

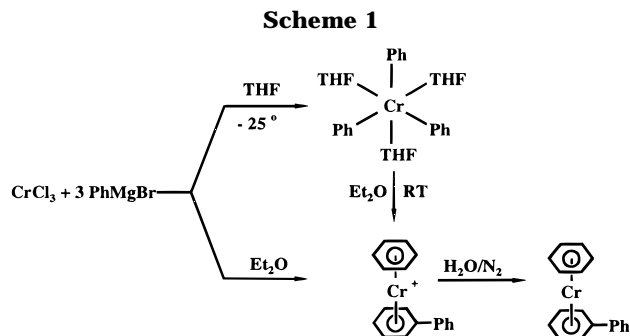
From Hein to Hexene: Recent Advances in the Chemistry of Organochromium π -Complexes

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Organochromium chemistry has its origins in the investigations of the German chemist *Franz Hein* who, in 1919 as a young man of 26 working on his *Habilita-tion* at the University of Leipzig, decided to reinvestigate the reaction of the then novel Grignard reagent PhMgBr with CrCl₃. After hydrolysis of the primary product, he isolated an orange compound which he identified “mit ziemlicher Sicherheit” as pentaphenylchromium bromide (Ph₅CrBr).¹ Thirty-five years later, in part as a result of his request in the original publication—“alles Nähere bleibt einer zusammenfassenden Publikation vorbehalten und ich richte daher an die verehrten Fachgenossen die Bitte, die Chromorganoverbindungen mir zur weiteren Bearbeitung überlassen zu wollen”²—the true nature of this species was still unknown, and it was not until the structure of ferrocene had been established that Zeiss and his graduate student Tsutsui decided to reinvestigate the system. In what is now a classical study, they were able to show that a mixture of (η^6 -arene)-chromium compounds had been formed.³ An indication of the course of the reaction for one of the products is shown in Scheme 1.



Soon after the discovery of ferrocene, chromocene was isolated⁴ and in the late 1960's Union Carbide developed a catalyst for the polymerization of ethylene by depositing chromocene onto silica.⁵ Sophisticated variations of this and a related process developed by Phillips Petroleum are still used to prepare much of the high-density polyethylene which is produced world wide.⁶

Parallel to this, G. Wilke was able to prepare tris(η^3 -allyl)chromium in 1963 and demonstrated that this

compound is an active, single-component homogeneous catalyst for the polymerization of ethylene under mild conditions and as such was among the first homogeneous, non-Ziegler catalysts for the polymerization of alkenes and dienes.⁷ Although there was considerable interest in commercially exploiting this system, notably in Japan, this faded with the discovery that other homoleptic η^3 -allyl-metal complexes (i.e. compounds in which the metal atom interacts solely with allyl groups) are more active, particularly when deposited on a carrier.⁸

The further development of organochromium chemistry in the next 20 years concentrated on the η^6 -arene compounds, CO-stabilized species, and the Fischer-carbene complexes.⁹

The initial impetus for this Account came from an interesting contribution by K. H. Theopold published in 1990 in this journal¹⁰ with the provocative title “Organochromium(III) Chemistry: A Neglected Oxidation State” in which the author summarized his results on the chromium(III)-alkyls. At the time this Account appeared, we already had considerable experience with organochromium(III) compounds but were much less familiar with the corresponding chemistry of chromium(II). Originally we intended to fill this gap, but it soon became apparent that it would be more useful to summarize our recent results on the π -complexes of chromium, regardless of the oxidation state of the metal.

We entered the field about a dozen years ago when we decided to attempt to resuscitate the chemistry of the homoleptic η^3 -allyl complexes of the group 6 metals. Initially we concentrated on molybdenum and were able to prepare a monochloride (**1**) by reacting

(1) Hein, F. *Ber. Dtsch. Ges.* **1919**, *52*, 195.

(2) “Further details will be reserved for an extensive publication ... and I therefore request my professional colleagues to leave the further investigation of the organochromium compounds to myself”.

(3) Zeiss, H. In *Organometallic Chemistry*; Zeiss, H., Ed; Reinhold: New York, 1960; p 380.

(4) Fischer, E. O.; Hafner, W. *Z. Naturforsch.* **1953**, *8b*, 444. Fischer, E. O.; Hafner, W. *Z. Naturforsch.* **1954**, *9b*, 503. Fischer, E. O.; Hafner, W.; Stahl, H. O. *Z. Anorg. Allg. Chem.* **1955**, *282*, 47. Cotton, F. A.; Wilkinson, G. *Z. Naturforsch.* **1954**, *9b*, 417.

(5) Karol, F. J.; Karapinka, G. L.; Wu, C.; Dow, A. W.; Johnson, R. N.; Carrick, W. L. *J. Polym. Sci.: Part A-1* **1972**, *10*, 2621. Karol, F. J.; Brown, G. L.; Davison, J. M. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 413. Karapinka, G. L. (Union Carbide Corp.). Ger. Offen. 1,808,388, 1967/70; *Chem. Abstr.* **1970**, *72*, 80105.

(6) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*, 2nd ed.; Wiley: New York, 1992; p 52.

(7) Oberkirch, W. Dissertation, Technische Hochschule Aachen, Germany, 1963. Wilke, G. *Angew. Chem.* **1963**, *75*, 10. Wilke, G.; Bogdanović, B.; Heimbach, P.; Keim, W.; Kröner, M.; Oberkirch, W.; Tanaka, K.; Steiner, E.; Walter, D.; Zimmermann, H. *Angew. Chem.* **1966**, *78*, 157.

(8) Ballard, D. G. H. *Adv. Catal.* **1973**, *23*, 263.

(9) Kirtley, S. W. *Compr. Organomet. Chem.* **1982**, *3*, 783. Davis, R.; Kane-Maguire, L. A. P. *Compr. Organomet. Chem.* **1982**, *3*, 953.

(10) Theopold, K. H. *Acc. Chem. Res.* **1990**, *23*, 263.

Peter W. Jolly was born in 1940 and educated in England (B.Sc. Imperial College, London; Ph.D. University of Bristol with F. G. A. Stone). After a postdoc at the University of Texas in Austin with the late Rolly Pettit, he joined the Max-Planck-Institut für Kohlenforschung in Mülheim an der Ruhr, initially as a postdoc with G. Wilke and later as a group leader. For over a decade he has been associated with the Vrije Universiteit in Amsterdam as an external professor. His research interests center on the role of organometallic intermediates in homogeneous catalysis, and he is presently investigating systems involving Cr, Fe, Ru, Co, Ni, and Pd.

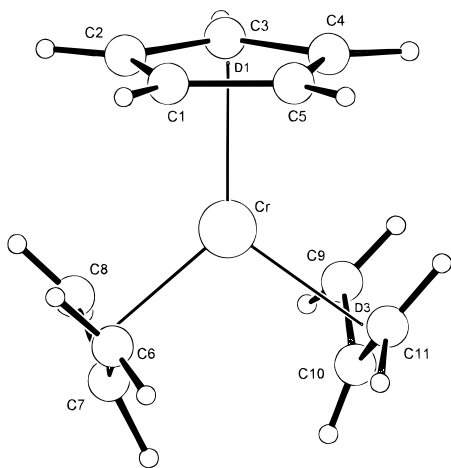
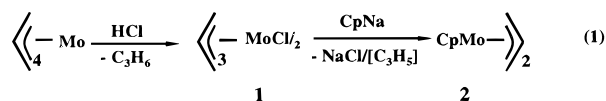


Figure 1. Molecular structure of $\text{Cp}(\eta^3\text{-C}_3\text{H}_5)_2\text{Cr}$ (**3**).¹² Bond distances (Å) and angles (deg): Cr–D1, 1.903; Cr–D2/D3, 1.908; C6–C7, 1.407(3); C7–C8, 1.408(3); C–C(Cp), 1.406(3)–1.418(3); C6–C7–C8, 120.0(2); D1–Cr–D2, 129; D2–Cr–D3, 102.9. Reprinted with permission from ref 12. Copyright 1986 American Chemical Society.

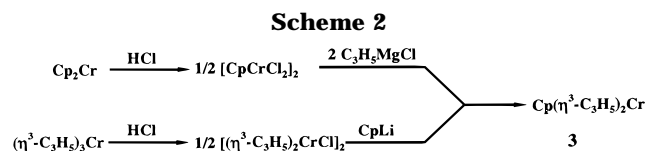
$(\eta^3\text{-C}_3\text{H}_5)_4\text{Mo}$ with HCl in pentane at low temperatures (eq 1). **1** proved to be a useful starting material and



reacted, for example, with cyclopentadienyl sodium with homolytic cleavage of an allyl–Mo bond to give the paramagnetic, 17-electron species $\text{Cp}(\eta^3\text{-C}_3\text{H}_5)_2\text{Mo}$ (**2**).¹¹ **2** proved depressingly unreactive, and as a consequence we decided to attempt to prepare the chromium analogue in the hope that this would be less stable and hence more reactive. Both expectations were realized, and a description of the further development is the subject of this Account.

Cyclopentadienyl(η^3 -allyl)₂chromium and Related Compounds

The target compound **3** may be prepared in high yield, as an orange-red solid which is soluble in all common solvents, starting from either chromocene or tris(η^3 -allyl)chromium (Scheme 2).^{12,13} The crystal structure (Figure 1) shows that the organic ligands are arranged in a trigonal-planar manner around the metal atom with a dihedral angle of 156° between the two allyl planes. As a result, the two *meso*-H atoms are separated by only 2.05 Å.



(11) Jolly, P. W.; Krüger, C.; Ramão, C. C.; Ramão, M. J. *Organometallics* **1984**, *3*, 936. Benn, R.; Holle, S.; Jolly, P. W.; Krüger, C.; Ramão, C. C.; Ramão, M. J.; Rufinska, A.; Schroth, G. *Polyhedron* **1986**, *5*, 461. Andell, A.; Goddard, R.; Holle, S.; Jolly, P. W.; Krüger, C.; Tsay, Y. H. *Polyhedron* **1989**, *8*, 203.

(12) Angermund, K.; Döhring, A.; Jolly, P. W.; Krüger, C.; Romão, C. C. *Organometallics* **1986**, *5*, 1268.

(13) Betz, P.; Döhring, A.; Emrich, R.; Goddard, R.; Jolly, P. W.; Krüger, C.; Romão, C. C.; Schönfelder, K. U.; Tsay, Y. Y. *Polyhedron* **1993**, *12*, 2651.

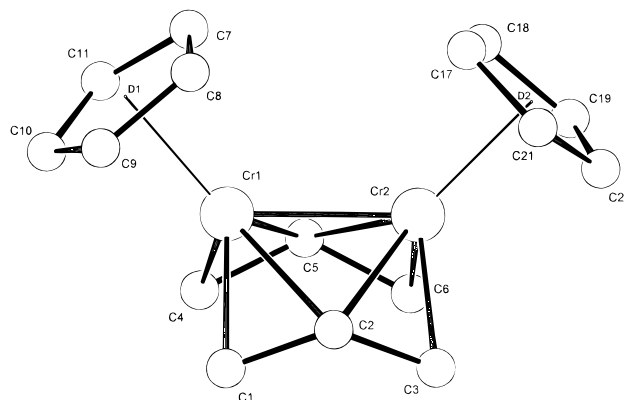
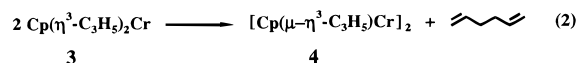


Figure 2. Molecular structure of $[\text{Cp}(\mu\text{-}\eta^3\text{-C}_3\text{H}_5)\text{Cr}]_2$ (**4**).¹³ Bond distances (Å) and angles (deg): Cr1–D1, 1.940; Cr1–Cr2, 2.299(1); Cr–C1, 2.098(3); Cr1–C2, 2.303(3); Cr2–C2, 2.308(3); Cr2–C3, 2.083(3); C1–C2, 1.405(5); C2–C3, 1.428(5); C–C(Cp), 1.359(6)–1.407(6); D1–Cr1–Cr2, 131.2(1); C1–C2–C3, 126.3(3). Reprinted with permission from ref 13. Copyright 1993 Elsevier Science.

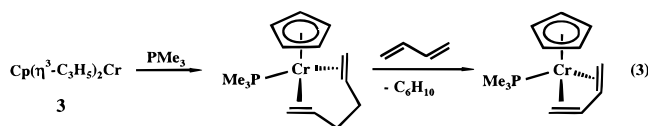
In contrast to the molybdenum analogue **2**, the chromium compound is thermally unstable, reacting further above ca. -15° in solution to give a brown, dinuclear species (**4**) (eq 2).¹³ **4** had been previously



isolated from the reaction of $[\text{CpCrCl}_2]_2$ with allylmagnesium chloride at room temperature,¹⁴ and the crystal structure (Figure 2) confirms the dinuclear nature, with the allyl groups (and not the Cp groups) bridging the Cr_2 fragment. The interplanar angle between the two allyl planes is 55° , and both *meso*-C atoms are pointing toward the metal–metal bond.

Reactions similar to those shown in Scheme 2 have been used to prepare a series of compounds related to **3** in which substituents are present in both the allyl and cyclopentadienyl groups, e.g., $\text{Cp}^*(\eta^3\text{-C}_3\text{H}_5)_2\text{Cr}$, $\text{Cp}(\eta^3\text{-2-MeC}_3\text{H}_4)_2\text{Cr}$, and $(\eta^5\text{-indenyl})(\eta^3\text{-2-MeC}_3\text{H}_4)_2\text{Cr}$.¹³

The synthetic utility of $\text{Cp}(\eta^3\text{-C}_3\text{H}_5)_2\text{Cr}$ (**3**) and related compounds rests on the ligand-induced reductive coupling of the two allyl groups to give a Cr-bonded 1,5-hexadiene molecule which can be readily substituted. The intermediate $(\eta^2, \eta^2\text{-1,5-hexadiene})\text{-Cr}$ species can be isolated from the reaction with P-donor ligands and substituted in a separate reaction by, for example, 1,3-butadiene (eq 3). The crystal structures of both compounds shown in eq 3 have been verified by X-ray diffraction.¹³



Polyenes react similarly, and for example, treatment of **3** with cyclooctatetraene gives $\text{Cp}(\eta^6\text{-C}_8\text{H}_8)\text{Cr}$ (**5**) in over 80% yield. The η^6 -complexation of the cyclooctatetraene molecule in **5**, with one uncomplexed double bond, has been confirmed by a crystal structure determination (Figure 3): the Cp and C1–C6 plane of the cyclooctatetraene molecules are essentially parallel (interplanar angle 4.4°) while the C1–C6 and

(14) Nieman, J.; Pattiasina, J. W.; Teuben, J. H. *J. Organomet. Chem.* **1984**, *262*, 157.

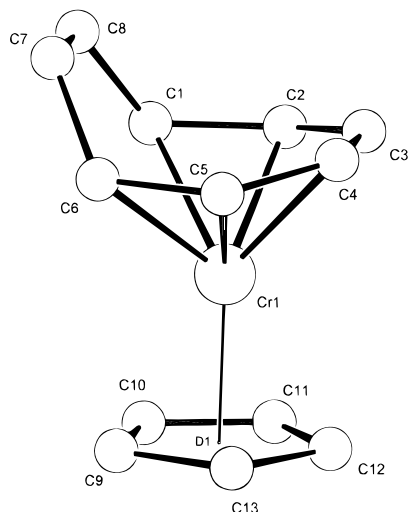
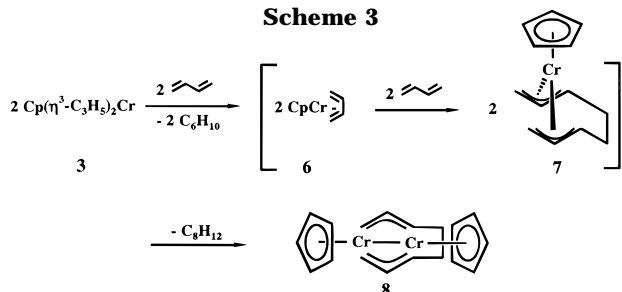


Figure 3. Molecular structure of $\text{Cp}(\eta^6\text{-C}_8\text{H}_8)\text{Cr}$ (**5**).¹⁵ Bond distances (Å) and angles (deg): Cr–D(C_8H_8), 1.346; Cr–D(Cp), 1.832(5); C–C (C1–C6), 1.40(2)–1.44(2); C6–C7, 1.49(1); C7–C8, 1.29(2); C–C(Cp), 1.37(3)–1.421(1). Reprinted with permission from ref 15. Copyright 1993 Elsevier Science.

C1–C8–C7–C6 planes form an angle of 63.7°. In some cases, the reaction proceeds with deprotonation of the polyene, and for example, the products of the reaction of **3** with cyclopentadiene, cycloheptatriene, and 1,3-cyclohexadiene are Cp_2Cr , $\text{Cp}(\eta^7\text{-C}_7\text{H}_7)\text{Cr}$, and $\text{Cp}(\eta^6\text{-C}_6\text{H}_6)\text{Cr}$ respectively.¹⁵

In the absence of a P-donor ligand, **3** reacts with 1,3-butadiene to give a dinuclear species (**8**) in which two butadiene molecules have dimerized and bridge the metal atoms in an η^3, η^3 -manner (Scheme 3). The mechanism for the formation of **8** suggested in the scheme is supported by the isolation of mononuclear compounds corresponding to **6** and **7** from the reaction of 1,3-butadiene with $\text{Cp}^*(\eta^3\text{-C}_3\text{H}_5)_2\text{Cr}$ ($\text{Cp}^* \equiv \eta^5\text{-C}_5\text{Me}_5$) while the product of the analogous reaction with *trans*-piperylene has been shown by X-ray diffraction to have the structure shown in Figure 4 in which two piperylene molecules have coupled at the metal atom to give an $\eta^3, \eta^3\text{-Me}_2\text{C}_8\text{H}_8$ fragment.¹⁶ The observed head–tail coupling of two piperylene molecules is unusual: head–head coupling has been observed at nickel¹⁷ and tail–tail coupling at zirconium.¹⁸

Scheme 3



Organo-transition-metal compounds in which two 1,3-diene molecules have dimerized at the metal center are believed to be involved as intermediates in

(15) Angermund, K.; Betz, P.; Döhring, A.; Jolly, P. W.; Krüger, C.; Schönfelder, K.U. *Polyhedron* **1993**, *12*, 2663.

(16) Döhring, A.; Emrich, R.; Goddard, R.; Jolly, P. W.; Krüger, C. *Polyhedron* **1993**, *12*, 2671.

(17) Benn, R.; Büssemeier, B.; Holle, S.; Jolly, P. W.; Mynott, R.; Tkatchenko, I.; Wilke, G. *J. Organomet. Chem.* **1985**, *279*, 63.

(18) Brauer, D. J.; Krüger, C. *Organometallics* **1982**, *1*, 207.

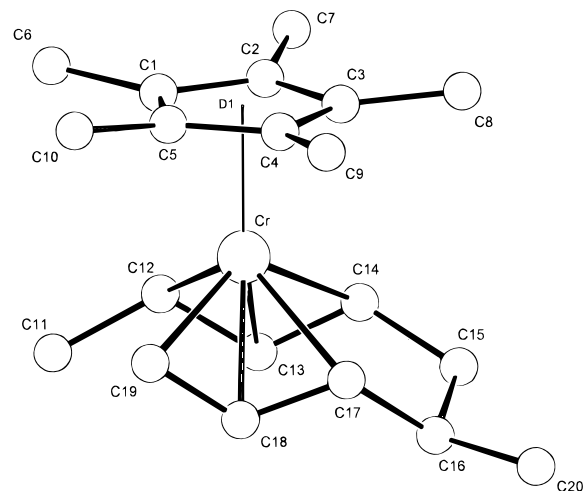


Figure 4. Molecular structure of $\text{Cp}^*(\eta^3, \eta^3\text{-1,5-Me}_2\text{C}_8\text{H}_8)\text{Cr}$.¹⁶ Bond distances (Å) and angles (deg): Cr–D(Cp^*), 1.916(2); Cr–C(allyl), 2.134(3)–2.187(3); C–C(allyl), 1.383(5)–1.403(5); C–C(Cp^*), 1.404(4)–1.411(3); C17–C18–C19, 122.0(3); C12–C13–C14, 123.5(3). Reprinted with permission from ref 16. Copyright 1993 Elsevier Science.

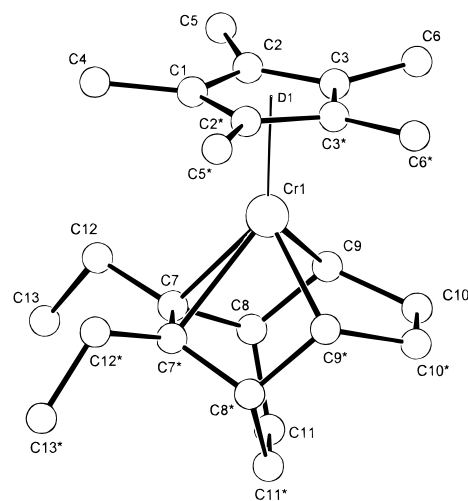
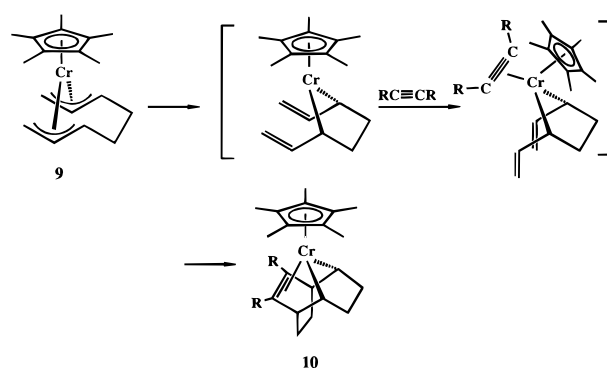


Figure 5. Molecular structure of $\text{Cp}^*(\eta^1, \eta^2, \eta^1\text{-1,2-Et}_2\text{C}_{10}\text{H}_{12})\text{-Cr}$ (**10**, R = Et).¹⁶ Bond distances (Å) and angles (deg): Cr–C7, 2.341(4); Cr–C9, 2.064(5); Cr–D(Cp^*), 1.926(6); C7–C8, 1.508(6); C8–C9, 1.542(7); C7–C7*, 1.364(6); C–C(Cp^*), 1.383(6)–1.402(5); C7–C8–C9, 106.6(4). Reprinted with permission from ref 16. Copyright 1993 Elsevier Science.

catalytic oligomerization and cooligomerization, and we therefore, investigated the reactions of $\text{Cp}^*(\eta^3, \eta^3\text{-C}_8\text{H}_{12})\text{Cr}$ (**9**) with alkynes: an unusual 2,6-addition of the alkyne across the C_8 fragment occurs with accompanying coupling to give the tricyclic species **10** (Scheme 4).¹⁶ The crystal structure of the product

Scheme 4



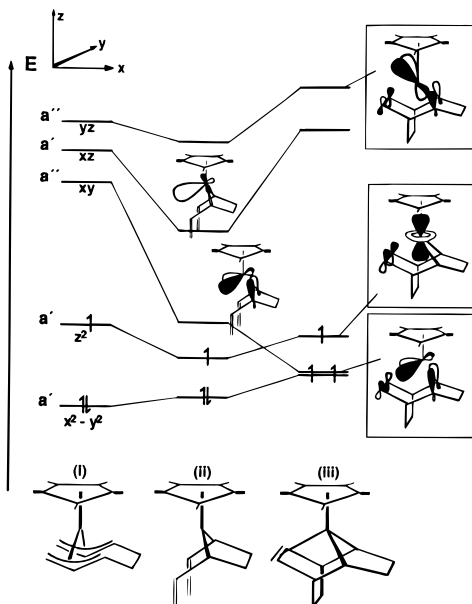
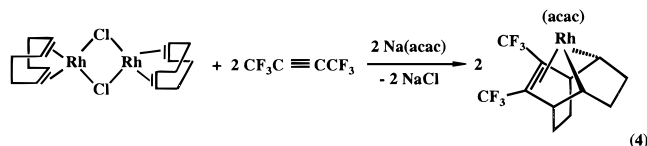
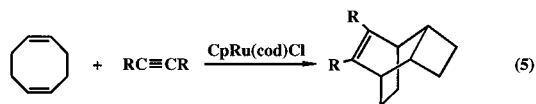


Figure 6. MO scheme illustrating the change in the energy of the Cr d-orbitals during the formation of $\text{Cp}^*(\eta^1, \eta^2, \eta^1\text{-C}_{12}\text{H}_{14})\text{-Cr}$ (**10**, R = H).¹⁶ Reprinted with permission from ref 16. Copyright 1993 Elsevier Science.

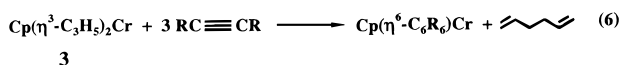
from the reaction with 3-hexyne (**10**, R = Et) has been confirmed by X-ray diffraction (Figure 5), and the suggested mechanism, involving a $(2\pi + 2\pi + 2\pi)$ -cycloaddition is supported by an extended-Hückel MO treatment. The MO scheme is shown in Figure 6, and the observed magnetic susceptibility of $3.1 \mu_{\text{B}}$ for **10** (R = Et) lends credibility to the description. The only reaction that we are aware of which might be related is that of $[(1,5\text{-cod})\text{RhCl}]_2$ (cod = cyclooctadiene) with hexafluorobutyne (eq 4).¹⁹ Whereas we have been



unable to turn the sequence shown in Scheme 4 into a catalytic cycle, Trost has recently developed a Ru-catalyzed process for converting 1,5-cod and alkynes into the tricyclic alkene (eq 5).²⁰



$\text{Cp}(\eta^3\text{-C}_3\text{H}_5)_2\text{Cr}$ (**3**) reacts readily with alkynes: cyclotrimerization at the metal occurs to give $\text{Cp}(\eta^6\text{-arene})\text{Cr}$ compounds in high yield (eq 6).¹⁵ The



reaction is general and may also be used to prepare compounds containing substituted cyclopentadienyl groups. Although this class of compound was first discovered over 30 years ago, no convenient synthesis

(19) Russell, D. R.; Tucker, P. A., *J. Chem. Soc., Dalton Trans.* **1976**, 841.

(20) Trost, B. M.; Imi, K.; Indolese, A. F. *J. Am. Chem. Soc.* **1993**, *115*, 8831.

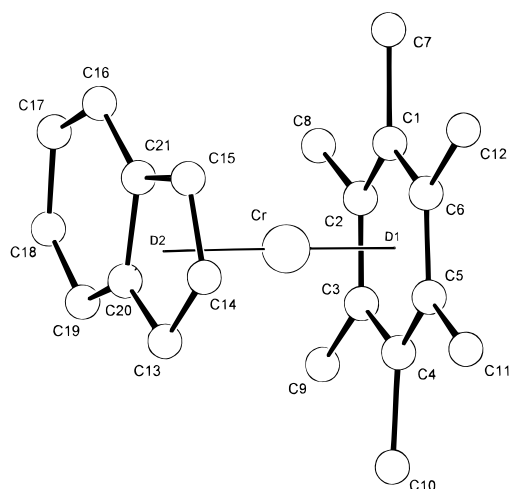
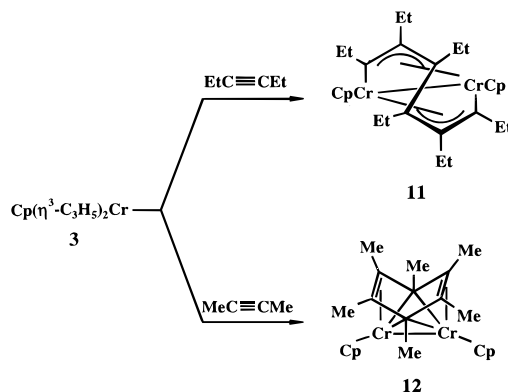


Figure 7. Molecular structure of $(\eta^5\text{-indenyl})(\eta^6\text{-C}_6\text{Me}_6)\text{Cr}$.¹⁵ Bond distances (Å) and angles (deg): Cr–D(C₆Me₆), 1.573(7); Cr–D(indenyl), 1.800(9); C–C(C₆Me₆), 1.387(9)–1.437(9); C13–C14, 1.40(2); C14–C15, 1.38(2); C15–C21, 1.47(1); C20–C21, 1.45(1). Reprinted with permission from ref 15. Copyright 1993 Elsevier Science.

was available (see also ref 21), while disorder in both rings had thwarted all attempts to determine a crystal structure. Fortunately, the crystal structure of the product of the reaction between $(\eta^5\text{-indenyl})(\eta^3\text{-C}_3\text{H}_5)_2\text{-Cr}$ and 2-butyne is not disordered and is shown in Figure 7: the two Cr-bonded rings are almost parallel (interplanar angle 6.3°), and there is no evidence for bond alternation within the hexamethylbenzene ring for which the C–C and Cr–C bond distances are similar to those observed for $(\eta^6\text{-C}_6\text{H}_6)_2\text{Cr}$.²² The formulation of the indenyl ligand as being bonded in an η^5 (and not an η^3) manner is supported by the planarity of this ligand.

The observation that the $\text{Cp}(\eta^6\text{-arene})\text{Cr}$ compounds are much less active than $\text{Cp}(\eta^3\text{-C}_3\text{H}_5)_2\text{Cr}$ for the catalytic cyclotrimerization of alkynes prompted us to look at this system more closely, and the results presented below suggest that the catalytically active species may well be dinuclear in nature. If the reaction with $\text{Cp}(\eta^3\text{-C}_3\text{H}_5)_2\text{Cr}$ is carried out in the presence of a deficiency of alkyne, then, in addition to the $\text{Cp}(\eta^6\text{-arene})\text{Cr}$ compounds, dinuclear species are formed, and it has been possible to isolate the flyover compound **11** from the reaction with 3-hexyne and the hexamethylbenzene compound **12** from the reaction with 2-butyne (Scheme 5).^{12,23}

Scheme 5



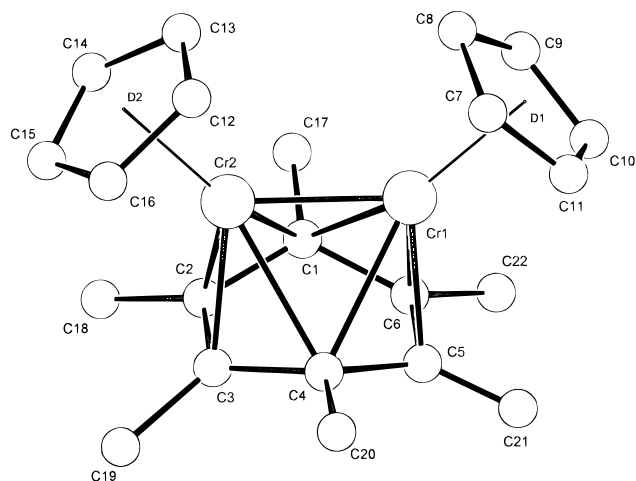
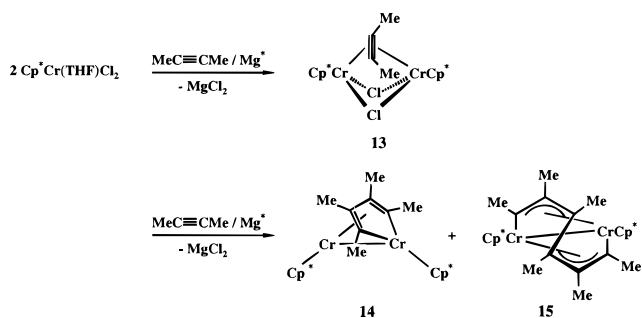


Figure 8. Molecular structure of $(\text{CpCr})_2(\mu\text{-C}_6\text{Me}_6)$ (**12**).²³ Cr1–Cr2, 2.193(2); Cr1–C1, 2.317(8); Cr1–C4, 2.342(7); Cr1–C5, 2.054(7); Cr1–C6, 2.060(7); C1–C6, 1.456(9); C4–C5, 1.459(9); C5–C6, 1.430(10); C–C(Cp), 1.32(2)–1.41(2).

Both compounds are diamagnetic, and as expected the ^1H - and ^{13}C -NMR spectra of **11** show signals for three magnetically inequivalent ethyl groups whereas those for **12** at low temperature show two signals for the methyl groups; at room temperature, the hexamethylbenzene molecule in **12** is fluxional and only one methyl signal is observed. The unusual bonding situation in **12** has been confirmed by a crystal structure determination (Figure 8). A syn-facial arrangement of an arene molecule at two metal atoms has been observed for complexes of Fe, V, Ru, Rh, Rh/Ir, and Co/Ir. An arrangement similar to that in **12** has been observed for $(\text{CpFe})_2(\mu\text{-C}_6\text{Me}_6)$ ²⁴ and $(\text{CpVH})_2(\mu\text{-C}_6\text{H}_6)$,²⁵ whereas the arene molecule is bonded in an η^2, η^2 -manner in $(\text{CpRu})_2(\mu\text{-PPh}_2)(\mu\text{-H})(\mu\text{-C}_6\text{H}_6)$ ²⁶ and in an η^3, η^3 -manner in $(\text{CpRh})_2(\mu\text{-C}_6\text{H}_6)$ ²⁷ and $\text{Cp}_2\text{-IrM}(\mu\text{-C}_6\text{H}_6)$ (M = Co, Rh)²⁸ as well as in $[(\eta^6\text{-C}_6\text{H}_5\text{-Me})\text{Fe}]_2(\mu\text{-C}_6\text{H}_5\text{Me})$.²⁹

Other plausible intermediates in the chromium-catalyzed cyclotrimerization of alkynes have been isolated by reacting $\text{Cp}^*\text{Cr}(\text{THF})\text{Cl}_2$ with activated Mg (Mg^*)³⁰ in the presence of 2-butyne (Scheme 6). The

Scheme 6



initial product of this reaction is a binuclear species (**13**) in which the two metal atoms are bridged by one butyne molecule,^{31,32} and this may be reduced further

(21) Köhler, F. H.; Metz, B.; Strauss, W. *Inorg. Chem.* **1995**, *34*, 4402.

(22) Keulen, E.; Jellinek, F. *J. Organomet. Chem.* **1966**, *5*, 490.

(23) Döhring, A.; Goddard, R.; Jolly, P. W.; Krüger, C. Unpublished results, 1992.

(24) Jonas, K.; Koepe, G.; Schieferstein, L.; Mynott, R.; Krüger, C.; Tsay, Y.-H. *Angew. Chem.* **1983**, *95*, 637.

(25) Jonas, K.; Wiskamp, V.; Tsay, Y.-H.; Krüger, C. *J. Am. Chem. Soc.* **1983**, *105*, 5480.

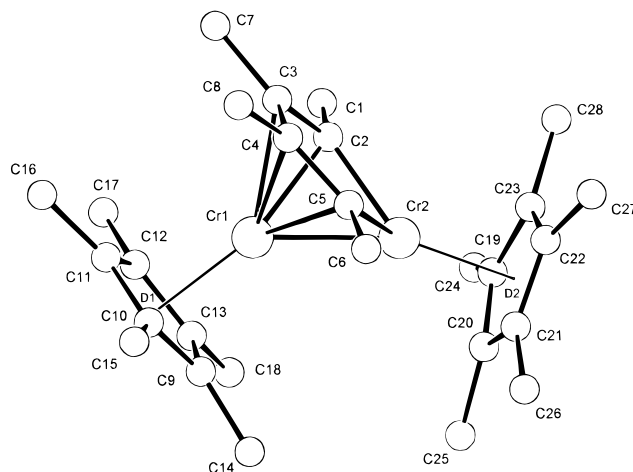


Figure 9. Molecular structure of $(\text{Cp}^*\text{Cr})_2(\mu\text{-}\eta^1, \eta^1, \eta^1\text{-C}_4\text{Me}_3)$ (**14**).^{33–35} Bond distances (Å) and angles (deg): Cr–Cr, 2.304(1); Cr2–C2, 2.010(4); Cr2–C5, 2.028(4); Cr1–C(C4Cr), 2.154(4)–2.176(4); C2–C3, 1.412(6); C3–C4, 1.459(6); C4–C5, 1.411(6); Cr1–D1(Cp*), 1.901(4); Cr2–D2(Cp*), 1.960(5); C2–Cr2–C5, 81.6(2); Cr2–Cr1–D1(Cp*), 138.9(1); Cr1–Cr2–D2(Cp*), 159.3(1). Reprinted with permission from ref 33. Copyright 1992 Elsevier Science.

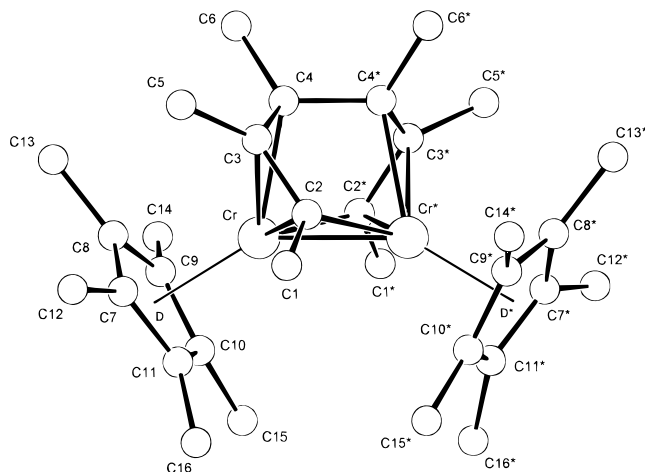


Figure 10. Molecular structure of $(\text{Cp}^*\text{Cr})_2(\mu\text{-}\eta^1, \eta^3, \eta^3, \eta^1\text{-C}_6\text{Me}_6)$ (**15**).³³ Bond distances (Å) and angles (deg): Cr–Cr*, 2.383(1); Cr–C2, 2.144(1); Cr–C3, 2.257(1); Cr–C4, 2.185(1); Cr–D(Cp*), 1.959(1); C2–C3, 1.417(2); C3–C4, 1.432(2); C4–C4*, 1.511(2); C2–C3–C4, 111.5(4); Cr*–Cr–D, 150.0(1). Reprinted with permission from ref 33. Copyright 1992 Elsevier Science.

to **14**, in which two alkyne molecules have reacted to give a chromacyclopentadiene fragment which is bonded in an η^4 -manner to a second metal atom, and to **15** which is the product of **14** with a third alkyne molecule.^{33–35} The crystal structures of **14** and **15** are shown as Figures 9 and 10. It should be noted that

(26) Müller, J.; Gaede, P. E.; Qiao, K. *Angew. Chem.* **1993**, *105*, 1809.

(27) Omari, H.; Suzuki, H.; Take, Y.; Moro-oka, Y. *Organometallics* **1989**, *8*, 2270.

(28) Müller, J.; Gaede, P. E.; Qiao, K. *J. Organomet. Chem.* **1994**, *213*, 480.

(29) Schneider, J. J.; Specht, U.; Goddard, R.; Krüger, C.; Ensling, J.; Gütllich, P. *Chem. Ber.* **1995**, *128*, 941.

(30) Bogdanović, B. *Acc. Chem. Res.* **1988**, *21*, 261. Aleandri, L. E.; Bogdanović, B. In *Active Metals*; Fürstner, A., Ed.; VCH: Weinheim, 1996.

(31) Emrich, R. Doctoral Dissertation, Ruhr-Universität Bochum, Germany, 1991. Emrich, R.; Jolly, P. W. Unpublished results, 1991.

(32) Swarat, K. Doctoral Dissertation, Ruhr-Universität Bochum, Germany, 1990. Jonas, K.; Swarat, K. Unpublished results, 1990.

(33) Wilke, G.; Benn, H.; Goddard, R.; Krüger, C.; Pfeil, B. *Inorg. Chim. Acta* **1992**, *198–200*, 741.

(34) Angermund, K.; Claus, K. H.; Goddard, R.; Krüger, C. *Angew. Chem.* **1985**, *97*, 241.

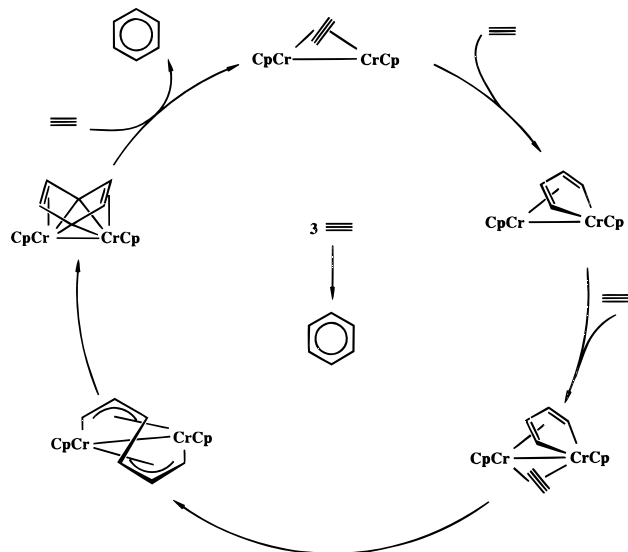


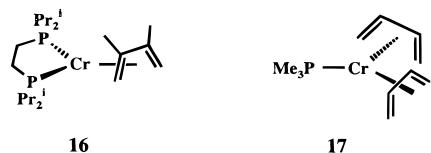
Figure 11. Cp_2Cr_2 -catalyzed cyclotrimerization of acetylene.

the C_6Me_6 chain in **15** adopts a syn-facial arrangement above the Cp^*_2Cr_2 fragment. Carbonyl-stabilized, dinuclear chromium compounds containing a metallocyclopentadiene group have been reported,^{36,37} while Mo analogues of the flyover compounds **11** and **15** have been investigated in detail.³⁸

The structures of the dinuclear compounds described above encourage us to propose the catalytic cycle shown in Figure 11 for the cyclotrimerization reaction. This suggestion has as its forerunner one made by G. Wilke in 1978 for the nickel-catalyzed cyclotetramerization of acetylene to cyclooctatetraene.^{39,40}

Phosphine-Stabilized Organochromium π -Complexes

The active Mg mentioned above as the reducing agent for CpCrCl_2 and related species is prepared by the thermolysis of MgH_2 ³⁰ and has proved invaluable for the preparation of thermally unstable zerovalent chromium compounds containing 1,3-dienes and alkynes since the reduction can be carried out at low temperatures. For example, the paramagnetic (η^4 -2,3-dimethylbutadiene)chromium compound **16** decomposes above -20°C but can be prepared by reduction with active Mg in the presence of the diene at -30°C . Related reactions in the presence of monodentate phosphines lead to the formation of compounds containing two η^4 -bonded diene molecules, e.g., **17**.⁴¹



(35) Wilke, G. *Proceedings of the 5th IUPAC Symposium in Organic Synthesis*, Freiburg, 1984; Blackwell Science Ltd., 1985; p 1.

(36) Bradley, J. S. *J. Organomet. Chem.* **1978**, *150*, C1.

(37) Knox, S. A. R.; Stansfield, R. F. D.; Stone, F. G. A.; Winter, M. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1982**, 173.

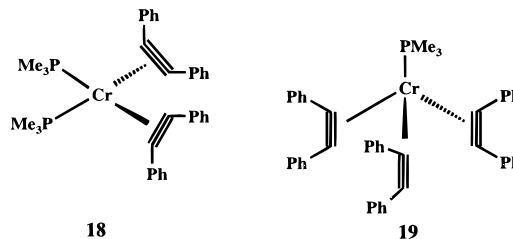
(38) Whiteley, M. W. *Compr. Organomet. Chem. II* **1995**, *5*, 331.

(39) Wilke, G. *Pure Appl. Chem.* **1978**, *50*, 677.

(40) Dieck, H. tom; Svoboda, M.; Kopf, J. *Z. Naturforsch., Teil B* **1978**, *33*, 1381.

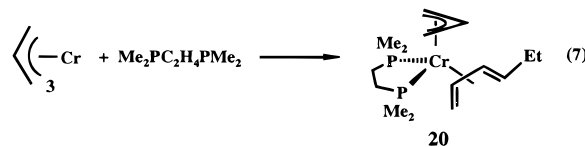
(41) Jolly, P. W.; Zakrzewski, U. *Polyhedron* **1991**, *10*, 1427.

Phosphine-stabilized, zerovalent chromium-alkyne compounds, e.g., **18** and **19**, can be prepared similarly. Both **18** and **19** are diamagnetic, the two alkyne

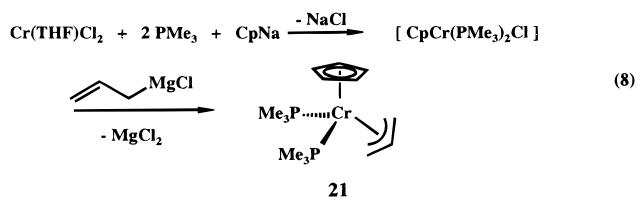


molecules in **18** donating 8 electrons and the three alkyne molecules in **19** donating 10 electrons to the zerovalent metal atom. This is reflected in the ^{13}C chemical shift and C-C stretching frequency of the complexed alkyne molecules which lie at 212.5 ppm and $1670/1650\text{ cm}^{-1}$ for **18** and 186.5 ppm and $2050/1700\text{ cm}^{-1}$ for **19**, respectively. A MO description of the bonding in compounds of this class has been developed.⁴²

Organochromium compounds containing a single η^3 -allyl group have been prepared by reacting tris(η^3 -allyl)chromium with bidentate ligands: two of the allyl groups undergo reductive coupling with subsequent isomerization to give an η^4 -bonded 1,3-hexadiene molecule (eq 7). Compound **20** is paramagnetic (17-

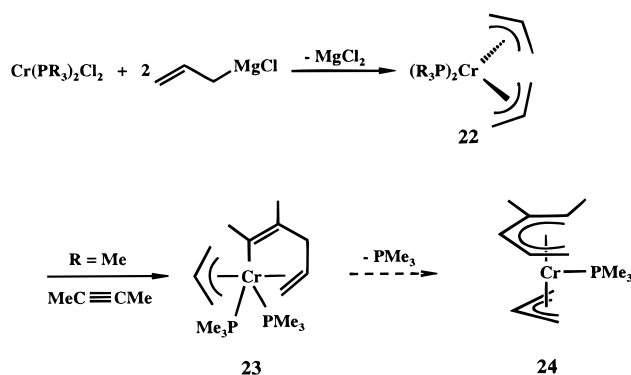


VE; VE = valence electron) and the structure has been confirmed by X-ray diffraction.⁴³ Substitution of the diene in **20** by a cyclopentadienyl group would lead to a diamagnetic, 18-electron species, and **21** has been prepared in a one-pot reaction (eq 8).⁴⁴



Thermally unstable, paramagnetic bis(η^3 -allyl)chromium compounds can be prepared by the conventional reaction between the metal halide and an allyl Grignard reagent (Scheme 7).⁴⁵ The decomposition tem-

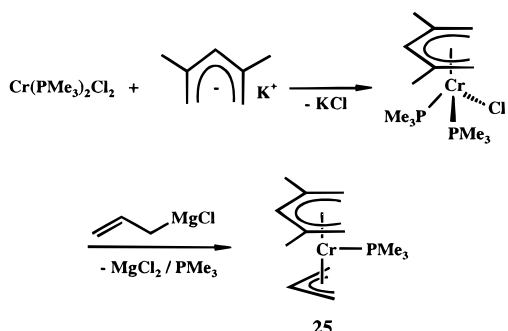
Scheme 7



perature of **22** is phosphine dependent, being ca. -70 °C where R is Et and -40 °C where R is Me, while the dimethylphenylphosphine-stabilized species decomposes at -10 °C. Crystal structure determinations show the ligands to be arranged in a pseudotetrahedral geometry around the central metal atom. **22** (R = Me) reacts with 2-butyne with insertion into one of the allyl groups to give **23** in which a 4-methyl-1,4-hexadienyl fragment is bonded in an η^1, η^2 -manner to the metal. **23** reacts further above -25 °C with loss of a donor ligand to give the substituted η^5 -pentadienylchromium compound **24** (Scheme 7).⁴⁵

η^5 -Pentadienylchromium compounds related to **24** can be prepared more conveniently by reacting a chromium halide successively with potassium 2,4-pentadienyl and allylmagnesium chloride (Scheme 8). A crystal structure determination of **25** shows that, in the crystal, the two organic groups are eclipsed and almost parallel (interplanar angle 5.6°).⁴⁴

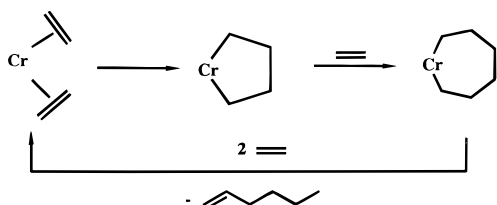
Scheme 8



Chromium-Catalyzed Trimerization of Ethylene to 1-Hexene

Although the intermediacy of metallacyclic intermediates has frequently been invoked to account for the *cyclic* oligomerization of alkenes and alkynes, these species are not generally believed to be involved in the *linear* oligomerization of alkenes;⁴⁶ see, however, refs 47–49. One exception is the chromium-catalyzed trimerization of ethylene to 1-hexene which, it has been suggested, involves the formation of metalla-five-membered and -seven-membered rings (Scheme 9).^{47,48} The key to this mechanism lies in the relative stability of the metallacyclopentane ring to β -H transfer compared to the metallacycloheptane ring.

Scheme 9



We have been able to obtain some support for this suggestion by preparing Cp*-stabilized chromacyclic

(42) Wink, D. J.; Creagan, B. T. *Organometallics* **1990**, *9*, 328. King, R. B. *Inorg. Chem.* **1968**, *7*, 1044. Tate, D. P.; Augl, J. M.; Ritchey, W. M.; Ross, B. L.; Grasselli, J. G. *J. Am. Chem. Soc.* **1964**, *86*, 3261.

(43) Iczek, F.; Jolly, P. W.; Krüger, C. *J. Organomet. Chem.* **1990**, *382*, C11.

(44) Jolly, P. W.; Krüger, C.; Zakrzewski, U. *J. Organomet. Chem.* **1991**, *412*, 371.

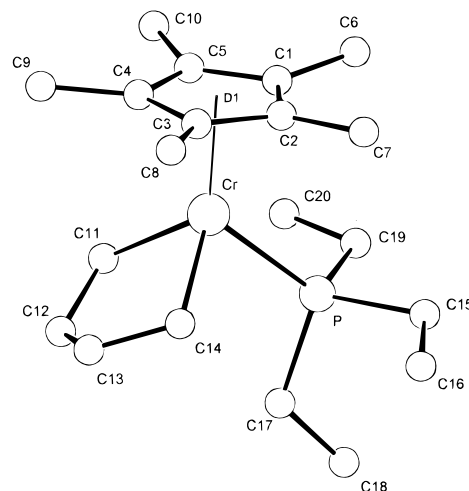


Figure 12. Molecular structure of $\text{Cp}^*\text{Cr}(\text{PEt}_3)\text{CH}_2\text{C}_2\text{H}_4\text{CH}_2$.³¹ Bond distances (Å) and angles (deg): Cr–C11, 2.089(3); Cr–C14, 2.091(3); Cr–P, 2.447(1); Cr–D(Cp*), 1.943; C11–C12, 1.470(7); C12–C13, 1.382(8); C13–C14, 1.490(6); C11–Cr–C14, 84.1(1).

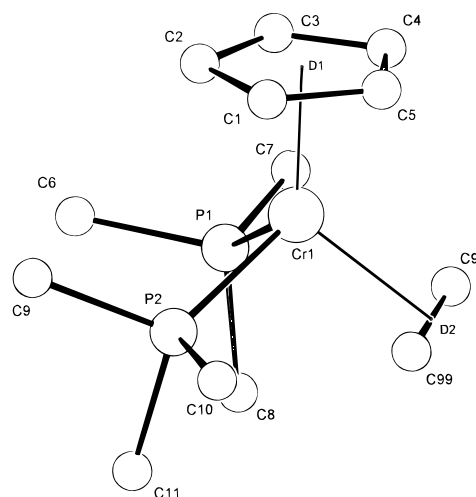


Figure 13. Molecular structure of $\text{CpCr}(\text{PMe}_3)_2(\text{CH}_2=\text{CH}_2)$.⁴⁹ Bond distances (Å) and angles (deg): Cr–D1(Cp), 1.844; Cr–D2(C₂H₄), 2.008; Cr–P, 2.308(1)/2.187(2); C–C(C₂H₄), 1.415(3); C–C(Cp), 1.404(3)–1.428(3); Cr–C(C₂H₄), 2.129(2); C–Cr–C, 38.8(1); P–Cr–P, 97.3(1).

compounds and studying their chemistry (Scheme 10).^{31,49} The crystal structure of the PEt_3 analogue of **26** has been determined (Figure 12) and confirms that the five-membered ring is essentially planar, with the β -H atoms directed away from the metal atom (the unusually short C12–C13 bond distance is an artifact associated with disorder). As anticipated, the chromacyclopentane species **26** is considerably more stable than the chromacycloheptane species **27** which decomposes above ca. 0 °C liberating 1-hexene. In addition, **26** reacts further with ethylene. Unfortunately, this last reaction occurs above the decomposition point of **27**, but it is encouraging that the organic

(45) Betz, P.; Jolly, P. W.; Krüger, C.; Zakrzewski, U. *Organometallics* **1991**, *10*, 3520.

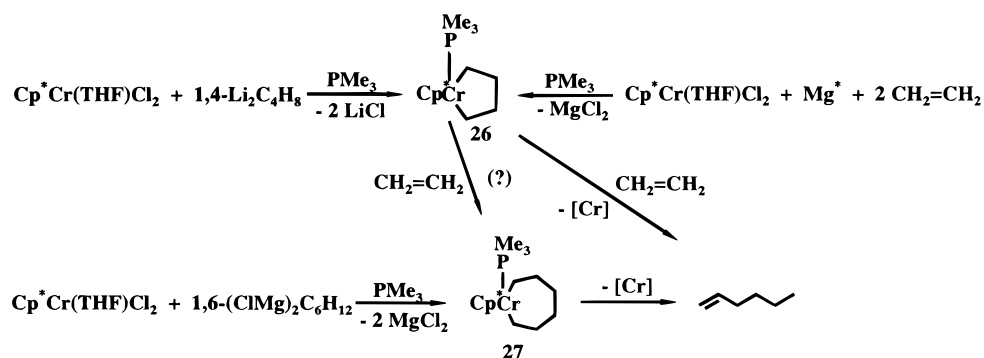
(46) Keim, W.; Behr, A.; Roper, M. *Compr. Organomet. Chem.* **1982**, *8*, 371.

(47) Briggs, J. R. *J. Chem. Soc., Chem. Commun.* **1984**, 674.

(48) Meijboom, N.; Schaverien, C. P.; Orpen, A. G. *Organometallics* **1990**, *9*, 774.

(49) Verhovnik, G. Doctoral Dissertation, Ruhr-Universität Bochum, Germany, 1996. Jolly, P. W.; Verhovnik, G. Unpublished results, 1996.

Scheme 10



product is again 1-hexene. Mechanistically relevant is also the observation that the chromacyclopentane compound **26** can be prepared by reducing the metal chloride in the presence of ethylene. Furthermore, if the reduction of CpCr(THF)Cl₂ is carried out in the presence of excess trimethylphosphine, the monoalkene compound CpCr(PMe₃)₂(CH₂=CH₂) can be isolated, and the structure has been confirmed by X-ray diffraction (Figure 13).⁴⁹

Outlook

Progress in the field of the organochromium π -complexes described here has been hampered by the thermal instability and paramagnetism of most of the compounds and has relied heavily upon X-ray crystallography. Since recent developments have made this technique almost routine, we can expect the rate to

become sufficient to satisfy both the student and the supervisor.

We have deliberately concentrated here on the role of organochromium compounds as intermediates in catalysis and have only occasionally mentioned their catalytic properties. However, the early indication that specific organochromium compounds have a role to play in the catalytic polymerization of alkenes is now beginning to bear fruit, and significant developments in this area will be the topic of a further paper.

I thank my co-workers who are mentioned in the references for their enthusiasm, perseverance, and skill, without which little would have been achieved. I am also indebted to my colleagues at the Institute for their support of our research and to the former director, Professor G. Wilke, for his long-term interest and encouragement.

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