.

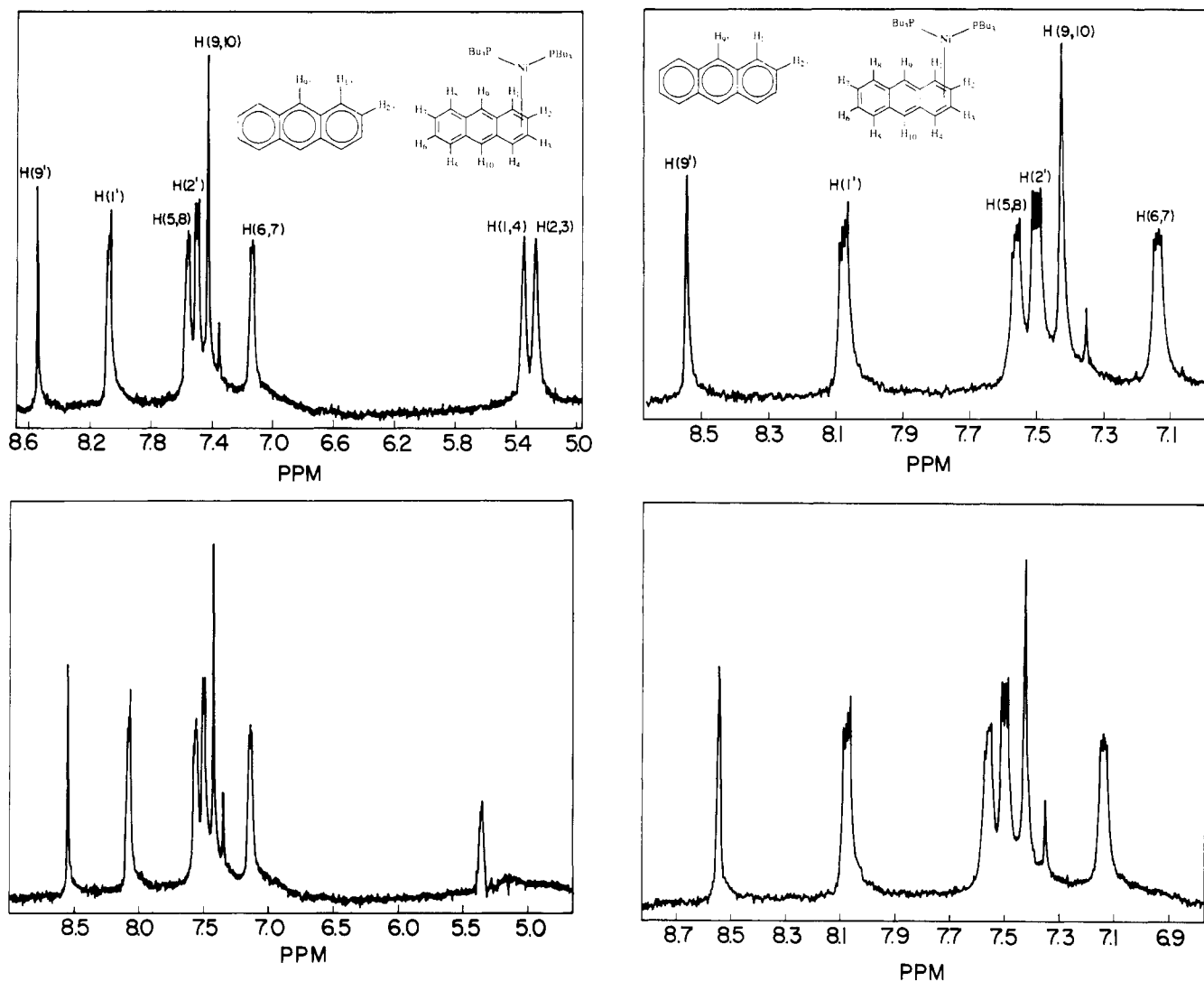


Figure 2. Mixture of bis(tributylphosphine)(anthracene)nickel (**3a**) and anthracene in THF- d_8 at $-70\text{ }^\circ\text{C}$ (a, top left) without saturation, (b, bottom left) with saturation of H_2 and H_3 , (c, top right) without saturation, the aromatic region only, and (d, bottom right) with saturation of H_2 and H_3 , the aromatic region only. Primed locants refer to anthracene ring positions and unprimed locants refer to **3a** ring positions.

a mixture of the complex and free anthracene should have shown line broadening or even coalescence at the anthracene region. Indeed, at $T \geq 60\text{ }^\circ\text{C}$ line broadening was observed, but at these temperatures the complex decomposes (to free anthracene and some phosphine nickel complexes), and thus the reason for the line broadening was not clear.

The application of spin saturation transfer techniques^{6a-c} seemed to be a good solution to the problem, since they are noninvasive and sensitive to rates that are 10^3 – 10^5 slower than those for line shape analysis, allowing the studies at lower temperatures. These techniques have been used quantitatively to determine reaction rates, both in 1D^{6,7} and 2D⁸ experiments. Qualitatively, these techniques have not been applied frequently,⁹ and the type of problems treated were different from the problem presented here. The method presented below is a natural extension of the above mentioned techniques. We use it here to determine the molecularity of the rearrangement in a simple, fast, inexpensive, and unambiguous way. To the best of our knowledge, spin saturation transfer experiments

have never been used for this purpose and can be applied for a large variety of reaction rates by controlling the reaction temperature.

The concept behind the method presented here is the opposite of that behind usual magnetization-transfer experiments.⁶⁻⁹ The basic idea is based on the knowledge that a given nucleus is exchanging. This nucleus is labeled by saturation, and by means of magnetization transfer one can determine to which other nucleus (or nuclei) the saturated nucleus is coupled. The experiment takes about 0.5 h, and the interpretation of the results is straightforward. The method is demonstrated by the study of the rearrangement **1a** \rightleftharpoons **1b**.

An NMR sample containing a mixture of ca. 1:1 **3b** and free anthracene in THF- d_8 was cooled to $-70\text{ }^\circ\text{C}$. The anthracene region of the spectrum is shown in Figure 2a. Figure 2b shows the same region under saturation of H_2 and H_3 . Figure 2c,d shows the aromatic region of the same respective spectra, and it is clear that no magnetization transfer is observed. The temperature was raised to $-50\text{ }^\circ\text{C}$, and the respective spectra were measured again. The results (shown in Figure 3b) are clear. The saturation of H_2 and H_3 (not shown) results in an intensity decrease of H_6 and H_7 , but the free anthracene's resonances are unchanged with respect to the spectrum measured under the

(7) (a) Mann, B. E. *Chem. Soc. Rev.* **1986**, *15*, 167. (b) Mann, B. E. *Adv. Organomet. Chem.* **1988**, *28*, 397.

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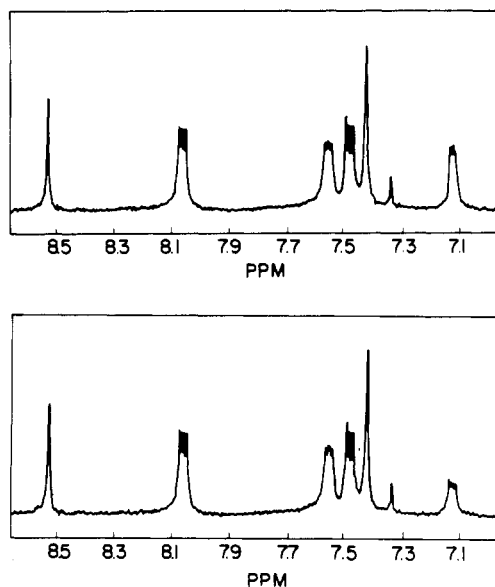


Figure 3. Mixture of bis(tributylphosphine)(anthracene)nickel (3a) and anthracene in THF- d_8 at $-50\text{ }^\circ\text{C}$ (a, top) without saturation and (b, bottom) with saturation of H_2 and H_3 . See the assignment of the resonances in Figure 2.

same conditions but without saturation (Figure 3a). Thus, we conclude that during the haptotropic process $1a \rightleftharpoons 1b$ intermolecular exchange of anthracene (which is the most labile ligand) does not take place, and the rearrangement is therefore intramolecular.

The method's main limitations are that the complex under study has to be stable to excess ligand¹⁰ and that the resonances which are exchanging must be sufficiently resolved to allow the specific saturation of only the desired resonance. In cases where the lines are poorly resolved, a 2D EXSY⁸ experiment must be carried out. However, we want to emphasize that in many cases it is unnecessary to run the 2D experiment, which is far more time consuming and presents technical difficulties, especially when measurements at low temperature for prolonged times are required.

Acknowledgment. This research was supported in part by the E. & J. Bishop research fund through the Technion VPR fund and by the Israeli ministry of absorbance. Dr. D. Igner is acknowledged for technical assistance.

(10) For example, 3 decomposes in the presence of Bu_3P to free anthracene and $(\text{Bu}_3\text{P})_n\text{Ni}$ ($n = 3$ or 4, depending on the amount of the phosphine introduced). Thus, a saturation-transfer experiment to determine a possible phosphine exchange (as suggested here) could not be performed.

$\text{Cu}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{B}_6\text{H}_9\text{Fe}(\text{CO})_4$: Rational Synthesis of a Heterobimetallaborane from B_6H_{10}

Lawrence Barton* and Dileep K. Srivastava

Department of Chemistry, University of Missouri—St. Louis, St. Louis, Missouri 63121

Received April 29, 1991

Summary: The heterobimetallaborane $\text{Cu}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{B}_6\text{H}_9\text{Fe}(\text{CO})_4$ is prepared by the reaction of $\text{K}[\text{Fe}(\text{CO})_4\text{B}_6\text{H}_9]$ with $[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{CuBr} \cdot 0.5\text{C}_6\text{H}_6$. The species forms by insertion of the Cu(I) moiety into a basal boron–boron bond in the $\text{Fe}(\text{CO})_4\text{B}_6\text{H}_{10}$ moiety generated by removal of a bridging hydrogen. This is the first report of a rational synthesis of a heterobimetallaborane from B_6H_{10} .

Hexaborane(10) and its conjugate base have several potential donor sites, but to date this aspect of its chemistry has not been exploited to any great extent,¹ and there are no known examples of simple dimetallaboranes in which a single hexaborane unit coordinates to two metal atoms. The direct basal B–B bond in B_6H_{10} is a basic site. This was demonstrated several years ago in proton affinity measurements,² and later, complexes of iron,^{3,4} rhodium, iridium, nickel, and platinum,^{4,5} in which this bond donates two electrons to the metal, were prepared. Also a bridging hydrogen atom in B_6H_{10} may be removed and replaced by electrophilic metal-containing moieties.⁶ Thus complexes

containing the metals Mg, Zn, Cd,⁷ Ti,⁸ Pt,⁹ and Cu^{10} have been prepared. The only example of a hexaborane(10)-based system in which these two bonding modes are found in a single B_6H_{10} moiety system is in the two related species $[(\text{CO})_4\text{FeB}_7\text{H}_{12}]^-$ and $(\text{CO})_4\text{FeB}_7\text{H}_{11}$. In these species,¹¹ a BH_3 moiety has been inserted into a site vacated by a proton and the B–B bond coordinates to a $\text{Fe}(\text{CO})_4$ group. There do exist metallaboranes in which a B_6H_9 moiety coordinates to two metal atoms, but these examples, $[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2\text{Pt}_2(\eta^3\text{-B}_6\text{H}_9)_2$,^{9,12} $[\text{Ti}(\text{B}_6\text{H}_9)(\text{C}_5\text{H}_5)_2]_2$,^{8,10b} and

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