Gas-Phase Ion Chemistry of (η^6-c-C$_7$H$_8$)Cr(CO)$_3$ by FT-ICR Spectroscopy: β-Hydride Transfer in Organometallic Ions

Ziyi Kan,[†] Sandra M. Taylor, and Melvin B. Comisarow*

Contribution from the Department of Chemistry, University of British Columbia, Vancouver, B.C., V6T 1Z1, Canada

Received September 24, 1993[®]

Abstract: The gas-phase ion chemistry of η^6-cycloheptatriene chromium tricarbonyl was studied by Fourier transform ion cyclotron resonance spectroscopy. The well-known trend that fragment-ion reactivity toward the parent neutral increases with increasing electron deficiency on the metal atom was, in general, observed. However, the reactivity of the fragment ions from (η^6-c-C$_7$H$_8$)Cr(CO)$_3$ shows the order Cr$^+$ > C$_5$H$_6$Cr$^+$ > C$_7$H$_8$Cr$^+$ $\approx$ C$_7$H$_8$Cr(CO)$^+$ > C$_7$H$_8$Cr(CO)$_2^+$ > C$_7$H$_8$Cr(CO)$_3^+$, in which C$_7$H$_8$Cr$^+$ has an anomalously low reactivity. Similarly, the secondary ion–molecule product ion, (C$_7$H$_8$Cr)$_2^+$, has an anomalously low reactivity when compared with that of (C$_7$H$_8$Cr)$_2$(CO)$_3^+$. A more quantitative analysis indicates that the ions C$_7$H$_8$Cr$^+$, C$_7$H$_8$Cr$_2$(CO)$^+$ and C$_7$H$_8$Cr$_2$(CO)$_2^+$ are less reactive than expected. All of these low reactivities can be explained by a β-hydride shift from the cycloheptatriene ring to the chromium atom that converts the cycloheptatriene ligand into an aromatic tropylium ligand. The coordination hapticity to chromium changes from η^6 to η^7 + η^1 and the electron deficiency of chromium drops by 2. Similarly, the reactivity of the fragment ion C$_5$H$_6$Cr$^+$ implies it has a hydrido-π-cyclopentadienyl structure. An additional driving force for these rearrangements appears to be the aromatization of the seven-membered cycloheptatriene ring to a tropylium ring and the aromatization of the five-membered cyclopentadiene ring to a cyclopentadienyl ring, as the fragment and secondary ion reactivity orders are normal in the otherwise analogous benzene chromium tricarbonyl and cyclopentadienyl vanadium tetracarbonyl systems. These latter systems have no possible corresponding aromatization reaction. Ions that have low reactivity and have metal–hydrogen bonds react with deuterium-labeled methanol to eliminate a molecule of molecular hydrogen in which one hydrogen atom comes from the hydroxyl group of methanol and the other hydrogen atom comes from the organometallic ion. In contrast, ions that have normal reactivity and do not have metal–hydrogen bonds give methanol adduct products when reacted with methanol.

Introduction

In the last fifteen years, many Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR)[1,2] investigations of the gas-phase ion–molecule reactions of bare and ligated transition metal ions have been reported.[3–9] Two aspects of this research are the study of ion–molecule condensation processes and the study of the activation of C–C and C–H bonds promoted by bare and ligated metal ions. Although most early work concerned condensation reactions, bond activation has received much recent attention due to its fundamental importance in catalysis. Many early studies focused on transition metal carbonyls[10–19] and

complexes with cyclopentadienyl or benzene ligands.[3,20–23] The hydrocarbon ligands in these systems generally retain their structural integrity throughout the ion–molecule reaction processes. For C–H and C–C bond activation studies, Allison, Freas, and Ridge[24] first observed the oxidative addition of gas-phase Fe$^+$ to isomeric butanes in 1979. They observed that a metal ion reacted with a hydrocarbon molecule to give elimination of molecular methane or molecular hydrogen via both C–C and C–H bond insertion. Since this early work, the activation of C–C and C–H bonds of hydrocarbons by gas-phase bare or ligated metal ions has been intensively studied.[25–38] The activation process involves coordination of the metal to the olefin and then

† Present address: H. C. Brown Laboratory of Chemistry, Purdue University, West Lafayette, IN 47907.
® Abstract published in *Advance ACS Abstracts*, April 1, 1994.
(1) Comisarow, M. B.; Marshall, A. G. *Chem. Phys. Lett.* **1974**, *25*, 282–283.
(2) Comisarow, M. B.; Marshall, A. G. *Chem. Phys. Lett.* **1974**, *26*, 489–490.
(3) Parisod, G.; Comisarow, M. B. In *Advances in Mass Spectrometry*; Quayle, A., Ed.; Heyden & Son: London, 1980; Vol. 8A, pp 212–223.
(4) Allison, J. *Prog. Inorg. Chem.* **1986**, *34*, 627–677.
(5) Squires, R. R. *Chem. Rev.* **1987**, *87*, 623–646.
(6) Russell, D. H. *Gas Phase Inorganic Chemistry*; Plenum Press: New York, 1989.
(7) Freiser, B. S. *Chemtracts* **1989**, *1*, 65–109.
(8) Freiser, B. S. In *Techniques for the Study of Ion Molecule Reactions*; Farrar, J. M., Saunders, W. H., Eds.; Wiley: New York, 1988; Vol. 20, pp 61–118.
(9) Eller, K.; Schwarz, H. *Chem. Rev.* **1991**, *91*, 1121–1177.
(10) Wronka, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 67–71.
(11) Meckstroth, W. K.; Ridge, D. P. *Int. J. Mass Spectrom. Ion Proc.* **1984**, *61*, 149–152.
(12) Fredeen, D. A.; Russell, D. H. *J. Am. Chem. Soc.* **1985**, *107*, 3762–3768.
(13) Fredeen, D. A.; Russell, D. H. *J. Am. Chem. Soc.* **1986**, *108*, 1860–1867.
(14) Fredeen, D. A.; Russell, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 3903–3909.
(15) Meckstroth, W. K.; Ridge, D. P.; Reents, W. D. J. *J. Phys. Chem.* **1985**, *89*, 612–617.
(16) Marshall, A. G. *Acc. Chem. Res.* **1985**, *18*, 316–322.
(17) Mullen, S. L.; Marshall, A. G. *J. Am. Chem. Soc.* **1988**, *110*, 1766–1774.
(18) Houriet, R.; Vulpius, T. *Chem. Phys. Lett.* **1989**, *154*, 454–457.
(19) Forbes, R. A.; Laukien, F. H.; Wronka, J. *Int. J. Mass Spectrom. Ion Proc.* **1988**, *83*, 23–44.
(20) Corderman, R. R.; Beauchamp, J. L. *Inorg. Chem.* **1976**, *15*, 665–668.
(21) Corderman, R. R.; Beauchamp, J. L. *Inorg. Chem.* **1977**, *16*, 3135–3139.
(22) Foster, M. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 4814–4817.
(23) Operti, L.; Vaglio, G. A.; Gord, J. R.; Freiser, B. S. *Organometallics* **1991**, *10*, 104–111.
(24) Allison, J.; Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 1332–1333.
(25) Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6624–6628.
(26) Fisher, E. R.; Armentrout, P. B. *J. Am. Chem. Soc.* **1992**, *114*, 2039–2049.
(27) Bjarnason, A.; Taylor, J. W. *Organometallics* **1990**, *9*, 1493–1499.
(28) Blum, O.; O'Bannon, P.; Schroder, D.; Schwarz, H. *Organometallics* **1993**, *12*, 980–981.
(29) Christ, C. S.; Eyler, J. R.; Richardson, D. E. *J. Am. Chem. Soc.* **1990**, *112*, 4778–4787.
(30) Huang, Y.; Freiser, B. S. *J. Am. Chem. Soc.* **1990**, *112*, 5085–5089.
(31) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 72–80.
(32) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 2605–2612.

rearrangement giving cleavage of a C–C bond or a C–H bond in the hydrocarbon–metal ion complex. The generally accepted mechanism involves a β-hydride transfer process yielding a hydrido-π-hydrocarbon intermediate, as generalized in eq 1.

(1)
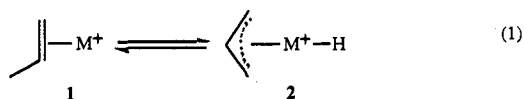
Many of the final (olefin)M^+ products produced in the activation processes, such as c-$C_5H_6M^+$ (M = Fe, Co) and $C_3H_6M^+$ (M = Fe, Co, Ni, Rh), have also been proposed to have hydrocarbon metal hydride structures that are formed by a further β-hydride transfer from the organic ligand to metal center.[31,39] The gas-phase ion $C_5H_5MeTi^+$,[40] for example, was produced in the reactions of Ti^+ with isomeric methylpentenes. It was suggested that this ion was a η^4-methylcyclopentadiene metal complex that underwent a β-hydride transfer rearrangement to form a η^5-methylcyclopentadienyl metal hydride.

While examples of the hydrido-π-allyl structure, **2**, have been observed directly in the condensed phase,[41,42] gas-phase metal hydride character has been probed by H/D exchange reactions with deuterated molecules, such as deuterium and ethene-d_4.[31,39,43–45] Reactions of ions with NH_3 have also been discovered that indicate the presence of hydrocarbon metal hydride structures in c-$C_5H_6M^+$ (M = Fe, Co) and $C_3H_6Rh^+$.[46,47]

In this study, the gas-phase ion condensation chemistry of cycloheptatriene chromium tricarbonyl, $(\eta^6$-c-$C_7H_8)Cr(CO)_3$ (**3**), is examined. Certain anomalously low ion reactivities can be explained by a hydrogen on a saturated carbon undergoing a β-hydride transfer to form ions with metal–hydrogen bonds and a low electron deficiency on the metal center. The presence of metal–hydrogen bonds is corroborated by reactions with methanol that give elimination of molecular hydrogen. The ion–molecule chemistry of **3** is contrasted with that of η^6-benzene chromium tricarbonyl, $(\eta^6$-c-$C_6H_6)Cr(CO)_3$ (**4**), and η^5-cyclopentadienyl vanadium tetracarbonyl, $(\eta^5$-c-$C_5H_5)V(CO)_4$ (**5**).

3   4   5
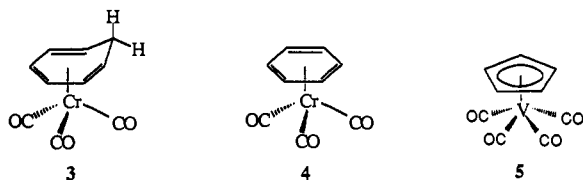
Experimental Section

The theory, instrumentation, and methodology of Fourier transform ion cyclotron resonance mass spectrometry have been discussed else-

(33) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 7484–7491.

(34) Peake, D. A.; Gross, M. L.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 4307–4316.

(35) Peake, D. A.; Gross, M. L. *Organometallics* **1986**, *5*, 1236–1243.

(36) Eller, K.; Karrass, S.; Schwarz, H. *Organometallics* **1992**, *11*, 1637–1646.

(37) Rope, R. M.; VanOrden, S. L.; Cooper, B. T.; Buckner, S. W. *Organometallics* **1992**, *11*, 2001–2003.

(38) MacMillan, D. K.; Gross, M. L. *Organometallics* **1992**, *11*, 2079–2087.

(39) Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 5944–5950.

(40) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1977**, *99*, 35–39.

(41) Scherman, E. O.; Schreiner, P. R. *J. Chem. Soc., Chem. Commun.* **1978**, 223–224.

(42) Tulip, T. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4201–4211.

(43) Christ, C. S.; Eyler, J. R.; Richardson, *J. Am. Chem. Soc.* **1990**, *112*, 596–607.

(44) Beauchamp, J. L.; Stevens, A. E.; Corderman, R. R. *Pure Appl. Chem.* **1979**, *51*, 967–978.

(45) Carlin, T. J.; Sallans, L.; Cassady, C. J.; Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 6320–6321.

(46) Buckner, S. W.; Freiser, B. S. *J. Am. Chem. Soc.* **1987**, *109*, 4715–4716.

(47) Buckner, S. W.; Freiser, B. S. *Polyhedron* **1989**, *8*, 1401–1406.

Table 1. FT-ICR Mass Spectrum of $(\eta^5$-c-$C_7H_8)Cr(CO)_3{}^a$

fragment ion	m/z	rel intensity(%)[b]
Cr^+	52	90.2
CH_2Cr^+	66	7.5
$C_5H_6Cr^+$	118	12.4
$C_7H_8Cr^+$	144	100.0
$C_7H_8Cr(CO)^+$	172	37.9
$C_7H_8Cr(CO)_2{}^+$	200	22.5
$C_7H_8Cr(CO)_3{}^+$	228	62.9
$C_5H_5{}^+$	65	2.8
$C_6H_7{}^+$	79	2.2
$C_7H_7{}^+$	91	18.9
$C_7H_8{}^+$	92	6.3

^{a} Electron impact ionization; 25 eV × 20 ms beam pulse at 1.0 × 10^{-7} Torr. ^{b} Relative to the base peak in the spectrum.

where.[48,49] All experiments were performed on a locally-constructed FT-ICR spectrometer[3,50] equipped with a Nicolet FTMS-1000 console and a 2.54-cm cubic trapping cell[51,52] situated in a Varian electromagnet that was operated at 1.9 T. The trapping voltage was set at +1 V for positive ions. A 25-eV electron ionization beam was employed to favor the formation of a variety of positive fragment ions. The background pressure of the vacuum system was kept below 5 × 10^{-9} Torr by continuous pumping with an ion pump. A Varian dual range ionization gauge (Model 971–1008) was used to measure static pressures. For the data processing, normalized intensities $(I_i/\Sigma I_i)$ were used. Nitrogen gas was used for collision-induced dissociation (CID)[53] experiments as the spectrometer's ion pump precludes using Argon as the collision gas. Standard FT-ICR ion ejection techniques[54] were used to determine reaction pathways.

$(\eta^6$-c-$C_7H_8)Cr(CO)_3$ (**3**) was obtained from Aldrich in high purity and used as supplied and was introduced into the vacuum system at room temperature through a leak valve and the system maintained at a pressure of 1.0 × 10^{-7} Torr. No impurities were found in its mass spectrum. Methanol, used as a secondary neutral reactant, was introduced into the system from a separate sample inlet. For those experiments with methanol, the total pressure of the two neutrals was kept at about 1.0 × 10^{-6} Torr. Four different deuterium-labeled methanol isotopomers (CH_3OH, CD_3-OH, CH_3OD, CD_3OD) were used as appropriate to verify the formulae of the products of the reactions with methanol. The isotopic methanols were purified by multiple freeze–pump–thaw cycles.

Results and Discussion

Table 1 gives the positive ion FT-ICR mass spectrum of $(\eta^6$-c-$C_7H_8)Cr(CO)_3$ (**3**). The FT-ICR mass spectrum of **3** matches that in King's[55] report with minor differences. The abundance of hydrocarbon ions is lower in our spectrum than in King's spectrum since our sample was introduced at room temperature rather than at over 200 °C. High-resolution FT-ICR exact mass measurements indicate that ion $m/z = 66$ is CH_2Cr^+ rather than $C_5H_6{}^+$, as reported by King. Metastable ion studies[55] showed that $C_5H_6Cr^+$ is formed from $C_7H_8Cr^+$ by ejection of C_2H_2 and that Cr^+ is formed from $C_7H_8Cr^+$ by ejection of the ligand. Müller and Fenderl[56] also observed the metastable ion for the transition from $C_7H_8Cr^+$ to Cr^+ as well as the metastable ion for the transition from $C_5H_6Cr^+$ to Cr^+.

Cr^+ **Reactions.** FT-ICR ion ejection experiments[54] identify the following reactions.

(48) Comisarow, M. B. *Anal. Chim. Acta* **1985**, *178*, 1–15.

(49) Marshall, A. G.; Grosshans, P. B. *Anal. Chem.* **1991**, *63*, 215A–229A.

(50) Aarstol, M.; Comisarow, M. B. *Int. J. Mass Spectrom. Ion Processes* **1987**, *76*, 287–297.

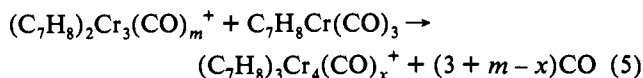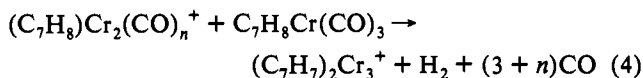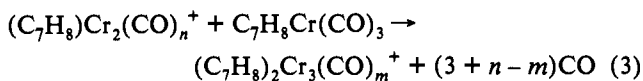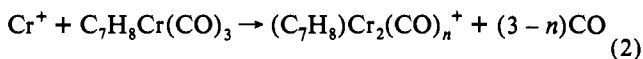(51) Comisarow, M. B. *Adv. Mass Spectrosc.* **1980**, *8*, 1698–1706.

(52) Comisarow, M. B. *Int. J. Mass Spectrom. Ion Phys.* **1981**, *37*, 251–257.

(53) Cody, R. B.; Burnier, R. C.; Freiser, B. S. *Anal. Chem.* **1982**, *54*, 96–101.

(54) Comisarow, M. B.; Grassi, V.; Parisod, G. *Chem. Phys. Lett.* **1978**, *57*, 413–416.
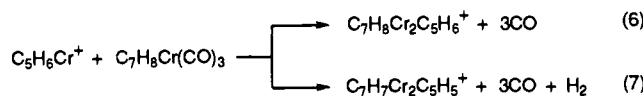
(55) King, R. B. *Appl. Spectrosc.* **1969**, *23*, 536–546.

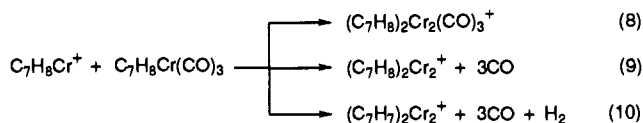(56) Muller, J.; Fenderl, K. *Chem. Ber.* **1970**, *103*, 3128–3140.

$$Cr^+ + C_7H_8Cr(CO)_3 \rightarrow (C_7H_8)Cr_2(CO)_n^+ + (3-n)CO \quad (2)$$

$$(C_7H_8)Cr_2(CO)_n^+ + C_7H_8Cr(CO)_3 \rightarrow$$
$$(C_7H_8)_2Cr_3(CO)_m^+ + (3+n-m)CO \quad (3)$$

$$(C_7H_8)Cr_2(CO)_n^+ + C_7H_8Cr(CO)_3 \rightarrow$$
$$(C_7H_7)_2Cr_3^+ + H_2 + (3+n)CO \quad (4)$$

$$(C_7H_8)_2Cr_3(CO)_m^+ + C_7H_8Cr(CO)_3 \rightarrow$$
$$(C_7H_8)_3Cr_4(CO)_x^+ + (3+m-x)CO \quad (5)$$

where $n = 1, 2$; $m = 0\text{-}3$; $x = 1\text{-}3$. These reactions are similar to reactions of Cr^+ with the analogous compounds, $(\eta^6\text{-arene})$-$Cr(CO)_3^{23}$ and $(\eta^6\text{-benzene})Cr(CO)_3$ (**4**).

**$C_5H_6Cr^+$ Reactions.** The ion reacts with the parent neutral **3** to form the dichromium products indicated in reactions 6 and 7. Note that a dehydrogenation product ion is observed as one of the two major condensation products.

$$C_5H_6Cr^+ + C_7H_8Cr(CO)_3 \longrightarrow$$
$$\longrightarrow C_7H_8Cr_2C_5H_6^+ + 3CO \quad (6)$$
$$\longrightarrow C_7H_7Cr_2C_5H_5^+ + 3CO + H_2 \quad (7)$$

$C_7H_8Cr^+$ Reactions. $C_7H_8Cr^+$ reacts with its neutral parent molecule to generate two major products, $(C_7H_8Cr)_2(CO)_3^+$ (reaction 8) and $(C_7H_8Cr)_2^+$ (reaction 9). The former product ion is unreactive toward the neutral parent molecule and the later ion shows very low reactivity. The association–dehydrogenation product of reaction 10 is only observed in small amounts.

$$C_7H_8Cr^+ + C_7H_8Cr(CO)_3 \longrightarrow$$
$$\longrightarrow (C_7H_8)_2Cr_2(CO)_3^+ \quad (8)$$
$$\longrightarrow (C_7H_8)_2Cr_2^+ + 3CO \quad (9)$$
$$\longrightarrow (C_7H_7)_2Cr_2^+ + 3CO + H_2 \quad (10)$$

$C_7H_8Cr(CO)_{1,2}^+$ Reactions. Reactions of $C_7H_8Cr(CO)^+$ and $C_7H_8Cr(CO)_2^+$ are summarized in eq 11. All the product ions of reaction 11 show very low reactivity toward the parent neutral.

$$C_7H_8Cr(CO)_{1,2}^+ + C_7H_8Cr(CO)_3 \rightarrow$$
$$(C_7H_8Cr)_2(CO)_{0\text{-}3}^+ + nCO \quad (n = 1\text{-}5) \quad (11)$$
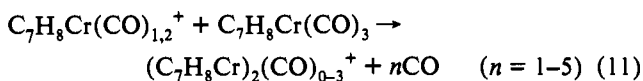
Rate Constants and Ion Structures. First-order rate constants for the reactions of ions were determined from the decay slopes of the curves of ion intensity vs reaction times. Figure 1 shows typical data for major ions in the $(\eta^6\text{-}c\text{-}C_7H_8)Cr(CO)_3$ system.

Table 2 summarizes the rate data. The relative rate constants for ions in the $C_7H_8Cr(CO)_3$ system are given as are the rates relative to that of Cr^+. The ion reactivity order is as follows: Cr^+ > $C_7H_8Cr^+$ $\cong$ $C_7H_8Cr(CO)^+$ > $C_7H_8Cr_2(CO)^+$ > $(C_7H_8)_2$-$Cr_3(CO)^+$ > $(C_7H_7Cr)_2^+$ $\cong$ $C_7H_8Cr(CO)_3^+$ $\cong$ $(C_7H_8Cr)_2(CO)_3^+$ $\cong$ 0. The ED column in Table 2 gives calculated electron deficiencies per chromium atom, relative to 18 valence electrons per metal atom, assuming single metal–metal bonds between two chromium atoms and assuming C_7H_8 to be a 6-electron donor, as it is in the neutral parent molecule, **3**. Note that the reactivity of $C_7H_8Cr^+$, **6** (ED = 7), is similar to that of $C_7H_8Cr(CO)^+$, **8** (ED = 5), even though the former is seemingly more electron deficient. This contradicts the general trend that rate constants increase with increasing electron deficiencies.[10–13] Another exceptional case is that of $(C_7H_8Cr)_2^+$, which is less reactive than $(C_7H_8Cr)_2(CO)^+$ or $(C_7H_8Cr)_2(CO)_2^+$.

Figure 2 is a plot of the rate constants for the ions of this work vs their electron deficiencies. The monotonic general trend that rate constants increase with increasing electron deficiencies[10–13]

is clearly evident. Those ions whose formulae are in outline font are off the monotonic curve due to an anomalously low reactivity. The data of Figure 2 indicate that, in addition to the ions C_7H_8-Cr^+ and $(C_7H_8Cr)_2^+$ mentioned above, the ions $C_5H_6Cr^+$, C_7H_8-$Cr_2(CO)^+$, and $C_7H_8Cr_2(CO)_2^+$ also have lower-than-expected reactivity.

To explain these observations, we propose a β-hydride transfer process that lowers the electron deficiency on chromium. Reaction 12 accounts for the first exceptional case. In this reaction, when


$$(12)$$
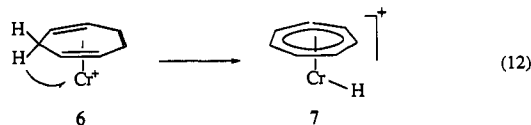
the third CO is ejected from the molecular ion to form ion **6**, hydride is intramolecularly transferred from the organic ring to the Cr atom, converting the cycloheptatriene ligand into an aromatic tropylium ligand. The coordination hapticity to Cr is converted from η^6 to $\eta^7 + \eta^1$ and the electron deficiency on the chromium atom drops by two. Thus, the Cr atom in each of $\eta^7,\eta^1\text{-}C_7H_7CrH^+$ (**7**) and $\eta^6\text{-}C_7H_8Cr(CO)^+$ (**8**) has the same


8
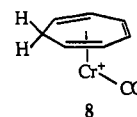
electron deficiency (ED* = 5), explaining why these two ions have similar reactivity. The ED* values in Table 2 are calculated using this proposal and triple metal–metal bond structures as appropriate. We believe that when the central Cr atom is highly electronically unsaturated, the cycloheptatriene ligand reacts so as to offer more than 6 electrons to the metal center.

Reaction 12 has a condensed phase counterpart,[57] reaction 13. In this reaction, the trityl cation abstracts a hydride from the cycloheptatriene ligand forming a stable tropylium cation ligand.

$$(13)$$
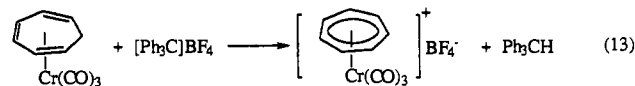
A related solution-phase process is the β-hydrogen transfer reaction from bonded alkyl groups. This β-hydride transfer has been observed directly by proton NMR spectroscopy and has been used as a typical mechanism to explain the decomposition of transition metal alkyls.[58,59]

Similarly, the low reactivity of ion $C_5H_6Cr^+$ (**9**, ED = 9) is explained by a rearrangement to ion $C_5H_5CrH^+$ (**10**, ED* = 7), reaction 14.

$$(14)$$
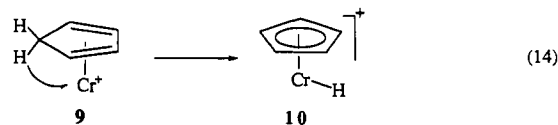
An additional driving force[60] for the above rearrangements appears to be the aromatization of the seven-membered ring (reaction 12) or aromatization of the five-membered ring (reaction 14). Consistent with this analysis is our observation that the fragment ions from benzene chromium tricarbonyl, $\eta^6\text{-}C_6H_6Cr$-$(CO)_3$ (**4**), have the normal condensation reactivity, $Cr^+ > C_6H_6$-

(57) Powell, P. *Principles of Organometallic Chemistry*, 2nd ed.; Chapman and Hall: New York, 1988; p 330.

(58) Powell, P. *Principles of Organometallic Chemistry*, 2nd ed.; Chapman and Hall: New York, 1988; pp 217–224.

(59) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1980; pp 1120–1255.

(60) Winstein, S.; Grunwald, E.; Ingraham, L. L. *J. Am. Chem. Soc.* **1948**, *70*, 821–828.
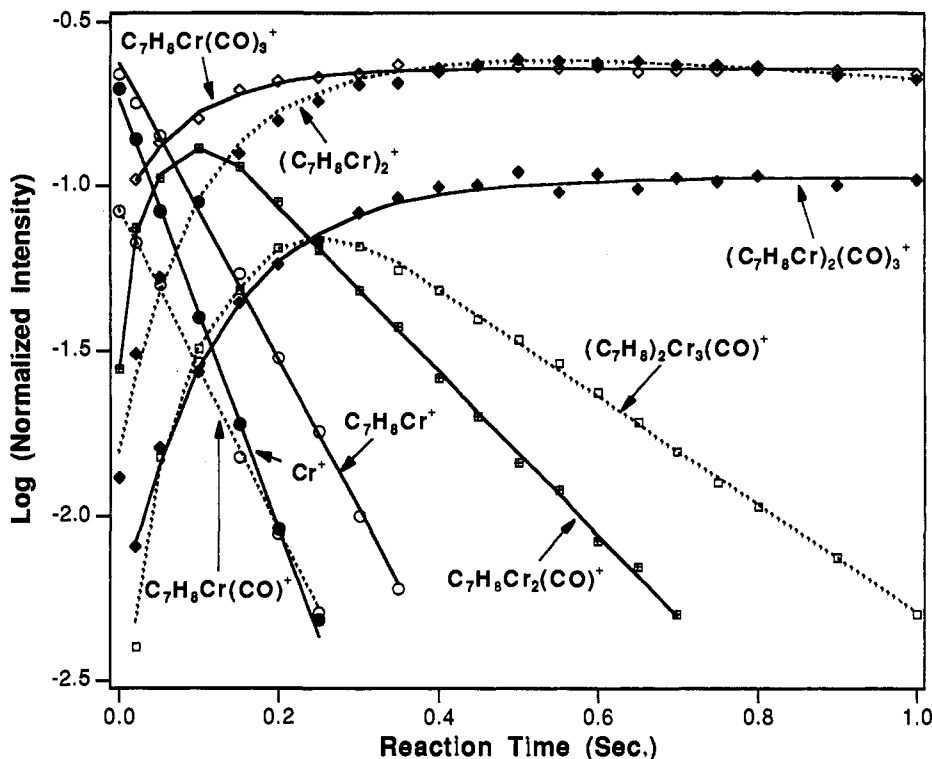
Figure 1. Temporal variation of ion abundances monitored by FT-ICR single resonance technique when fragment ions from $(\eta^6\text{-}c\text{-}C_7H_8)Cr(CO)_3$ undergo clustering reactions with the parent molecule.

Table 2. Rate Constants and Electron Deficiencies

species	ED[b]	ED*[b]	rel reactivity[a]
Cr^+	13		1.0
$C_5H_6Cr^+$	9 (9)	7 (10)	0.85
$C_7H_8Cr^+$	7 (6)	5 (7)	0.70
$C_7H_8Cr(CO)^+$	5 (8)	5	0.74
$C_7H_8Cr(CO)_2^+$	3	3	0.50
$C_7H_8Cr(CO)_3^+$	1	1	0.00
$C_7H_8Cr_2(CO)^+$	7.5	4.5[c], 5.5[d] (11)	0.57
$C_7H_8Cr_2(CO)_2^+$	6.5	3.5[c], 4.5[d] (12)	0.33
$(C_7H_8Cr)_2^+$	5.5	1.5[c] (13)	0.017
$(C_7H_8Cr)_2(CO)^+$	4.5	2.5[d] (14)	0.091
$(C_7H_8Br)_2(CO)_2^+$	3.5	1.5[d] (15)	0.041
$(C_7H_8Cr)_2(CO)_3^+$	2.5	0.5[d] (16)	0.00
$(C_7H_8)_2Cr_3(CO)^+$	5.7	2.7[d]	0.24
$(C_7H_8)_2Cr_3(CO)_2^+$	5.0	2.0[d]	0.11

[a] Relative to the rate constant of Cr^+. [b] Chemical structures corresponding to the bold face numerals are given in the text. ED is the calculated electron deficiency assuming no hydride transfer and single metal–metal bonding in polymetallic ions. ED* is the adjusted electron deficiency. [c] Assuming a triple metal–metal bond and tropylium–hydride bonding. [d] Assuming only a triple metal–metal bond.

$Cr^+ > C_6H_6CrCO^+ > C_6H_6Cr(CO)_2^+$, with their parent molecule. The fragment ions from $\eta^5\text{-}C_5H_5V(CO)_4$ (5) also have the normal reactivity order, $V^+ > C_5H_5V^+ > C_5H_5V(CO)^+ > C_5H_5V(CO)_2^+$, with their parent neutral. These systems have no possible corresponding aromatization reaction as each of **4** and **5** already contains an aromatic ring.

The data in Figure 2 imply that the highly electron deficient secondary product ions, $C_7H_8Cr_2(CO)^+$ and $C_7H_8Cr_2(CO)_2^+$, have structures **11** and **12**, formed via a β-hydride transfer and a hydrogen shift to the more electron deficient metal center.
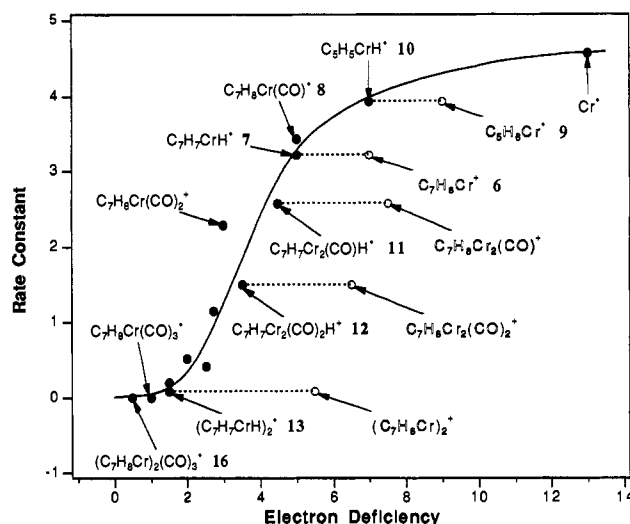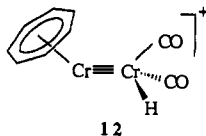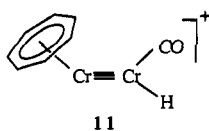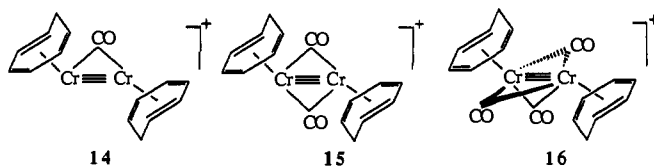

11   **12**

Figure 2. Ion reactivity versus electron deficiency. The data are from Table 2. Each ion whose reactivity is anomalously low is indicated in outline font. The solid dots correspond to the ED* values and the outline dots correspond to the ED values. The bold face numerals correspond to the structures in the text.

Similarly, the secondary product ion, $(C_7H_8Cr)_2^+$, is proposed to have a double hydrido structure, **13**, to explain its low reactivity.


13
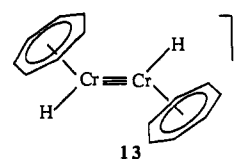
This triple metal–metal bond tropylium hydride structure, **13**, has a low electron deficiency (Table 2), explaining the ion's low reactivity. Triple metal–metal bond structures can also be ascribed to ions **14–16**.

Gas-Phase Ion Chemistry of (η^6-c-C_7H_8)Cr(CO)$_3$

J. Am. Chem. Soc., Vol. 116, No. 10, 1994 4453

14   **15**   **16**

In polymetallic ions, loss of H_2 is most easily explained by loss from a single metal center. The loss of H_2 from polymetallic ions in reactions 4, 7, and 10 indicates that the hydrogen atoms in ions such as **13** are labile within the polymetallic ion.

This study and previous work on the gas-phase ion–molecule chemistry of organometallic molecules have revealed that molecular ions are generally unreactive toward their neutral parent molecule.[22,23] This is because a molecular ion lacks only one electron compared to its stable neutral counterpart. As the molecular ion $C_7H_8Cr(CO)_3^+$ is an unreactive ion in the system, we suggest that the unreactive ion, $(C_7H_8Cr)_2(CO)_3^+$, has structure **16** and is the molecular ion of the as-yet-unprepared 18-electron compound *bis(η^6-cycloheptatriene) dichromium tricarbonyl*. Ion **16** would have a triple metal–metal bond by analogy to a known 18-electron complex—bis(η^5-cyclopentadienyl) dichromium tetracarbonyl[61,62] (**17**). Ions **11–15** can be considered to be fragment ions of this molecular ion with the triple metal-metal bond in their structures.
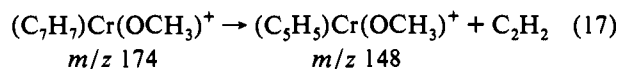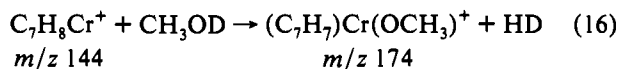

17
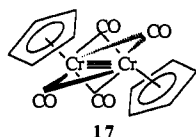
Probing the Hydrido-π-tropylium and Hydrido-π-cyclopentadienyl Structures. As $C_7H_8Cr^+$ is the prototypical ion of this study, it was selected for FT-ICR collision-induced dissociation (CID) experiments with nitrogen as the collision gas. We found that Cr$^+$ was the only CID product, with no CrH$^+$ or $C_7H_7Cr^+$ being seen.

$$C_7H_8Cr^+ \xrightarrow{\text{CID}} Cr^+ + C_7H_8 \qquad (15)$$
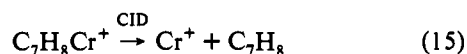
It has been demonstrated previously[31] that the only pathway for FTICR-CID on $C_5H_6Fe^+$ eliminates C_5H_6 to give Fe$^+$ as the only ionic product. It appears that FTICR-CID experiments are not definitive for detecting the metal–hydrogen bonds resulting from β-hydride transfer reactions such as reactions 12 and 14. We also observed that $C_7H_8Cr^+$ does not undergo H/D exchange with D_2. Gas-phase metal hydride ions that do not react with deuterium have been reported previously.[31,45] Therefore, the lack of exchange with D_2 does not preclude a hydrido-π-tropylium structure for $C_7H_8Cr^+$.

Methanol was reacted with the fragment and product ions from complex **3**. Reactions 16 and 17 were observed for the fragment ion $C_7H_8Cr^+$.

$$C_7H_8Cr^+ + CH_3OD \rightarrow (C_7H_7)Cr(OCH_3)^+ + HD \quad (16)$$
$$m/z \; 144 \qquad\qquad\qquad m/z \; 174$$

$$(C_7H_7)Cr(OCH_3)^+ \rightarrow (C_5H_5)Cr(OCH_3)^+ + C_2H_2 \quad (17)$$
$$m/z \; 174 \qquad\qquad\qquad m/z \; 148$$

$C_7H_8Cr^+$ reacts with methanol to form an addition–dehydrogenation ionic product that ejects C_2H_2. Using CD$_3$OH and CD$_3$OD as reactants, we determined that one of the two hydrogen atoms eliminated in reaction 16 is from $C_7H_8Cr^+$ and the other
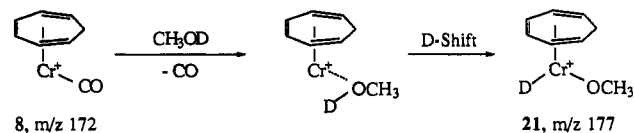
(61) Hackett, P.; O'Neill, P. S.; Manning, A. R. *J. Chem. Soc. Dalton Trans.* **1974**, 1625–1627.

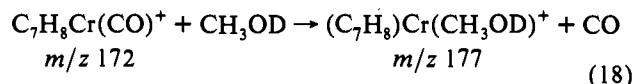(62) Curtis, M. D.; Butler, W. M. *J. Organomet. Chem.* **1978**, *155*, 131–145.

Scheme 1

7, m/z 144   **18**

20, m/z 174   **19**

Scheme 2

8, m/z 172   **21**, m/z 177
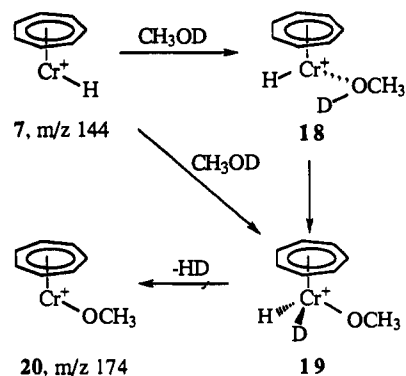
is from the hydroxyl group of methanol. In contrast, the monocarbonyl fragment ion $C_7H_8Cr(CO)^+$ reacts differently with methanol (reaction 18) to form a substitution product that does not self dehydrogenate.

$$C_7H_8Cr(CO)^+ + CH_3OD \rightarrow (C_7H_8)Cr(CH_3OD)^+ + CO$$
$$m/z \; 172 \qquad\qquad\qquad m/z \; 177 \qquad (18)$$

Reactions 16 and 18 confirm that $C_7H_8Cr^+$ has a hydrido-tropylium moiety consistent with structure **7**, before the ion reacts with methanol, and that $C_7H_8Cr(CO)^+$ has structure **8** with an unrearranged cycloheptatriene ligand. A mechanism for the addition–dehydrogenation reaction of ion **7**, reaction 16, is proposed in Scheme 1. Fragment ion $C_7H_7CrH^+$ (**7**) reacts with methanol to form a double metal hydride ion **19** by either direct ion insertion into the O–D bond of methanol (**7** to **19**) or ion association with methanol followed by a D-shift[63] to metal (**7** to **19** via **18**). The double hydride ion, **19**, undergoes rapid reductive elimination of hydrogen to form the final metal–oxygen bonded product, **20**. The reductive elimination of hydrogen via a gas-phase double metal hydride ion has been demonstrated repeatedly.[9]

Similarly, the mechanism of the substitution reaction (reaction 18) of the monocarbonyl fragment ion $C_7H_8Cr(CO)^+$ (**8**) is given in the Scheme 2. As ion **8** does not have an original metal–hydrogen linkage before the reaction, the final product **21** is a monohydride ion that does not self-dehydrogenate as does the double metal hydride ion **19** of Scheme 1.

Ion **20** undergoes a facile fragmentation process that ejects C_2H_2 from its tropylium ligand to form ion $C_5H_5Cr(OCH_3)^+$ (**22**, m/z 148, reaction 17), as shown below.

20, m/z 174   **22**, m/z 148
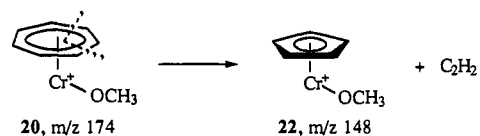
Uncoordinated tropylium ion has been observed to lose C_2H_2 to form $C_5H_5^+$.[64–66] Consistent with the presence of a tropylium ligand, the organometallic ion **20** undergoes an analogous fragmentation to give a fairly large amount of ion **22**. In

(63) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1976**, *98*, 7445–7447.

(64) Grubb, H. M.; Meyerson, S. *Mass Spectrometry of Organic Ions*; McLafferty, F. W., Ed.; Academic Press Inc.: New York, 1963; p 453.

(65) McLafferty, F. W.; Bockhoff, F. M. *J. Am. Chem. Soc.* **1979**, *101*, 1783–1786.

(66) Ausloos, P. *J. Am. Chem. Soc.* **1982**, *104*, 5259–5265.

4454   *J. Am. Chem. Soc., Vol. 116, No. 10, 1994*

Kan et al.

contrast, the product of $C_7H_8Cr(CO)^+$ (**21**) does not undergo this fragmentation. This also indicates that the C_7H_8Cr moiety is not the same in the fragment ions $C_7H_8Cr^+$ and $C_7H_8Cr(CO)^+$.

$C_6H_6Cr^+$ generated by EI on $(\eta^6\text{-c-}C_6H_6)Cr(CO)_3$ (**4**) was also reacted with methanol. Only an adduct-formation product (reaction 19) is observed as the hydrogen atom in benzene does not readily undergo β-hydride transfer.

$$+ \ CH_3OD \ \rightarrow \ (C_6H_6)Cr(CH_3OD)^+ \quad (19)$$

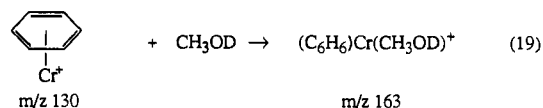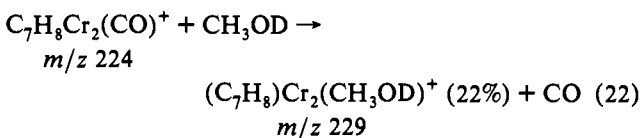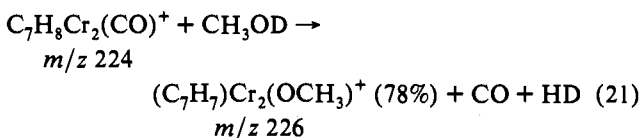$$m/z \ 130 \qquad\qquad\qquad m/z \ 163$$

Figure 2 indicates that $C_5H_6Cr^+$ has a low reactivity. However, the monotonic curve in Figure 2 could have been drawn to indicate that ion $C_5H_6Cr^+$ had normal reactivity and so had structure **9** rather than **10**. That is, the reactivity of $C_5H_6Cr^+$ (Table 2) could be interpreted to be consistent with ED = 9. That C_5H_6-Cr^+ actually has structure **10** is indicated definitively by reaction 20 which leads to the formation of an HD product by the reaction with methanol-d_1, reaction 20.

$$C_5H_6Cr^+ + CH_3OD \rightarrow (C_5H_5)Cr(OCH_3)^+ + HD \quad (20)$$
$$m/z \ 118 \qquad\qquad m/z \ 148$$
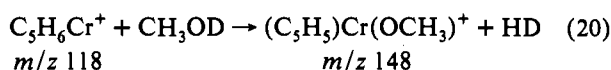
When $C_7H_8Cr_2(CO)^+$ is reacted with methanol two different reactions are observed, of which the dominant one is the dehydrogenation reaction, reaction 21.

$$C_7H_8Cr_2(CO)^+ + CH_3OD \rightarrow$$
$$m/z \ 224$$
$$(C_7H_7)Cr_2(OCH_3)^+ \ (78\%) + CO + HD \quad (21)$$
$$m/z \ 226$$

$$C_7H_8Cr_2(CO)^+ + CH_3OD \rightarrow$$
$$m/z \ 224$$
$$(C_7H_8)Cr_2(CH_3OD)^+ \ (22\%) + CO \quad (22)$$
$$m/z \ 229$$

Some CO-displacement product is also seen, reaction 22. This may indicate that under our reaction conditions, $C_7H_8Cr_2(CO)^+$ exists as an equilibrium mixture of the tropylium–hydrido structure **11** and its cycloheptatriene isomer. The reactions of this ion are summarized in Scheme 3.

Conclusions

The ion reactivities in the $C_7H_8Cr(CO)_3$ system are shown to be dependent upon electron deficiencies of the central metal atoms

Scheme 3
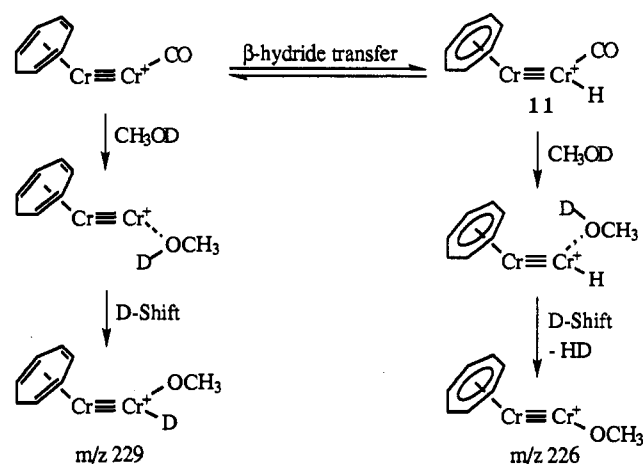
in the present system. The common trend that ion reactivities of organometallic ions increase with increasing electron deficiency on the metal atom is observed. Ions whose reactivity deviates from this general trend are believed to have undergone structural changes in their ligands and/or possess multiple metal–metal bonds. For example, the fragment ions $C_7H_8Cr^+$ and C_7H_8Cr-$(CO)^+$ show similar reactivity toward their neutral parent even though the former is seemingly more electron deficient. An intramolecular β-hydride transfer process that decreases the electron deficiency on the central metal is proposed for $C_7H_8Cr^+$. Thus, $C_7H_8Cr^+$ has a hydrido-π-tropylium structure whereas the cycloheptatriene ligand in $C_7H_8Cr(CO)^+$ retains its structural integrity. As a result, the two ions have the same electron deficiency, explaining their similar reactivity. The hydride and/ or multiple metal–metal bond structures are also assigned to those ions with anomalously low reactivities. The unreactive secondary product $(C_7H_8Cr)_2(CO)_3^+$ is believed to be the molecular ion of an as-yet-unprepared complex, *bis(η^6-cycloheptatriene) dichromium tricarbonyl*. This complex would have a triple metal–metal bond by analogy with previously known organometallic compounds.

Reaction with methanol was used to probe the hydride structures proposed in this study. Ions with probable metal hydride character formed adduct–dehydrogenation ionic products in their reactions with methanol, providing strong proof for the presence of hydrido-π-tropylium chromium and hydrido-π-cyclopentadienyl chromium structures in the present system.