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Steric Stabilization of a High-Spin Chromium(II) Indenyl Complex, [1,3-$(C_3H_7)_2C_9H_5]_2Cr$

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Summary: The monomeric bis(indenyl) complex [1,3-$(C_3H_7)_2C_9H_5)]_2Cr$ is high spin from 20 K to room temperature. The isopropyl groups block the dimerization that occurs with the unsubstituted $(C_9H_7)_2Cr$ complex but do not affect its spin state.

Among the structurally characterized bis(indenyl) complexes of the first-row transition metals, only that of chromium is a dimer.[1−5] Complete alkylation of the indenyl rings, as in $(C_9Me_7)_2Cr$,[6] blocks the dimerization and generates a low-spin ($\mu_{eff} = 2.67 \pm 0.05\ \mu_B$ (5−235 K)) monomer. Our interest in steric effects on the structural and magnetic properties of organometallic complexes[7] led us to investigate the consequences of partial substitution of the indenyl ligand with sterically demanding groups. We have found that appropriate indenyl substitution can inhibit dimerization of Ind′$_2$-Cr but still preserve a *high-spin* Cr(II) electron configuration.

Organometallic compounds of Cr(II) with π-bound ligands, including almost all cyclopentadienyl-containing complexes, are generally low-spin species.[8] Given the bonding parallels between cyclopentadienyl and indenyl complexes,[9,10] it seems reasonable that (π-indenyl)chromium species would also be low-spin. This is true for $(C_9Me_7)_2Cr$,[6] but the other indenyl complexes of chromium(II) that have been described in the literature are dimers in the solid state, including the chloride-bridged $(indenyl)_3Cr_2Cl$,[1] the mixed indenyl/allyl complex $[(\eta^5\text{-indenyl})(\mu\text{-}\eta^3\text{-}C_3H_5)Cr]_2$,[11] and bis(indenyl)chromium itself ($(indenyl)_4Cr_2$).[1] In the dimeric compounds, spin pairing can occur through Cr···Cr′ interactions, leading to diamagnetic compounds.[12] The question then arises whether the permethylation of the indenyl ligand in $(C_9Me_7)_2Cr$ serves only to inhibit dimerization or whether the greater electron donating ability of the $[C_9Me_7]^-$ ligand affects the electronic configuration of the complex; i.e., would a monomeric "$(C_9H_7)_2Cr$" complex actually be high-spin?

We investigated the influence of partial substitution on bis(indenyl)chromium with the 1,3-$(C_3H_7)_2C_9H_5$ ligand (Ind^{2i}).[13] Chromium(II) chloride reacts in a 1:2 molar ratio with K[Ind^{2i}][14] in THF to form violet (Ind^{2i})$_2$Cr in moderate yield.[15] The complex displays high solubility in hydrocarbon and ethereal solvents and is extremely air- and moisture-sensitive. In C_6D_6 at room temperature, (Ind^{2i})$_2$Cr displays a magnetic moment of 4.9 μ_B, a value appropriate for a high-spin configuration with four unpaired electrons. A similar, although slightly lower, value is observed in the solid state (4.4 ± 0.2 μ_B) from 20 to 350 K (Figure 1).[16]

To determine what structural effect the isopropyl substituents were having on the complex, (Ind^{2i})$_2$Cr was examined with single-crystal X-ray diffraction.[17] The molecules are monomeric, with a metallocene-like sand-

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(1) Heinemann, O.; Jolly, P. W.; Krüger, C.; Verhovnik, G. P. J. *Organometallics* **1996**, *15*, 5462−5463.

(2) Ind$_2$Ti has not been reported, and the structure of Ind$_2$Mn[3] is unknown; Ind$_2$V,[4] Ind$_2$Fe,[5] Ind$_2$Co,[5] and Ind$_2$Ni[5] are monomers.

(3) (a) Shapiro, H.; DeWitt, E. G.; Brown, J. E. U.S. Patent 2,839,-552, 1956. (b) Brown, J. E.; DeWitt, E. G.; Shapiro, H. U.S. Patent 2,964,548, 1957.

(4) Bocarsly, J. R.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1987**, *26*, 1871−1875.

(5) Westcott, S. A.; Kakkar, A. K.; Stringer, G.; Taylor, N. J.; Marder, T. B. *J. Organomet. Chem.* **1990**, *394*, 777−794.

(6) O'Hare, D.; Murphy, V. J.; Kaltsoyannis, N. *J. Chem. Soc., Dalton Trans.* **1993**, 383−392.

(7) Hays, M. L.; Burkey, D. J.; Overby, J. S.; Hanusa, T. P.; Yee, G. T.; Sellers, S. P.; Young, V. G., Jr. *Organometallics* **1998**, *17*, 5521−5527.

(8) Sitzmann has recently reported that solid octaisopropylchromocene displays sterically induced spin crossover from 2.83 to 4.90 μB on warming from 15 to 300 K (Sitzmann, H.; Schar, M.; Dormann, E.; Kelemen, M., *Z. Anorg. Allg. Chem.* **1997**, *623*, 1850−1852).

(9) Cauletti, C.; Green, J. C.; Kelly, M. R.; Powell, P.; Van Tilborg, J.; Robbins, J.; Smart, J. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *19*, 327−353.

(10) Evans, S.; Green, M. L. H.; Nagy, A.; Stringer, G. *J. Chem. Soc., Faraday Trans. 2* **1972**, 1847−1865.

(11) Betz, P.; Döhring, A.; Emrich, R.; Goddard, R.; Jolly, P. W.; Krüger, C.; Romão, C. C.; Schönfelder, K. U.; Tsay, Y. H. *Polyhedron* **1993**, *12*, 2651−2662.

(12) A Cr═Cr double bond in $(indenyl)_4Cr_2$ would allow the metal centers to achieve formal 18-electron counts. The existence of such a bond is consistent with the chromium−chromium separation of 2.173(1) Å.

(13) Overby, J. S.; Hanusa, T. P. *Organometallics* **1996**, *15*, 2205−2212.

(14) Prepared from the reaction of K[N(SiMe$_3$)$_2$] and HInd^{2i} in toluene (Overby, J. S.; Hanusa, T. P. Unpublished results).

(15) Chromium (II) chloride (0.22 g, 1.9 mmol) and potassium diisopropylindenide (0.90 g, 3.8 mmol) were dissolved in 25 mL of THF in a 50 mL Erlenmeyer flask containing a magnetic stirring bar. The mixture, initially green, turned deep violet after 1 h. This solution was stirred overnight, after which time it was evaporated to dryness and extracted with two 15 mL portions of hexane. Removal of precipitated KCl through a medium-porosity glass frit and evaporation of the filtrate left a dark violet-black solid. Fractional sublimation (120−150 °C, 10^{-6} Torr) of this led to the isolation of violet (Ind^{2i})$_2$Cr (0.52 g, 1.1 mmol) in 61% yield, mp 173−175 °C. Anal. Calcd for $C_{30}H_{38}Cr$: C, 79.96; H, 8.50; Cr, 11.54. Found: C, 78.98; H, 8.97; Cr, 11.52. Principal IR bands (KBr, cm^{-1}): 3062 (w), 2960 (vs), 2873 (m), 1600 (w), 1458 (m), 1376 (w), 1260 (m), 1095 (vs), 1022 (vs), 803 (s), 761 (w), 598 (w), 444 (w). Magnetic susceptibility (C_6D_6): $\mu_{cor} = 4.9\ \mu$B.

(16) Magnetic moment measurements were performed on a 5 T Quantum Design MPMS-5 SQUID magnetometer in a field of 5000 G as previously described.[7]

(17) Crystals of (Ind^{2i})$_2$Cr are orthorhombic, space group $P2_12_12_1$, with $a = 14.944(5)$ Å, $b = 15.616(1)$ Å, $c = 11.028(1)$ Å, $V = 2573.5(9)$ Å^3, $Z = 4$, and $\rho_{calcd} = 1.063$ g cm^{-3} for fw = 454.48. Refinement of 1461 reflections collected at 293 K with Cu Kα radiation and $I > 3.0\sigma(I)$ led to residuals of R1(F) = 0.046 and wR2(F) = 0.055.

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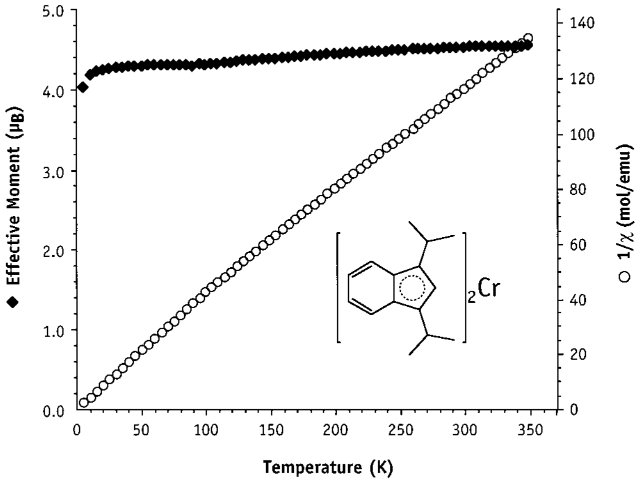

Figure 1. Magnetic susceptibility and 1/χ_M data as a function of temperature for (Ind^{2i})$_2$Cr in a field of 5000 G. The magnetic moment is essentially temperature independent to 20 K.

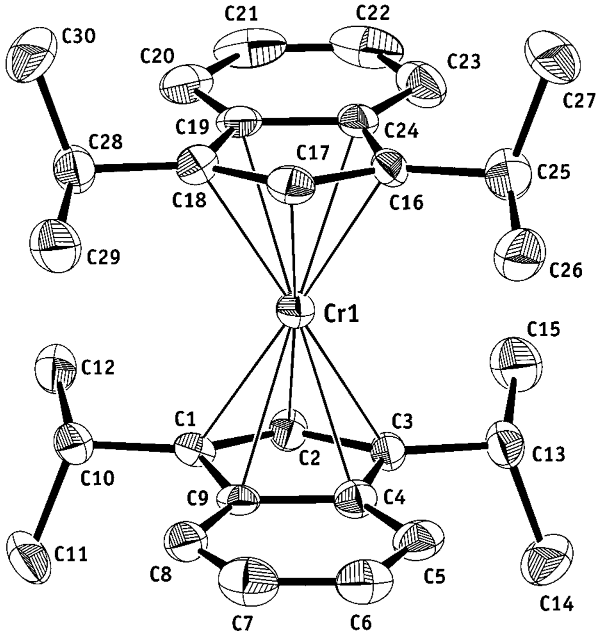

Figure 2. ORTEP plot of the non-hydrogen atoms of (Ind^{2i})$_2$Cr. Thermal ellipsoids are displayed at the 30% level.

wich geometry and an approximate C_2 rotational axis through the metal atom, although it is not crystallographically imposed. An ORTEP view of the complete molecule is provided in Figure 2. The rings are in a fully staggered orientation with respect to each other. The average chromium−carbon distance of 2.32(2) Å is substantially greater than that found in the low-spin (C$_9$Me$_7$)$_2$Cr (2.18(1) Å)[6] and in all structurally characterized chromocenes (e.g., 2.151(4) Å in (C$_5$H$_5$)$_2$Cr,[18] 2.17(1) Å in (1,2,4-C$_5$(i-Pr)$_3$H$_2$)$_2$Cr,[19] and 2.197(5) Å in (C$_5$Ph$_4$H)$_2$Cr[20]). The larger average distance in (Ind^{2i})$_2$Cr correlates well with the high-spin state; for comparison, the Mn−C bonds in high-spin manganocenes are typically 0.2−0.3 Å longer than those of low-spin manganese compounds.[21−23]

As is characteristic for indenyl complexes, there is a notable spread in the Cr−C distances in (Ind^{2i})$_2$Cr, which range from 2.226(8) to 2.420(7) Å. However, the slip parameter[5] Δ_{M-C} for the complex (0.138(10) Å) is only slightly greater than the value of 0.097(9) Å found in (C$_9$Me$_7$)$_2$Cr.[6] These Δ_{M-C} values are far below the value of ≤0.7 found for true η^3-bound ligands; consequently, the bonding arrangement in (Ind^{2i})$_2$Cr is appropriately described as "distorted η^5".[6]

In the case of recently described high-spin manganocenes containing the bulky [(C$_5$(i-Pr)$_4$H] ligand, distortions in the solid-state structure make it obvious that steric influences are responsible for the high spin state.[7] This is not the case with (Ind^{2i})$_2$Cr. The isopropyl substituents are bent out of the C$_5$ plane by an average of only 0.079 Å; for comparison, the isopropyl groups in the more highly substituted, low-spin complex (1,2,4-C$_5$(i-Pr)$_3$H$_2$)$_2$Cr show an average displacement of 0.10 Å.[19] In addition, there are no short contacts between isopropyl groups, as the closest approach is 4.16 Å, well outside the sum of the van der Waals radii of two methyl groups.[24] The closest intermolecular C···C′ contact is 3.80 Å between the isopropyl substituent (C15) and a carbon in the C$_6$ ring of the other indenyl ligand (C23′). The isopropyl groups in (Ind^{2i})$_2$Cr evidently serve only to block the dimerization that occurs with monomeric "Ind$_2$Cr," without causing the spin pairing that is found in (C$_9$Me$_7$)$_2$Cr.[6,25]

In summary, we have found that (Ind^{2i})$_2$Cr is a monomeric high-spin Cr(II) species with four unpaired electrons. The presence of the isopropyl groups prevents the dimerization that occurs with the unsubstituted indenyl ligand in Ind$_2$Cr but does not influence the spin state of the complex through steric crowding. The use of selective ligand substitution may be an attractive synthetic strategy for generating other reactive organometallic radicals without altering their magnetic properties.

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Supporting Information Available: Tables giving atomic fractional coordinates, bond distances and angles, and anisotropic thermal parameters for (Ind^{2i})$_2$Cr. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Flower, K. R.; Hitchcock, P. B. *J. Organomet. Chem.* **1996**, *507*, 275−277.

(19) Overby, J. S.; Schoell, N. J.; Hanusa, T. P. *J. Organomet. Chem.* **1998**, *560*, 15−19.

(20) Castellani, M. P.; Geib, S. J.; Rheingold, A. L.; Trogler, W. C. *Organometallics* **1987**, *6*, 1703−1712.

(21) Switzer, M. E.; Wang, R.; Rettig, M. F.; Maki, A. H. *J. Am. Chem. Soc.* **1974**, *96*, 7669−7674.

(22) Ammeter, J. H.; Bucher, R.; Oswald, N. *J. Am. Chem. Soc.* **1974**, *96*, 7833−7835.

(23) Hebendanz, N.; Köhler, F. H.; Müller, G.; Riede, J. *J. Am. Chem. Soc.* **1986**, *108*, 3281−3289.

(24) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(25) There is some computational support for this conclusion. Although the energy difference is likely overestimated, semiempirical MO calculations (PM3) place the energy of high-spin (quintet) (C$_9$H$_7$)$_2$Cr 21 kcal/mol below the energy of the low-spin (triplet) species (Hanusa, T. P. Unpublished results).