Heterobimetallic cycloheptatrienyl and cycloheptatrienylidene complexes

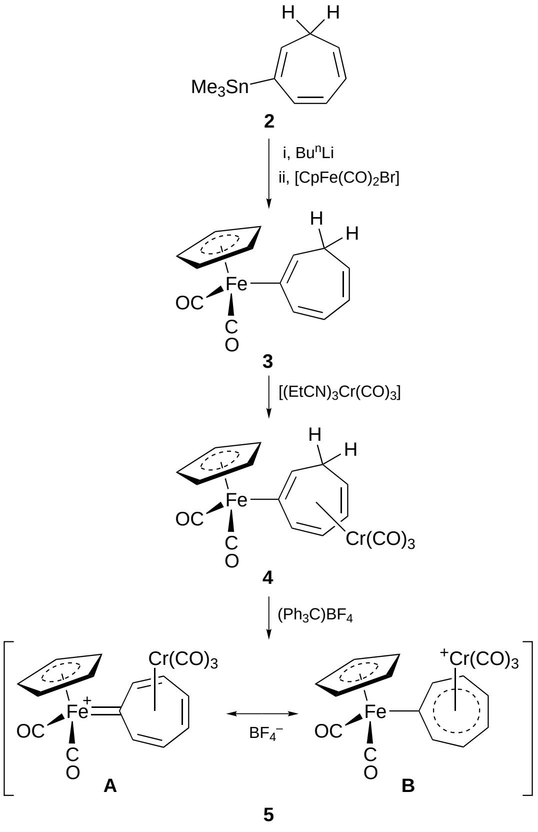
Matthias Tamm,* Alexander Grzegorzewski, Irene Brüdgam and Hans Hartl

Institut für Anorganische und Analytische Chemie, Freie Universität Berlin, Fabeckstraße 34-36, D-14195 Berlin, Germany

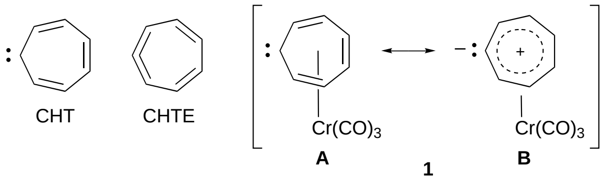
The heterobimetallic μ-(η^1 : η^6-1,3,5-cycloheptatrien-2-yl) complex 4 is obtained from 2-trimethylstannyl-1,3,5-cycloheptatriene 2 and [CpFe(CO)$_2$Br] followed by reaction with [(EtCN)$_3$Cr(CO)$_3$]; hydride abstraction results in the formation of the first heterobimetallic cycloheptatrienylidene (CHT) complex [CpFe(CO)$_2${μ-(η^1 : η^7-CHT)}Cr(CO)$_3$]BF$_4$ 5; the crystal structure of 4 is reported.

Cycloheptatrienylidene (CHT) and 1,2,4,6-cycloheptatetraene (CHTE) are well known isomers of the C_7H_6 potential-energy surface. Experimentally[1] and theoretically,[2] CHTE is the most stable species among the monocyclic C_7H_6 isomers. On the other hand, in transition metal complexes the ground state varies with the metal, and several η^1-CHT and η^2-CHTE complexes have been reported by Jones and coworkers.[3]

In addition, these ligands offer the option to synthesize heterobimetallic complexes by coordination of the seven-membered ring to a second metal fragment.[4] Whereas the first heterobimetallic CHTE complex, [(PPh$_3$)$_2$Pt{μ-(η^2 : η^6-CHTE)}Mo(CO)$_3$], has been reported only recently,[5] heterobimetallic CHT complexes have not yet been prepared. Attempts to generate and trap free [(η^7-CHT)Cr(CO)$_3$] **1** were unsuccessful.[6] In the course of our work on ligands containing cycloheptatrienylium rings,[7] we have recently synthesized 2-trimethylstannyl-1,3,5-cycloheptatriene **2**,[7c] which can be used in a Stille coupling reaction. Here, we wish to report on the suitability of **2** for the preparation of heterobimetallic 1,3,5-cycloheptatrien-2-yl and cycloheptatrienylidene complexes.



Scheme 1



Complex **3** was prepared by lithiation of **2** with Bu^{n}Li and reaction with [CpFe(CO)$_2$Br] in THF at low temperature (Scheme 1).†,[8] The ^{1}H NMR spectrum clearly shows the exclusive formation of the 1,3,5-cycloheptatrien-2-yl derivative exhibiting a doublet of doublets for the allylic protons and five resonances for the vinylic protons in a 2 : 1 : 1 : 1 : 1 : 1 ratio. In order to avoid isomerization, **3** was treated with [(EtCN)$_3$Cr(CO)$_3$] at room temp., to form heterobimetallic **4** as stable red–orange crystals.† The ^{1}H NMR spectrum exhibits five resonances due to the vinylic protons and two resonances due to the allylic *exo-* and *endo*-protons. As **4** is a racemic mixture of two enantiomers, two ^{13}C NMR resonances are observed for the diastereotopic FeCO carbon atoms. The molecular structure of **4** is depicted in Fig. 1.‡ The 1,3,5-cycloheptatriene-2-yl ring is coordinated in a μ-(η^1 : η^6)-fashion. The bond lengths and angles about the iron atom fall in the range observed for other alkenyl complexes,[9] and the Cr(CO)$_3$ coordination is similar to that reported for a manganese–chromium hydrosesquifulvalenyl complex.[7c]

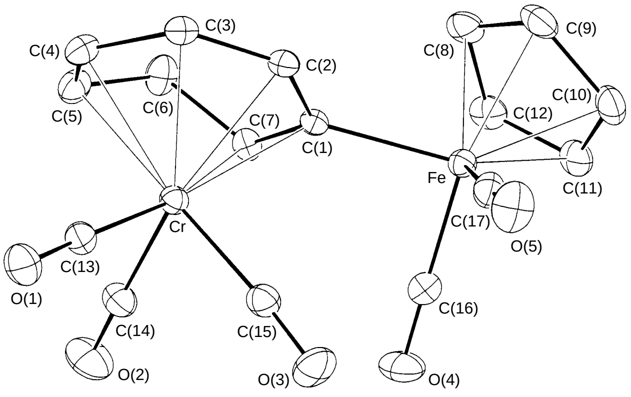


Fig. 1 ORTEP drawing of **4**. Selected bond lengths (Å) and angles (°): Fe–C(1) 2.014(4), Fe–C(8) 2.139(6), Fe–C(9) 2.110(6), Fe–C(10) 2.117(4), Fe–C(11) 2.116(4), Fe–C(12) 2.125(5), Fe–C(16) 1.767(5), Fe–C(17) 1.761(5), Fe–C(17) 1.761(5), Cr–C(1) 2.272(3), Cr–C(2) 2.233(4), Cr–C(3) 2.220(5), Cr–C(4) 2.223(5), Cr–C(5) 2.386(6), Cr–C(7) 2.317(4), Cr–C(13) 1.847(4), Cr–C(14) 1.859(5), Cr–C(15) 1.848(5), O(1)–C(13) 1.151(5), O(2)–C(14) 1.138(7), O(3)–C(15) 1.139(7), O(4)–C(16) 1.132(6), O(5)–C(17) 1.140(7), C(1)–C(2) 1.446(5), C(1)–C(7) 1.397(7), C(2)–C(3) 1.406(5), C(3)–C(4) 1.449(7), C(4)–C(5) 1.385(7), C(5)–C(6) 1.514(5), C(6)–C(7) 1.516(7), C(8)–C(9) 1.434(9), C(8)–C(12) 1.434(7), C(9)–C(10) 1.458(8), C(10)–C(11) 1.415(8), C(11)–C(12) 1.425(8); C(1)–Fe–C(16) 90.8(2), C(1)–Fe–C(17) 94.3(2), C(16)–Fe–C(17) 95.7(2), Fe–C(1)–C(2) 119.3(3), Fe–C(1)–C(7) 118.2(2), Fe–C(16)–O(4) 178.5(4), Fe–C(17)–O(5) 176.2(4), Cr–C(13)–O(1) 177.4(4), Cr–C(14)–O(2) 178.5(3), Cr–C(15)–O(3) 175.7(4).

In **4** the 7-*exo*-hydrogen atom is easily accessible for hydride abstraction, and the carbene complex [CpFe(CO)$_2$**1**]BF$_4$ **5** was formed quantitatively upon reaction with (Ph$_3$C)BF$_4$.† To the best of our knowledge, **5** represents the first heterobimetallic cycloheptatrienylidene complex. The carbene carbon resonance (δ 159.1) is observed at high field due to coordination of the Cr(CO)$_3$-unit to the μ-(η^1 : η^7-CHT) ligand. A direct relationship between the chemical shift of the cyclopentadienyl group and the degree of electron richness at the metal site has been suggested.[10] Consequently, the ^{1}H cyclopentadienyl resonance of **5** is observed at substantially higher field (δ 5.14) than that of [CpFe(CO)$_2$(η^1-CHT)]PF$_6$ (δ 5.50),[3a] thus indicating that [(η^7-CHT)Cr(CO)$_3$] **1** is a weaker π-acceptor than cycloheptatrienylidene and that the canonical form **B** contributes more strongly to the ground-state electronic structure of **5**.

Here, we have presented a new route for the preparation of isomerically pure mono- and bi-metallic cycloheptatrienyl complexes as suitable precursors for the synthesis of cycloheptatrienylidene complexes. In continuation of this program, we are currently studying the possibility to synthesize various bimetallic mono- and poly-carbene complexes by this method.

Footnotes and References

* E-mail: tammm@chemie.fu-berlin.de

† *Spectroscopic data*: **3**: IR (CH$_2$Cl$_2$): $\bar{\nu}$ 2013, 1956 cm^{-1} (CO). ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.70 (d, 1 H, 3-CH), 6.12 (dd, 1 H, 4-CH), 6.05 (dd, 1 H, 5-CH), 5.30 (td, 1 H, 6-CH), 5.14 (t, 1 H, 1-CH), 4.64 (s, 5 H, C$_5$H$_5$), 2.23 (dd, 2 H, 7-CH$_2$). ^{13}C NMR (62.9 MHz, CDCl$_3$): δ 216.3 (Fe-CO), 146.2 (C-3), 133.0 (C-2), 126.7 (C-1), 124.8 (C-5), 122.8 (C-4), 120.7 (C-6), 85.8 (C$_5$H$_5$), 32.3 (C-7).

4: IR (CH$_2$Cl$_2$): $\bar{\nu}$ 2025, 1972, 1958, 1893, 1860 cm^{-1} (CO). ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.08 (d, 1 H, 3-CH), 5.63 (dd, 1 H, 4-CH), 4.88 (s, 5 H, C$_5$H$_5$), 4.78 (dd, 1 H, 5-CH), 3.25 (dd, 1 H, 1-CH), 3.16 (m, 1 H, 6-CH), 2.90 (m, 1 H, 7-*endo*-CH), 1.46 (m, 1 H, 7-*exo*-CH). ^{13}C NMR (62.9 MHz, CD$_3$CN): δ 235.1 (CrCO), 217.5, 216.7 (FeCO), 128.4 (C-2), 115.3, 100.7, 97.1 (C$_7$ ring: CH), 87.7 (C$_5$H$_5$), 64.6, 56.1 (C$_7$ ring: CH), 26.9 (C-7).

5: IR (MeCN): $\bar{\nu}$ 2052, 2025, 1999 cm^{-1} (CO). ^{1}H NMR (250 MHz, CD$_3$CN): δ 6.69 (d, 2 H, C$_7$ ring: CH), 6.35 (m, 2 H, C$_7$ ring: CH), 6.05 (m, 2 H, C$_7$ ring: CH), 5.14 (s, 5 H, C$_5$H$_5$). ^{13}C NMR (62.9 MHz, CD$_3$CN): δ 225.2 (CrCO), 214.8 (FeCO), 159.1 (C-1), 119.0, 105.6, 104.0 (C$_7$ ring: CH), 89.0 (C$_5$H$_5$). UV–VIS (MeCN) λ/nm (log [ε/dm^3 mol^{-1} cm^{-1}]) 322 (3.74), 348 (sh), 420 (sh).

‡ *Crystal data* for C$_{17}$H$_{12}$CrFeO$_5$ **4**: M = 404.12, triclinic, space group $P\bar{1}$ (no. 2), a = 7.859(2), b = 9.320(2), c = 12.403(4) Å, α = 99.94(4), β = 102.55(4), γ = 109.13(4)°, U = 808.0(5) Å^3, Z = 2, D_c = 1.66 g cm^{-3}, Mo-Kα radiation (λ = 0.710 73 Å), μ = 16.44 cm^{-1}. 4652 unique data collected on a CAD-4 four-circle diffractometer at 20(3) °C in the range 4.8 < 2θ < 60°. Structure solution with direct methods, refined to R = 0.053, R_w = 0.066 for 3879 absorption corrected (ψ-scan) structure factors [$F_0 \geqslant 2\sigma(F_0)$] and 217 variables. CCDC 182/617.

1 For a review, see: R. P. Johnson, *Chem. Rev.*, 1989, **89**, 1111.

2 For recent reviews, see: S. Matzinger, T. Bally, E. V. Patterson and R. J. McMahon, *J. Am. Chem. Soc.*, 1996, **118**, 1535; M. W. Wong and C. Wentrup, *J. Org. Chem.*, 1996, **61**, 7022; P. R. Schreiner, W. L. Karney, P. von Ragué Schleyer, W. T. Borden, T. P. Hamilton and H. F. Schaefer III, *J. Org. Chem.*, 1996, **61**, 7030.

3 (*a*) N. T. Allison, Y. Kawada and W. M. Jones, *J. Am. Chem. Soc.*, 1978, **100**, 5224; (*b*) P. E. Riley, R. E. Davies, N. T. Allison and W. M. Jones, *J. Am. Chem. Soc.*, 1980, **102**, 2458; (*c*) F. J. Manganiello, M. D. Radcliffe and W. M. Jones, *J. Organomet. Chem.*, 1982, **228**, 273; (*d*) W. R. Winchester and W. M. Jones, *Organometallics*, 1985, **4**, 2228; (*e*) Z. Lu, W. M. Jones and W. R. Winchester, *Organometallics*, 1993, **12**, 1344; (*f*) Z. Lu, K. A. Abboud and W. M. Jones, *Organometallics*, 1993, **12**, 1471.

4 M. L. H. Green and D. K. P. Ng, *Chem. Rev.*, 1995, **95**, 439.

5 J. Klosin, X. Zheng and W. M. Jones, *Organometallics*, 1996, **15**, 3788.

6 R. W. Hoffmann, M. Lotze, M. Reiffen and K. Steinbach, *Liebigs Ann. Chem.*, 1981, 581.

7 (*a*) M. Tamm, A. Grzegorzewski and I. Brüdgam, *J. Organomet. Chem.*, 1996, **519**, 217; (*b*) M. Tamm, A. Grzegorzewski, T. Steiner, W. Werncke and T. Jentzsch, *Organometallics*, 1996, **15**, 4984; (*c*) M. Tamm, A. Grzegorzewski and T. Steiner, *Chem. Ber./Recueil*, 1997, **130**, 225; (*d*) M. Tamm, W. Werncke and T. Jentzsch, *Organometallics*, 1997, **16**, 1418.

8 Alternatively, **3** could also be isolated after Pd^0-catalyzed coupling between **2** and [CpFe(CO)$_2$I], albeit in much lower yield. For palladium-catalyzed metal–carbon bond formation, see: P. Cianfriglia, V. Narducci, C. Lo Sterzo, E. Viola, G. Bocelli and T. A. Kodenkandath, *Organometallics*, 1996, **15**, 5220 and references therein.

9 See, for example: M. J. Heeg, *Acta Crystallogr., Sect. C*, 1988, **44**, 361; R. P. Hughes, R. T. Carl, S. J. Doig, R. C. Hemond, D. E. Samkoff, W. L. Smith, L. C. Stewart, R. E. Davis, K. D. Holland, P. Dickens and R. P. Kashyap, *Organometallics*, 1990, **9**, 2732, R. D. Adams and M. Huang, *Organometallics*, 1995, **14**, 2887.

10 E. S. Bolton, G. R. Knox and C. G. Robertson, *Chem. Commun.*, 1969, 664.

Received in Cambridge, UK, 29th July 1997; 7/05502A