Bis(indenyl)chromium Is a Dimer

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*Summary: The reduction of chromium(III) chloride with sodium indenyl leads initially to chromium (II) chloride, which then gives the dimeric compounds (indenyl)$_3$Cr$_2$Cl (**1**) and (indenyl)$_4$Cr$_2$ (**2**), both of which have been shown to contain μ-η^3-indenyl groups. **2** is catalytically active for the polymerization of ethylene and the hydrogenation of styrene to ethylbenzene.*

Shortly after the discovery of chromocene,[2] (indenyl)$_2$Cr formed the subject of a short, sharp polemic concerning the bonding situation;[3] however, the compound was not actually isolated until 1976, when scientists at the Union Carbide Corp. reported its preparation by the reduction of CrCl$_3$ with 3 equiv of sodium indenyl[4] and patented its use, supported on silica, as a catalyst for the polymerization of ethylene.[5] We have had occasion to repeat the preparation and report here the true structure.

Initial experiments indicated that the reaction of Cr(THF)$_3$Cl$_3$ with 1 equiv of sodium indenyl results solely in the reduction of the chromium salt to CrCl$_2$. Further reaction with sodium indenyl occurs in a stepwise manner: initially a brown compound is formed whose spectroscopic data indicate the formation of (indenyl)$_3$Cr$_2$Cl (**1**), and this reacts further to give a red-bown species having the composition (indenyl)$_4$Cr$_2$ (**2**) (Scheme 1).

Treatment of CrCl$_2$ with 1 equiv of sodium indenyl in THF at room temperature, followed by removal of the solvent under vacuum and crystallization from hot toluene, gave (indenyl)$_3$Cr$_2$Cl (**1**) as black crystals in 30% yield; mp 136 °C. Treatment of CrCl$_2$ with 2 equiv of sodium indenyl in the same manner as described above gave (indenyl)$_4$Cr$_2$ (**2**) as brown crystals in 59% yield, which decompose at 150 °C.[6] **2** can also be obtained in 67% yield by reacting **1** with 1 equiv of sodium indenyl.

The molecular structures of both **1** and **2** have been determined by single-crystal X-ray diffraction analysis (Scheme 1)[7] and show the compounds to be dinuclear and to contain both η^5- and μ-η^3-indenyl groups; the latter bonding arrangement is apparently unique among the indenyl−metal compounds. The structure is related to that of [(η^5-indenyl)(μ-η^3-C$_3$H$_5$)Cr]$_2$ (**3**), which we have reported earlier.[8] The ^{13}C NMR spectra[9] suggest that the structures of **1** and **2** in solution and in the crystal are similar: for example, the observation of two signals for C8/C9 confirms the nonsymmetric structure of **1**, while the chemical shifts of the bridging allylic C atoms in **2** are similar to those observed for (η^3-C$_3$H$_5$)$_4$Cr$_2$ (**4**).[10]

The structure of **2** should be contrasted to that of the permethylated indenyl compound (η^5-C$_9$Me$_7$)$_2$Cr[11] and to that of the 1-cyclo-C$_6$H$_{11}$CH$_2$-substituted species (η^5-1-CyCH$_2$C$_9$H$_6$)$_2$Cr,[12] both of which have conventional metallocene structures, suggesting that steric factors play a role in the adoption of a dinuclear structure by **2**.

Mechanistically interesting is the observation that a toluene solution of (indenyl)$_4$Cr$_2$ (**2**) is an active single-component catalyst for the polymerization of ethylene into linear polyethylene with a crystallinity of 77%[13] at room temperature; in contrast, both of the related

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(6) Analytical data for **1** and **2** are as follows. Anal. Calcd for C$_{27}$H$_{21}$ClCr$_2$ (**1**): C, 66.88; H, 4.37; Cr, 21.45; Cl, 7.31. Found: C, 66.80; H, 4.31; Cr, 21.58; Cl, 7.37. Calcd. for C$_{36}$H$_{28}$Cr$_2$ (**2**): C, 76.58; H, 5.00; Cr, 18.42. Found: C, 76.46; H, 4.89; Cr, 18.56.

(7) Crystal data for **1**: C$_{27}$H$_{21}$ClCr$_2$, $M_r = 484.9$, black, crystal size $0.11 \times 0.35 \times 0.39$ mm, $a = 8.409(1)$ Å, $b = 12.985(2)$ Å, $c = 19.869(2)$ Å, $V = 2169.6$ Å^3, $T = 293$ K, $D_c = 1.48$ g cm^{-3}, $\mu = 11.13$ cm^{-1}, $F(000) = 992$, $Z = 4$, orthorhombic, P2$_1$2$_1$2$_1$ (No. 19), Enraf-Nonius CAD4 diffractometer, $\lambda = 0.710\,69$ Å, measuring method $\omega{-}2\theta$, 4481 measured reflections ($\pm h,+k,+l$), $[(\sin\theta)/\lambda]_{\max} = 0.65$ Å^{-1}, 4032 independent reflections, 3225 observed reflections ($I \geq 2\sigma(I)$) for 355 refined parameters, structure solved by heavy-atom methods, non-hydrogen atoms refined anisotropically, H atom positions were found and refined isotropically in the final refinement stages, $\sum w(F_o - F_c)$ minimized, $R = 0.036$, $R_w = 0.039$ ($w = 1/\sigma^2(F_o)$], maximum shift/error 0.46, final difference Fourier $\rho = 0.85$ e Å^{-3}. Selected bond distances (Å) and angles (deg) are as follows: Cr1−Cr2 = 2.317(1), Cr1−D1 = 1.941, Cr1−D3 = 2.148, Cr1−C1 = 2.335(1), C1−C2 = 1.424(7), C11−C12 = 1.399(8), C13−C14 = 1.351(9); Cr1−Cl−Cr2 = 59.5(1), D1−Cr1−C1 = 128.6, D3−Cr1−Cl = 101.8, C1−C2−C3 = 110.6(4), C1−C9−C7 = 130.2(5), C10−C11−C12 = 109.2(5), C12−C17−C13 = 133.3(4). Crystal data for **2**: C$_{36}$H$_{28}$Cr$_2$, $M_r = 564.6$, dark red-black, crystal size $0.25 \times 0.67 \times 0.11$ mm, $a = 21.140(4)$ Å, $b = 7.577(1)$ Å, $c = 33.603(3)$ Å, $\beta = 98.83°$, $V = 5318.9$ Å^3, $T = 293$ K, $D_c = 1.41$ g cm^{-3}, $\mu = 8.20$ cm^{-1}, $F(000) = 2336$, $Z = 8$, monoclinic, $C2/c$ (No. 15), Enraf-Nonius CAD4 diffractometer, $\lambda = 0.710\,69$ Å, measuring method $\omega{-}2\theta$, 5145 measured reflections ($\pm h,+k,+l$), $[(\sin\theta)/\lambda]_{\max} = 0.59$ Å^{-1}, 4661 independent reflections, 3120 observed reflections ($I \geq 2\sigma(I)$) for 343 refined parameters, structure solved by direct methods, non-hydrogen atoms refined anisotropically, H atom positions were calculated in the final refinement stages, $\sum w(F_o - F_c)$ minimized, $R = 0.052$, $R_w = 0.057$ ($w = 1/\sigma 2(F_o)$), max shift/error 0.02, final difference Fourier $\rho = 0.73$ e Å^{-3}. Selected bond distances (Å) and angles (deg) are as follows: Cr1−Cr2 = 2.175(1), Cr1−D1 = 1.999, Cr1−D3 = 2.127, C1−C2 = 1.411(8), C1−C9 = 1.448(7), C11−C12 = 1.388(9), C13−C14 = 1.353(9); Cr1−C2−Cr2 = 56.3(1), D1−Cr1−D3 = 118.2, D1−Cr1−D5 = 131.4, C1−C2−C3 = 110.0(4), C1−C9−C7 = 130.8(5), C10−C11−C12 = 109.1(5), C12−C17−C13 = 133.3(5).

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(9) ^{13}C NMR spectrum of **1** (THF-d_8, 240 K): δ 82.69/82.35 (C1/C3), 107.60 (C2), 126.78−120.26 (C4−C7/C23−C26), 146.36/145.18 (C8/C9), 107.60/102.35 (C20/C22), 123.40/116.69 (C27/C28), 89.14/88.48 (C21/C11). ^{13}C NMR spectrum of **2** (THF-d_8, 300 K): δ 82.29 (C1, J(C,H) = 167 Hz), 108.33 (C2, J(C,H) = 168 Hz), 126.63−120.50 (C4/C5/C23-C26/C33/C34), 146.66/145.49 (C8/C38), 107.53/102.11 (C20/C22, J(C,H) = 172/176 Hz), 87.42 (C21, J(C,H) = 173 Hz), 122.66/117.34 (C27/C28), 88.33 (C31, J(C,H) = 167 Hz).

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(13) The crystallinity was determined from the IR spectra: Hendus, H.; Schnell, G. *Kunststoffe* **1961**, *51*, 69.

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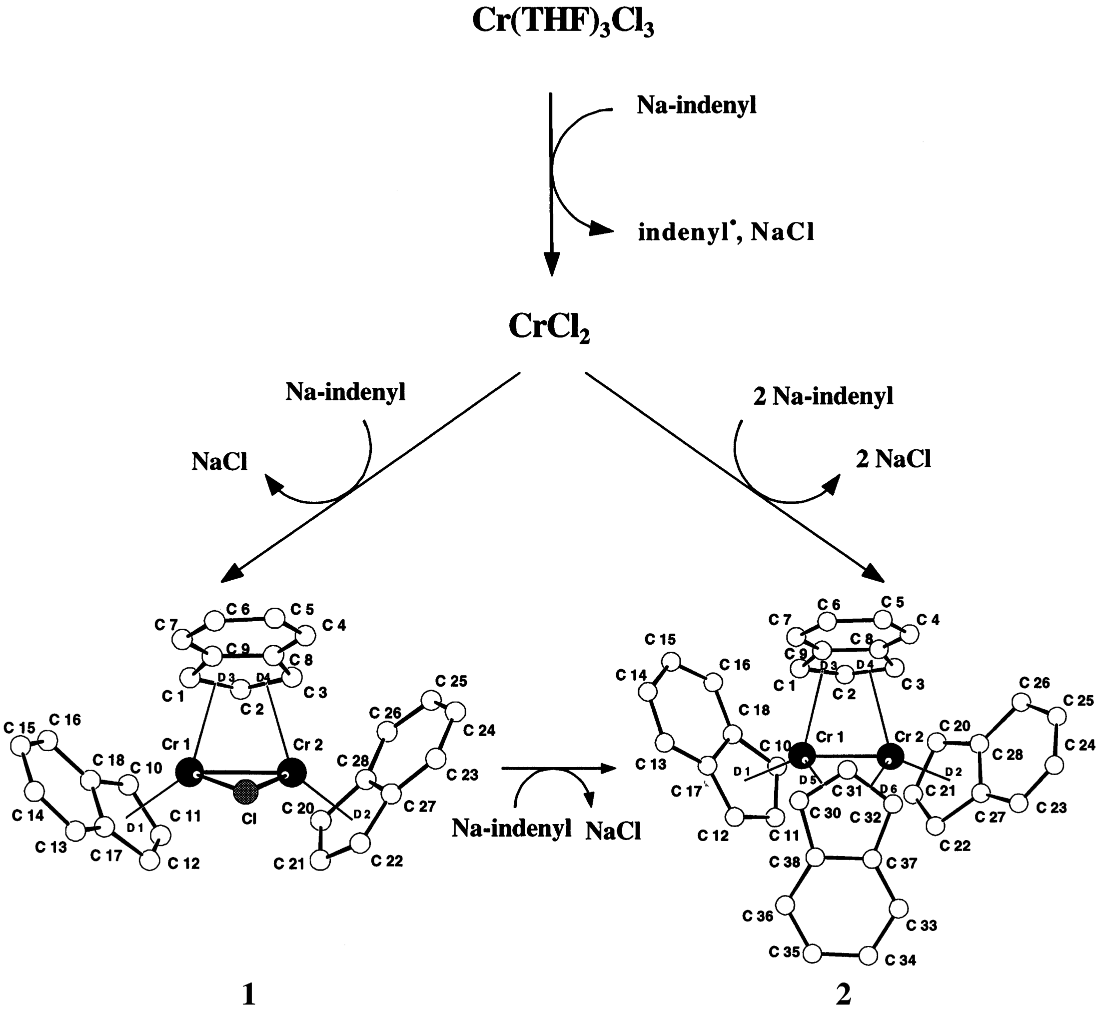
Scheme 1



species **3** and **4** are inactive.[14] Presumably, this activity results from the ready displacement of the μ-η^3-indenyl groups, whereas the μ-η^3-allyl group in **3** and **4** is more firmly bonded. Styrene can be hydrogenated into ethylbenzene at room temperature and 40 bar of hydrogen in the presence of a solution of **2** in toluene.

Supporting Information Available: Tables giving crystal data and details of the data collection, bond distances and angles, atomic coordinates, and thermal parameters for **1** and **2** (16 pages). Ordering information is given on any current masthead page.

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(14) Polymerization of ethylene with **2**: the reaction was carried out in a 200 mL steel autoclave containing a solution of 0.252 mmol of **2** in 20 mL of toluene with an initial pressure of 50 bar of ethylene at room temperature. After 3 h the polymerization was quenched with 200 mL of ethanol and the polymer was isolated by filtering, washing with ethanol, and then drying; 4.61 g polyethylene (mp 133 °C) was obtained. The IR spectra show high linearity. The average molecular weight ($M_w = 1.0 \times 10^7$) was determined by gel permeation chromatography.