812 *Organometallics* **2003,** *22,* 812−817

Reaction of Chromium(III) Chloride with the Cycloheptadienyl Anion: Susceptibility of Edge Bridges To C−H Activation Reactions

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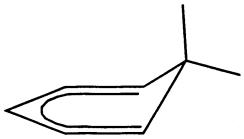
Received December 9, 2002

The reaction of $CrCl_3$ with 3 equiv of the cycloheptadienyl anion leads to $Cr(\eta^7\text{-}C_7H_7)(\eta^4\text{-}C_7H_{10})$ (C_7H_{10} = cycloheptadiene), through a process in which one ligand loses two hydrogen atoms while the other ligand gains one. The same complex had been reported from an entirely different route, involving the reaction of chromium(III) salts with Grignard reagents in the presence of cycloheptadiene and cycloheptatriene. The formulation of the complex has been confirmed by a low-temperature X-ray diffraction study. Related reactions have been found to lead to $M(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)$ (M = Ti, V; C_7H_9 = cycloheptadienyl) complexes. The preferential formation of one aromatic $\eta^n\text{-}C_nH_n$ ligand seems to provide the driving force favoring the isolated products and related species having other values of *n*.

Introduction

While the electronic and structural natures of open and half-open metallocenes have been examined in detail for complexes containing comparatively simple pentadienyl ligands,[1] far less has been done for related complexes with edge-bridged pentadienyls, such as 6,6-dimethylcyclohexadienyl (6,6-dmch; **1**), cycloheptadienyl (*c*-C_7H_9; **2**), or cyclooctadienyl (*c*-C_8H_{11}; **3**). Wolczanski et al. have reported the syntheses and spectroscopic studies of M(6,6-dmch)$_2$ complexes of titanium, vanadium, chromium, and iron,[2] and the last three have recently been structurally characterized.[3] A related series of $M(c\text{-}C_8H_{11})_2$ complexes (M = Ti, V, Cr, Fe) has also been reported and structurally characterized.[4] As the series of open metallocenes for both the six- and eight-membered edge-bridged pentadienyl ligands have been studied in detail, it was of interest to examine intermediate species derived from the cycloheptadienyl ligand. In fact, $Fe(c\text{-}C_7H_9)_2$ has been reported[5] and recently characterized structurally,[6] revealing a gauche-eclipsed conformation (**4**) reasonably similar to that adopted by simple open ferrocenes such as $Fe(2,4\text{-}C_7H_{11})_2$ (**5**) and $Fe(2,3,4\text{-}C_8H_{13})_2$ (C_7H_{11} = dimethylpentadienyl; C_8H_{13} = trimethylpentadienyl).[7] We have therefore attempted to prepare other $M(c\text{-}C_7H_9)_2$ complexes, for M = Ti, V, Cr, so that such species could be compared with their six- and eight-membered analogues. Herein we report on our results, which reveal the formation of unexpected products, in which one of the seven-membered ligands has become converted to an $\eta^7\text{-}C_7H_7$ ligand. It appears that this transformation is driven by the high degree of delocalization in an $\eta^n\text{-}C_nH_n$ ligand and that this is part of a general trend for a variety of other ring sizes.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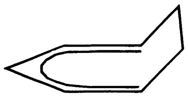
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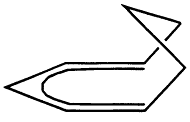
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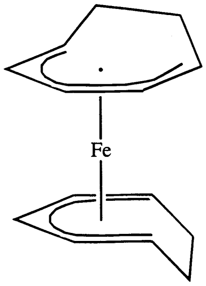

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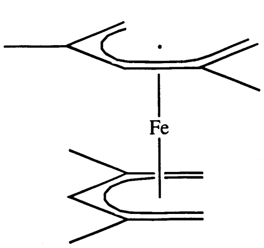

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Experimental Section

Unless otherwise stated, all reactions were carried out in Schlenk apparatus under a nitrogen atmosphere. Organic

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[1] Ernst, R. D. *Chem. Rev.* **1988**, *88*, 1255.
[2] Di Mauro, P. T.; Wolczanski, P. T. *Organometallics* **1987**, *6*, 1947.
[3] Basta, R.; Arif, A. M.; Ernst, R. D. Unpublished results.
[4] (a) Kulsomphob, V.; Tomaszewski, R.; Yap, G. P. A.; Liable-Sands, L. M.; Rheingold, A. L.; Ernst, R. D. *J. Chem. Soc., Dalton Trans.* **1999**, 3995. (b) See also: Müller, J.; Holzinger, W.; Köhler, F. H. *Chem. Ber.* **1976**, *109*, 1222.
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[7] (a) Wilson, D. R.; Ernst, R. D.; Cymbaluk, T. H. *Organometallics* **1983**, *2*, 1220. (b) Han, J.-C.; Hutchinson, J. P.; Ernst, R. D. *J. Organomet. Chem.* **1987**, *321*, 389.

10.1021/om020991k CCC: $25.00
Publication on Web 01/18/2003

solvents were dried and deoxygenated by distillation from benzophenone ketyl under a nitrogen atmosphere. 1,3-Cycloheptadiene was prepared by a published procedure[8] and converted to the cycloheptadienyl anion using $KO(t\text{-}C_4H_9)$/Li($n\text{-}C_4H_9$).[9] Mass spectral peaks are only given when their intensities are at least 10% that of the most abundant peak. Elemental analyses were obtained from Desert Analytics and E&R Microanalytical Labs.

(η^5-Cycloheptadienyl)(η^7-cycloheptatrienyl)titanium, Ti(η^7-C_7H_7)(η^5-C_7H_9). To a mixture of 50 mL of THF and 70−80 mesh magnesium metal (0.15 g, 6.15 mmol) at −78 °C was added $TiCl_4$ (0.56 mL, 5.13 mmol). The mixture was warmed to room temperature and was then refluxed for 2 h to give a black slurry of "$TiCl_2$". The slurry was then cooled to −78 °C, and a solution of K(c-C_7H_9) (1.50 g, 11.3 mmol) in 40 mL of THF was added dropwise. The resulting black-red mixture was warmed to room temperature and stirred for 3 h. Next, the solvent was removed in vacuo. The crude solid was extracted with ∼150−180 mL of hexane, and then the extracts were filtered through a Celite pad on a coarse frit. Concentration in vacuo of the olive green filtrate to ca. 15 mL and cooling to −30 °C resulted in air-sensitive green needle-shaped crystals (0.28 g, 23%). The identity of this compound was confirmed by ^1H NMR and mass spectroscopy. Mass spectrum (EI, 70 eV; *m/z* (relative intensity)): 232 (48), 231 (11), 230 (15), 204 (29), 152 (11), 140 (14), 139 (14), 138 (11), 126 (26), 113 (12), 93 (14), 92 (41), 91 (100), 79 (14), 78 (22), 77 (17), 65 (21), 39 (14).

(η^5-Cycloheptadienyl)(η^7-cycloheptatrienyl)vanadium, V(η^7-C_7H_7)(η^5-C_7H_9). To a magnetically stirred slurry of $VCl_3(THF)_3$ (1.47 g, 4.02 mmol) in 20 mL of THF at −78 °C was slowly added a solution of K(c-C_7H_9) (1.70 g, 12.8 mmol) in 40 mL of THF. The resulting blue-green solution changed to red-orange upon warming to room temperature. The mixture was stirred for 2 h. The solvent was removed in vacuo. The crude solid was extracted with ∼150−180 mL of hexane, and then the extracts were filtered through a Celite pad on a coarse frit. The brown-orange solution was concentrated to ∼20 mL and was cooled to −30 °C, yielding brown crystals (0.49 g, 54%). Single crystals of V(η^7-C_7H_7)(η^5-C_7H_9) were obtained by sublimation (ca. 0.1 Torr, 40 °C). Anal. Calcd for $C_{14}H_{16}V$: C, 71.49; H, 6.86. Found: C, 71.20; H, 6.61. Mass spectrum (EI, 70 eV; *m/z* (relative intensity)): 236 (14), 235 (100), 234 (29), 233 (29), 207 (19), 155 (15), 143 (16), 142 (55), 129 (17), 116 (24), 51 (12).

(η^4-Cycloheptadiene)(η^7-cycloheptatrienyl)chromium, Cr(η^7-C_7H_7)(η^4-C_7H_{10}). To a magnetically stirred slurry of $CrCl_3(THF)_3$ (2.00 g, 5.33 mmol) in 30 mL of THF at −78 °C was slowly added a solution of K(c-C_7H_9) (2.13 g, 16.0 mmol) in 40 mL of THF. The resulting blue-green solution changed to orange-brown upon warming to room temperature. The mixture was stirred for 6 h. The solvent was removed in vacuo. The crude orange-brown solid was extracted with ∼100−150 mL of hexane, and then the extracts were filtered through a Celite pad on a coarse frit. The orange-brown solution was cooled to −30 °C, yielding an orange to dark brown (depending on crystal thickness) air-sensitive crystalline solid (0.65−0.89 g, 51−70% yield). Anal. Calcd for $C_{14}H_{17}Cr$: C, 70.86; H, 7.22. Found: C, 70.72; H, 7.47. Mass spectrum (EI, 70 eV; *m/z* (relative intensity)): 238 (13), 237 (55), 144 (16), 143 (100), 91 (59), 52 (19).

X-ray Diffraction Study. Single crystals of Cr(η^7-C_7H_7)(η^4-C_7H_{10}) were obtained by sublimation (ca. 0.1 Torr, 60 °C). Crystal data and data collection and refinement parameters are given in Table 1. A suitable crystal was selected and mounted onto a glass fiber using Paratone oil. The structure was solved by direct methods and subsequent difference Fourier syntheses and least-squares refinements. Except for the hydrogen atoms attached to the minor component of the disordered C(13) atom, the hydrogen atoms were refined isotropically. All non-hydrogen atoms were refined anisotropically. The systematic absences in the diffraction data were uniquely consistent with the reported space group. All software and sources of the scattering factors are contained in the SHELXTL (5.3) program library (G. Sheldrick, Siemens XRD, Madison, WI).

Table 1. Crystal Data and Refinement Parameters for Cr(η^7-C_7H_7)(η^4-C_7H_{10})

formula	$CrC_{14}H_{17}$
fw	237.28
temp (K)	200
λ, Å	0.71073
cryst syst	orthorhombic
space group	*Pcab*
unit cell dimens	
a, Å	9.1650(2)
b, Å	10.2601(3)
c, Å	23.6460(7)
V, Å^3; *Z*	2223.5; 8
density (calcd), g cm^{-3}	1.418
abs coeff, cm^{-1}	9.90
θ range, deg	3.9−32.6
limiting indices	13; 15; 35
no. of rflns collected	7058
no. of indep rflns; n ($I > n\sigma(I)$)	3957; 2
$R(F)$	0.0452
$R(wF^2)$	0.0959
max/min diff Fourier peaks, e Å^{-3}	+0.37/−0.42

Structures of the M(η^7-C_7H_7)(η^5-C_7H_9) (M = Ti, V) complexes were similarly determined. While the η^7-C_7H_7 ligand coordinations were well-defined, in each case there was a serious disorder of the C_7H_9 ligands, such that four of the metal-bound carbon atoms were reasonably well localized, but the adjacent two atomic images were each a composite of a metal-bound (e.g., dienyl terminus) carbon atom and a saturated CH_2 group. Due to the severity of the disorder, and the fact that it results in each apparent carbon atom being a composite image, the observed bonding parameters are considered to be of limited interest and are not discussed further (see Supporting Information).

Results

Although the reaction of ferrous chloride with the cycloheptadienyl anion leads straightforwardly to Fe(c-C_7H_9)$_2$ and the reactions of chromium chlorides with the 6,6-dimethylcyclohexadienyl and cyclooctadienyl anions lead to the expected open chromocenes Cr(6,6-dmch)$_2$[2] and Cr(c-C_8H_{11})$_2$,[4] respectively, the analogous reaction of chromium(III) chloride with the cycloheptadienyl anion proceeds quite differently (eq 1). The

$$CrCl_3 + 3K(c\text{-}C_7H_9) \rightarrow Cr(\eta^7\text{-}C_7H_7)(\eta^4\text{-}C_7H_{10}) \quad (1)$$

paramagnetic, 17-electron product **6** does contain two seven-membered ligands, but one has lost two hydrogen atoms, while the other has gained one. Notably, the same product had originally been reported as arising from the reaction of chromium halides with Grignard reagents in the presence of 1,3-cycloheptadiene and cycloheptatriene;[5,10] however, large excesses of diene and triene were employed, and the yield of product under these conditions was lower, ca. 5−10.7% vs 51−70%.

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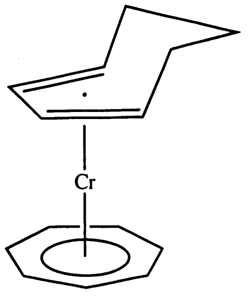
(8) Ter Borg, A. P.; Bickel, A. F. *Recl. Trav. Chim. Pays-Bas* **1961**, *80*, 1229.

(9) Wilson, D. R.; Stahl, L.; Ernst, R. D. *Organomet. Synth.* **1986**, *3*, 136.

(10) Fischer, E. O.; Reckziegel, A.; Müller, J.; Göser, P. *J. Organomet. Chem.* **1968**, *11*, P13.



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A structural study was carried out in order to provide a better understanding of the bonding in the complex. The result is presented in Table 2 and Figures 1 and 2.

Table 2. Pertinent Bonding Parameters for $Cr(\eta^7\text{-}C_7H_7)(\eta^4\text{-}C_7H_{10})$

Bond Distances (Å)			
Cr−C1	2.171(2)	C1−C2	1.393(3)
Cr−C2	2.173(2)	C1−C7	1.393(3)
Cr−C3	2.184(2)	C2−C3	1.389(4)
Cr−C4	2.151(3)	C3−C4	1.412(4)
Cr−C5	2.163(3)	C4−C5	1.418(6)
Cr−C6	2.192(2)	C5−C6	1.390(5)
Cr−C7	2.169(2)	C6−C7	1.377(4)
Cr−C8	2.196(2)	C8−C9	1.419(3)
Cr−C9	2.107(2)	C9−C10	1.400(3)
Cr−C10	2.112(2)	C10−C11	1.422(3)
Cr−C11	2.198(2)		
Bond Angles (deg)			
C2−C1−C7	127.8(2)	C9−C8−C14	125.3(2)
C1−C2−C3	129.4(2)	C8−C9−C10	120.3(2)
C2−C3−C4	128.4(3)	C9−C10−C11	120.6(2)
C3−C4−C5	127.5(3)	C10−C11−C12	126.3(2)
C4−C5−C6	128.1(3)	C11−C12−C13	118.4(2)
C5−C6−C7	129.2(3)	C12−C13−C14	115.4(3)
C6−C7−C1	129.4(3)	C13−C14−C8	117.8(2)

As can be seen, there is a disorder involving the unique methylene group of the η^4-C_7H_{10} ligand. In the principal orientation (ca. 75%, Figure 1), it generates something of a chair conformation with the remainder of the ligand, whereas in the minor form (Figure 2), there is a boatlike arrangement. The latter alternative actually resembles the arrangement (**3**) typically displayed by η^5-cyclooctadienyl ligands.[4,11] This form has been proposed to be stabilized through C−H/π interactions,[4] and the reduced tendency for the analogous arrangement here suggests that the geometry of an η^4-C_7H_{10} ligand is not as amenable to such interactions as is an η^5-C_8H_{11} ligand. Quite possibly the stronger C−H/π interactions in the M(c-C_8H_{11})$_2$ complexes of titanium, vanadium, and chromium greatly hinder potential C−H activations, thereby leading to the stability of these species, by restricting access of the edge bridges to the metal centers.

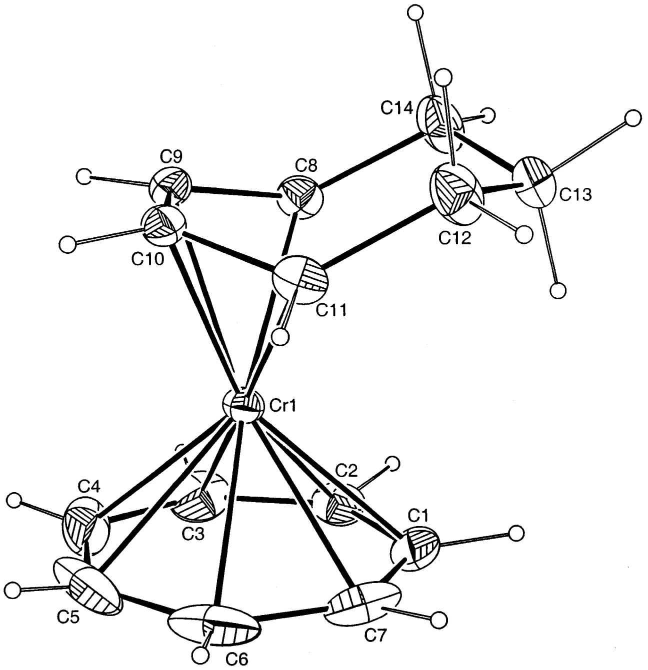

Figure 1. Solid-state structure of $Cr(\eta^7\text{-}C_7H_7)(\eta^4\text{-}C_7H_{10})$ in its major form.

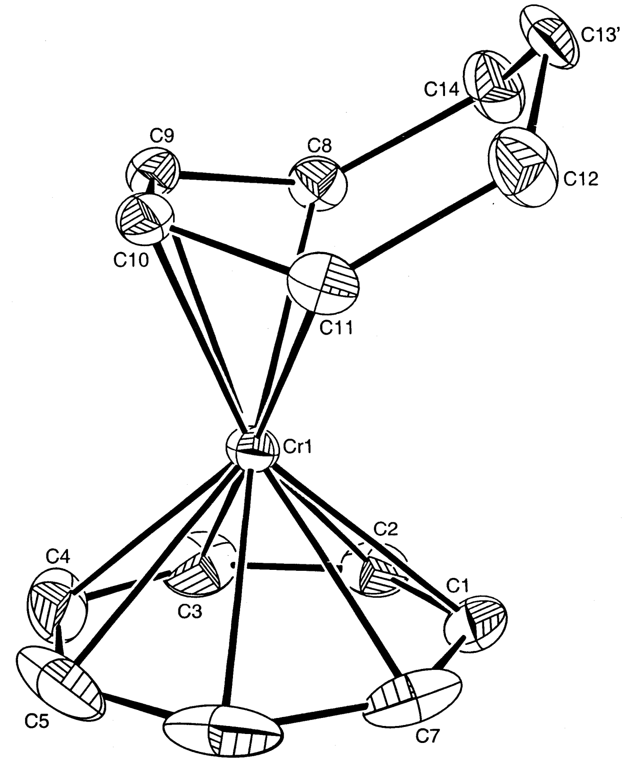

Figure 2. Solid-state structure of $Cr(\eta^7\text{-}C_7H_7)(\eta^4\text{-}C_7H_{10})$ in its minor form.

The data for **6** provide some worthwhile information concerning the Cr−C_7H_7 bonding.[12] The maximum deviation by a carbon atom from the C_7H_7 ligand is 0.032 Å, and the chromium atom lies 1.459 Å above this

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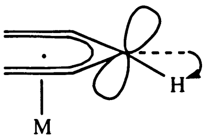
[11] (a) Fischer, M. B.; James, E. J.; McNeese, T. J.; Nyburg, S. C.; Posin, B.; Wong-Ng, W.; Wreford, S. S. *J. Am. Chem. Soc.* **1980**, *102*, 4941. (b) Blackborow, J. R.; Eady, C. R.; Grevels, F.-W.; Koerner von Gustorf, E. A.; Scrivanti, A.; Wolfbeis, O. S.; Benn, R.; Brauer, D. J.; Krüger, C.; Roberts, P. J.; Tsay, Y.-H. *J. Chem. Soc., Dalton Trans.* **1981**, 661. (c) Trimarchi, M. C. L.; Green, M. A.; Huffman, J. C.; Caulton, K. G. *Organometallics* **1985**, *4*, 514. (d) Ashworth, T. V.; Chalmers, A. A.; Liles, D. C.; Meintjies, E.; Singleton, E. *Organometallics* **1987**, *6*, 1543. (e) Stebler-Röthlisberger, M.; Salzer, A.; Bürgi, H. B.; Ludi, A. *Organometallics* **1986**, *5*, 298. (f) Osakada, K.; Grohmann, A.; Yamamoto, A. *Organometallics* **1990**, *9*, 2092. (g) Charpin, P.; Nierlich, M.; Vigner, D.; Lance, M.; Ephritikhine, M. *Acta Crystallogr.* **1990**, *C46*, 1735. (h) Frosin, K. M.; Dahlenberg, L. *Inorg. Chim. Acta* **1990**, *167*, 83. (i) Bouachir, F.; Chaudret, B.; Dahan, F.; Agbossou, F.; Tkatchenko, I. *Organometallics* **1991**, *10*, 455. (j) Yang, S.-M.; Cheng, W.-C.; Cheung, K.-K.; Che, C.-M.; Peng, S.-M. *J. Chem. Soc., Dalton Trans.* **1995**, 227. (k) Hitchcock, P. B.; Nixon, J. F.; Sakarya, N. *J. Chem. Soc., Chem. Commun.* **1996**, 2751. (l) Feiken, N.; Pregosin, P. S.; Trabesinger, G.; Scalone, M. *Organometallics* **1997**, *16*, 537.

plane. The hydrogen atom substituents are consistently tilted out of the plane[13] toward the chromium atom by 6.9−12.1°, averaging 9.7(5)°. Tilting of this sort occurs for ferrocene[14] and many related complexes and has been ascribed to an attempt by the ligand to direct its p orbitals more toward the metal center,[15] as in **7**. The much larger tilt in this case as compared to ferrocene (3.7(9)°) is consistent with the greater girth of the C_7H_7 ring. The Cr−C bond lengths range from 2.151 to 2.192 Å, averaging 2.172(5) Å, while the C−C bond lengths are also fairly regular and average 1.396(5) Å.



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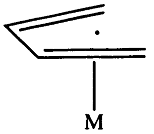
The bonding in the η^4-C_7H_{10} ligand is somewhat curious, and the situation is partly obscured by the oxidation state ambiguities that characterize C_7H_7 complexes. Diene ligands may coordinate to metal centers as diene (**8**) or enediyl (**9**) units, or somewhere in between. The shorter Cr−C bonds for the internal (C9, 10) rather than external (C8, 11) carbon atoms, 2.110(2) vs 2.197(1) Å, would suggest more of a diene contribution, but on the other hand the shorter internal (C9−C10) vs external (C8−C9, C10−C11) carbon−carbon bonds, 1.400(3) vs 1.420(2) Å, would suggest more of an enediyl contribution. Since it is possible that the steric demands of the trimethylene bridge prevent the terminal diene/enediyl carbon atoms from making the closer approach to the metal center, it seems most likely that **9** provides a greater contribution than **8**. As was observed for the η^7-C_7H_7 ligand, the hydrogen substituents on the diene ligand are tilted down toward the metal center. The tilts are, surprisingly, even larger, averaging 18.9° for the terminal substituents and 13.3° for the internal ones. An average tilt of 41.4° is experienced by C(12) and C(14), in the opposite direction.



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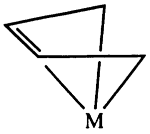

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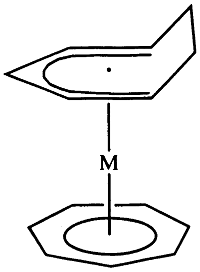
Discussion

Clearly of major interest is the origin of the Cr(η^7-C_7H_7)(η^4-C_7H_{10}) complex and the explanation for the formation of the same species from an entirely different reaction.[5,10] That the isolation of identical products is not coincidental is suggested by the fact that reactions of titanium or vanadium halides with the cycloheptadienyl anion also lead to η^7-C_7H_7 complexes, M(η^7-C_7H_7)(η^5-C_7H_9) (see Experimental Section), and such complexes had also been observed previously from metal halide/Grignard/cycloheptadiene/cycloheptatriene reactions.[10,16] It would seem therefore that all these reactions experience some element of thermodynamic control, at least regarding the transfer of hydrogen atoms to and from the organic ligands. In particular, each of these products contains one η^7-C_7H_7 ligand, with the chromium complex having an accompanying η^4-C_7H_{10} ligand and the titanium and vanadium complexes having an accompanying η^5−C_7H_9 ligand, as in **10**. Especially in the chromium complex there is something of an imbalance in the number of electrons donated by each ligand, and it might have seemed better to have one η^5- and one η^6-bound ligand instead. However, the sizable extra degree of delocalization (alternatively, "aromaticity") experienced by an η^7-C_7H_7 ligand should provide a substantial driving force for its formation.



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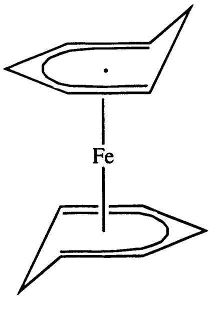
Indeed, a variety of analogous transformations has been reported for cyclic delocalized ligands in general. Both the 17- and the 18-electron Mo(η^6-C_7H_8)$_2{}^{0/+}$ complexes (C_7H_8 = cycloheptatriene) undergo a related reaction, yielding the corresponding Mo(η^7-C_7H_7)(η^5-C_7H_9)$^{0/+}$ species.[17] Further, while Fe(η^5-C_6H_7)$_2$ (**11**) can be isolated at room temperature,[2] it undergoes a slow transformation to an η^4:η^6 complex (**12**). Clearly the



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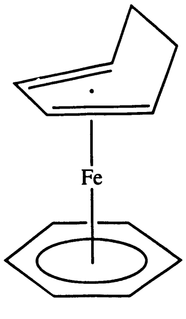

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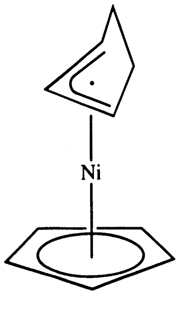
C−H (and even C−C[18]) bonds in these edge bridges are quite susceptible to bond activation reactions, as can also be seen by the isolation of Ti(C_5H_5)(C_8H_8) from reactions of mono(cyclopentadienyl)titanium halides with the cyclooctadienyl anion[19] and by the observed, facile insertion of an alkyne into a C−H bond in the bridge of a (cyclooctadienyl)titanium complex.[20] The selective formation of Ni(C_5H_5)(η^3-C_5H_7) (**13**; C_5H_7 = cyclopentenyl) on hydrogenation of nickelocene[21] and the observation of structures such as Nb(η^7-C_7H_7)(η^4-C_7H_8)-(PMe_3),[22] Fe(η^5-C_5H_5)(η^1-C_5H_5)$(CO)_2$,[23] Ti$(\eta^5$-$C_5H_5)_2(\eta^1$-$C_5H_5)_2$,[24] and Sc$(\eta^5$-$C_5H_5)_2(\eta^1$-$C_5H_5)$[25] provide additional cases demonstrating the favorability of having at least one aromatic ligand. While one could question the relative magnitude of stabilization experienced by a complexed aromatic π system as compared to an uncomplexed one, it is notable that some evidence suggests that the aromaticities of complexed π systems may exceed those of the uncomplexed ones.[26]



13

There is, however, also reason to invoke some kinetic control over the products' formations in these reactions. One can note that none of the η^7-C_7H_7 complexes discussed herein is an 18-electron complex. One could especially consider why an 18-electron Cr(η^7-C_7H_7)(η^5-C_7H_9) complex was not formed under the same conditions, since the titanium and vanadium analogues formed readily. To convert the η^4-C_7H_{10} ligand in **6** into an η^5-C_7H_9 ligand, one clearly needs to bring about an oxidative addition of a C−H bond. Such a process could be difficult for the 17-electron Cr(η^7-C_7H_7)(η^4-C_7H_{10}) complex, as a 19-electron intermediate would be expected (at least in the absence of a ligand slip process as has been proposed in other situations[17]), whereas it should be much easier to bring about for the more electron deficient titanium and vanadium analogues. Indeed, other reactions at higher temperatures have been found to produce Cr(η^7-C_7H_7)(η^5-C_7H_9), although still in low yields.[27]

While there appears to be additional stabilization for η^n-C_nH_n ("aromatic") ligands, there are nonetheless limitations to the favorabilities of their formations. Thus, the complex Ru(η^5-C_7H_7)(η^5-C_7H_9) is known,[28] rather than Ru(η^7-C_7H_7)(η^3-C_7H_9)—indicating a dramatic reversal relative to Cr(η^7-C_7H_7)(η^4-C_7H_{10}). Likewise, one finds M(η^6-C_8H_8)(η^4-C_8H_8) complexes for M = Fe, Ru,[29] although here the metal sizes may also contribute through an inability to sustain η^8-C_8H_8 coordination. It needs to be considered, however, that these trends do not solely reflect hapticity differences. In this regard, one can note the existence of the complex Ti(η^8-C_8H_8)[N(*t*-C_4H_9)] with remarkable η^8 and η^1 hapticities.[30] Although this represents an amazing difference, there is a far smaller imbalance in terms of electrons donated, 8 vs 4, which is not too different from the 7:4 ratio in **6**. Thus, the imbalance of importance here is that which pertains to the number of electrons donated (or alternatively, to the number of metal orbitals engaged in bonding), and while it is possible that there will be no absolute rule in this regard, it appears from the observed complexes to date that a substantial drop in stability occurs close to a 2:1 ratio.[31]

There does seem to be a driving force that often promotes the presence of at least one η^n-C_nH_n ligand in transition-metal polyene or polyenyl complexes,[32] and it is not clear to what extent the generality of this preference may have been appreciated in the past. That the hydrogen atom transfer processes which lead to the formation of C_nH_n ligands can be not only quite facile but also important should be clear from the fact that some metal complexes may bring about the catalytic dehydrogenation or disproportionation of cycloalkenes, leading to arenes,[11a,33] as well as the reverse process, arene hydrogenation.[34] It seems likely that greater synthetic advantage could be taken of these edge-bridge activations, and additional efforts in this regard are underway.

Acknowledgment. R.D.E. is grateful to the University of Utah and the National Science Foundation for partial support of this work.

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Supporting Information Available: Tables of positional coordinates, anisotropic thermal parameters, additional bonding parameters, and mass spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020991K