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# Steric Stabilization of Homoleptic Bis($\pi$-allyl) Complexes of Chromium(II) and Iron(II)

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Most first-row transition metal complexes containing only the sterically compact $\pi$-allyl ligand are coordinately unsaturated and highly reactive. This contributes to their usefulness as catalysts for olefin polymerization (e.g., $[(C_3H_5)_2Cr]_2$, $(C_3H_5)_3Cr$)[1] and as reagents in organic and materials chemistry (e.g., $(C_3H_5)_2Ni$),[2] but it also means that many homoleptic 3*d* $(C_3H_5)_nM$ compounds either possess low thermal stability (M = V, Co),[3] or are unknown (M = Mn, Fe).[4] Sterically demanding ligand substituents have often been used to improve the kinetic stability of unsaturated organometallic complexes,[5] but this strategy has not been generally employed with first-row allyl compounds.[6] We have now used such an approach to generate the first monomeric bis($\pi$-allyl)chromium(II) complex[7] and the first bis($\pi$-allyl)iron(II) complex;[8] both are thermally stable at room-temperature despite their low formal 12- and 14-electron counts.

The 1,3-bis(trimethylsilyl)allyl anion[9] reacts with $CrCl_2$ or $FeCl_2$ in THF at −78 °C to produce red-orange $[C_3(SiMe_3)_2H_3]_2Cr$ (**I**)[10] or orange $[C_3(SiMe_3)_2H_3]_2Fe$ (**II**)[11] in good yields. The complexes are highly soluble in ethers and both aliphatic and aromatic hydrocarbons. Although air-sensitive, **I** and **II** are neither pyrophoric nor shock-sensitive, and are indefinitely stable under a nitrogen atmosphere at room temperature. The complexes are usually isolated as oils from hydrocarbon solution, but will solidify after standing for several days at room temperature.

The thermal stability conferred on the allyl complexes by the trimethylsilyl substituents is striking. The Cr complex melts at 54 °C, is stable in boiling toluene solution, and can be sublimed without decomposition at 65 °C and $10^{-2}$ Torr; such stability is unknown in monomeric $(C_3H_5)_2Cr(PR_3)_2$ complexes, which decompose above −10 °C.[7] The Fe complex melts at 72 °C, in contrast to $(C_3H_5)_2Fe(PR_3)_2$ species, which decompose above 0 °C.[8] Sublimation of the Fe compound requires higher vacuum than does the Cr complex (80 °C, $10^{-8}$ Torr), but it also occurs without decomposition.

The solution magnetic moment of 4.5 $\mu_B$ for **I** at room temperature corresponds to the presence of four unpaired electrons on a Cr(II) center. Compound **II** has a solution magnetic moment of 2.9−3.0 $\mu_B$ through the temperature range of 210−303 K; this value is consistent with two unpaired electrons.

The solid-state structure of **I** was obtained at 173(2) K on a red-orange crystal grown from hexane solution.[12] The complex crystallizes as a monomer with the $\eta^3$-allyl ligands flanking the metal center, and has approximate $C_2$ symmetry (Figure 1). The two allyl ligands are in a staggered configuration, and the angle between the $C_3$ planes is 10.4°. The carbon atoms that constitute the C4−C6−C13−C15 plane generate a pseudosquare-planar coordination environment for the Cr; this is favored by the $S = 2$ spin state.[13] The $SiMe_3$ groups are in a *syn*, *anti* arrangement on each allyl; this is unlike the *syn*, *syn* configuration found in $[C_3(SiMe_3)_2H_3]_2Ca(thf)_2$.[14]

The allyl ligands are clearly bound in a *trihapto* manner to the metal, but the bonding is slightly asymmetric, with Cr−C distances ranging from 2.1930(6) to 2.257(1) Å ($\Delta_{Cr-C} = 0.06$ Å). The Cr−C distances are on the short end of the range observed in the dimeric tetraallyldichromium (2.19−2.31 Å),[6] although they are similar to the 2.175(3)−2.259(3) Å variation found in $(\eta^5\text{-}2,4\text{-}Me_2C_5H_5)(\eta^3\text{-}C_3H_5)CrPMe_3$,[15] despite the differences in coordination geometry.

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(1) (a) Novakov, P. P.; Kuckling, D.; Fedorova, L.; Adler, H. J. P. *Macromol. Symp.* **1998**, *128*, 195−201. (b) Bade, O. M.; Blom, R.; Ystenes, M. *Organometallics* **1998**, *17*, 2524−2533. (c) Sneeden, R. P. A.; Zeiss, H. H. *J. Organomet. Chem.* **1971**, *28*, 259−263. (d) Fedorova, L. A.; Yakimansky, A. V.; Erussalimsky, B. L. *Macromol. Rep.* **1995**, *A32*, 175−187. (e) Karol, F. J.; Johnson, R. N. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 1607−1617.

(2) (a) Chance, J. M.; Linebarrier, D. L.; Nile, T. A. *Transition Met. Chem. (London)* **1987**, 12, 276−277. (b) Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 185−206. (c) Bogdanovic, B.; Claus, K. H.; Guertzgen, S.; Spliethoff, B.; Wilczok, U. *J. Less-Common Met.* **1987**, *131*, 163−172. (d) Hierso, J.-C.; Feurer, R.; Kalck, P. *Coord. Chem. Rev.* **1998**, *178−180*, 1811−1834.

(3) The instability is observed regardless of formal electron count; e.g., $(\pi\text{-}C_3H_5)_3V$ (14 $e^-$) deflagrates > −30 °C, and $(\pi\text{-}C_3H_5)_3Co$ (18 $e^-$) decomposes > −40 °C. Even $(\pi\text{-}C_3H_5)_2Ni$ (16 $e^-$) decomposes at 20 °C (for an early review, see: Wilke, G.; Bogdanovic, B.; Hardt, P.; Heimbach, P.; Keim, W.; Kroner, M.; Oberkirch, W.; Tanaka, K.; Walter, D. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 151−164).

(4) Second- and third-row-based allyl complexes (e.g., $(C_3H_5)_2Pd$, $(C_3H_5)_3Rh$, $(C_3H_5)_3Ir$) are typically much more stable than their first-row counterparts. See, for example: John, K. D.; Salazar, K. V.; Scott, B. L.; Baker, R. T.; Sattelberger, A. P. *Organometallics* **2001**, *20*, 296−304.

(5) (a) Jimenez-Catano, R.; Niu, S.; Hall, M. B. *Organometallics* **1997**, *16*, 1962−1968. (b) Elschenbroich, C.; Salzer, A. *Organometallics: A Concise Introduction*, 2nd ed.; VCH Publishers: New York, 1992. (c) Janiak, C.; Schumann, H. *Adv. Organomet. Chem.* **1991**, *33*, 291−393.

(6) Methyl- and ethyl-substituted bis(allyl)nickel complexes are known (Batich, C. D. *J. Am. Chem. Soc.* **1976**, *98*, 7585−7590), but stability is not always improved (e.g., $(1\text{-}MeC_3H_5)_2Ni$ decomposes at room temperature (ref 3)).

(7) Bis(allyl)chromium(II) is a dimer in the solid state with a formal Cr−Cr quadruple bond (Aoki, T.; Furusaki, A.; Tomie, Y.; Ono, K.; Tanaka, K. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 545−547). Thermolabile phosphine adducts of monomeric $(C_3H_5)_2Cr$ have been described (Betz, P.; Jolly, P. W.; Krueger, C.; Zakrzewski, U. *Organometallics* **1991**, *10*, 3520−3525).

(8) The parent bis(allyl)iron(II) is unknown; various phosphine adducts have been prepared and characterized in solution (Gabor, B.; Holle, S.; Jolly, P. W.; Mynott, R. *J. Organomet. Chem.* **1994**, *466*, 201−209).

(9) Fraenkel, G.; Chow, A.; Winchester, W. R. *J. Am. Chem. Soc.* **1990**, *112*, 1382−1386.

(10) $CrCl_2$ (0.245 g, 2.00 mmol) was suspended in THF (50 mL) under nitrogen at −78 °C. A solution of $K[C_3(SiMe_3)_2H_3]$ (0.901 g, 4.00 mmol) in THF (100 mL) was added dropwise with stirring over 30 min. After the reaction mixture was warmed to room temperature, it was stripped to dryness, and the residue extracted with hexanes. The extract was filtered and evaporated to an oil, and the oil was allowed to stand at room temperature under an $N_2$ atmosphere. The crude product could be sublimed at 65 °C and $70 \times 10^{-3}$ Torr to yield $[C_3(SiMe_3)_2H_3]_2Cr$ as air-sensitive red-orange needles (0.53 g, 63%), mp 54−56 °C. Anal. Calcd for $C_{18}H_{42}CrSi_4$: C, 51.11; H, 10.03. Found: C, 50.77; H, 10.23. Principal IR bands (KBr, $cm^{-1}$): 2960 (m), 1598 (w), 1472 (w, br), 1248 (m), 1030 (w), 1015 (w), 853 (s), 550 (w, br). Magnetic susceptibility (tol-$d_8$) $\mu^{corr} = 4.5\ \mu_B$ at 296 K, $\mu^{corr} = 5.1\ \mu_B$ at 200 K.

(11) In a procedure similar to that used for **I**, $FeCl_2$ (0.254 g, 2.00 mmol) was suspended in THF (50 mL) under nitrogen at −78 °C. A solution of $K[C_3(SiMe_3)_2H_3]$ (0.900 g, 4.00 mmol) in THF (100 mL) was added dropwise with stirring over 30 min. Workup as for **I** left an oil that on standing left air-sensitive orange needles of $[C_3(SiMe_3)_2H_3]_2Fe$, (0.606 g, 71%) mp 72−75 °C. Anal. Calcd for $C_{18}H_{42}FeSi_4$: Fe, 13.1. Found (complexometric): Fe, 12.5. Principal IR bands (KBr), $cm^{-1}$, 2953 (s), 2896 (s), 2363 (w), 1600 (s), 1430 (s), 1260 (s), 1090 (s), 1020 (s), 870 (s), 800 (s), 690 (m), 480 (m). Magnetic susceptibility (tol-$d_8$) $\mu^{corr} = 2.9\ \mu_B$ at 303 K, $\mu^{corr} = 3.0\ \mu_B$ at 210 K.

(12) Crystals of $[C_3(SiMe_3)_2H_3]_2Cr$ are triclinic, space group $P\bar{1}$, with $a = 10.3040(7)$ Å, $b = 10.9844(8)$ Å, $c = 12.1807(9)$ Å, $\alpha = 90.817(1)°$, $\beta = 103.047(1)°$, $\gamma = 91.924(1)°$, $V = 3612.72(7)$ Å$^3$, $Z = 2$, and $\rho_{calc} = 1.021$ g $cm^{-3}$ for fw = 422.88. Refinement of 4039 reflections collected at the University of Minnesota at 173 ± 2 K with $I > 2.0\sigma(I)$ led to residuals of $R(F^2) = 0.0370$ and $R_w(F^2) = 0.106$.

(13) (a) Hermes, A. R.; Morris, R. J.; Girolami, G. S. *Organometallics* **1988**, *7*, 2372−2379. (b) Fryzuk, M. D.; Leznoff, D. B.; Rettig, S. J. *Organometallics* **1995**, *14*, 5193−5202.

(14) Harvey, M. J.; Hanusa, T. P.; Young, V. G., Jr. *Angew. Chem., Int. Ed.* **1999**, *38*, 217−219.

(15) Jolly, P. W.; Krueger, C.; Zakrzewski, U. *J. Organomet. Chem.* **1991**, *412*, 371−380.

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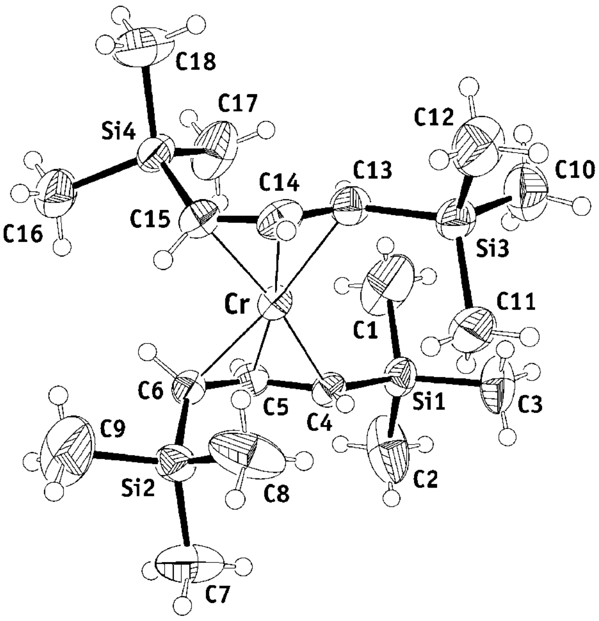

**Figure 1.** ORTEP plot of $[C_3(SiMe_3)_2H_3]_2Cr$ (**I**) with ellipsoids drawn at the 50% probability level. Selected bond distances [Å] and angles [deg]: Cr−C4, 2.257(2); Cr−C5, 2.195(2); Cr−C6, 2.212(2); Cr−C13, 2.255(2); Cr−C14, 2.193(2); Cr−C15, 2.206(2); C4−C5−C6, 125.7(2); Si1−C4−C5, 121.74(15), Si2−C6−C5, 127.99(15); C13−C14−C15, 125.9(2); Si3−C13−C14, 122.7(2); Si4−C15−C14, 130.0(2).

The solid-state structure of **II** was obtained at 173(2) K on an orange crystal grown from hexane solution.[16] Like **I**, **II** crystallizes as a monomer with $\eta^3$-allyl ligands on the metal center; it has crystallographically imposed $C_2$ symmetry (Figure 2). Unlike the chromium compound, however, the two allyl ligands in **II** are in an *eclipsed* configuration, and the angle between the $C_3$ planes is 52.7°. This represents an unprecedented arrangement for a homoleptic bis($\pi$-allyl) complex.[17] The Fe atom lies 0.21 Å out of the C4−C6−C4′−C6′ plane, and it can be envisioned to be in a distorted square pyramidal environment. The $SiMe_3$ groups are again oriented in a *syn, anti* arrangement on each allyl. The allyl ligands, although clearly bound in a *trihapto* manner to the metal, display a nearly 0.09 Å variation in the Fe−C distances, from 1.998(2) to 2.084(2) Å. These are marginally shorter than the 2.058(11) and 2.126(8) Å distances found in, for example, ($\eta^3$-$C_3H_5$)Fe(CO)$_3$Br,[18] although the different electronic environments in the complexes make strict comparisons difficult. Despite the formal electron deficiencies of both **I** and **II**, there is no clear structural evidence for α-CH agostic interactions with the metal centers.[19]

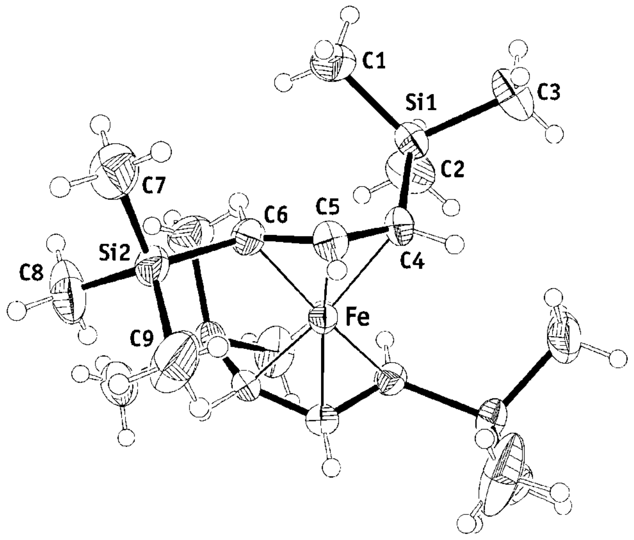

**Figure 2.** ORTEP plot of $[C_3(SiMe_3)_2H_3]_2Fe$ (**II**) with ellipsoids drawn at the 50% probability level. Selected bond distances [Å] and angles [deg]: Fe−C4, 2.079(2); Fe−C5, 1.998(2); Fe−C6, 2.084(2); C4−Si1, 1.865(3); C6−Si2, 1.857(3); C4−C5−C6, 122.3(2); Si1−C4−C5, 126.39(19), Si2−C6−C5, 122.98(19); Si1−C4−C5−C6, 49.9(3); C4−C5−C6−Si2, 174.32(19); C4−Fe−C4′, 166.8; C5−Fe−C5′, 156.4; C6−Fe−C6′, 170.3.

The *syn*, *anti* arrangement of the trimethylsilyl groups in both complexes minimizes the intramolecular impact of their steric bulk. Even so, there are substantial distortions in the placement of the silyl substituents. In **I**, Si2 and Si4 are bent out of their respective $C_3$ planes by 29.9° and 28.4°, respectively, and in **II**, Si1 is bent out of the allyl plane by 38.0°. As a consequence of these distortions, however, there are no intramolecular Me···Me′ contacts closer than the sum of their van der Waals' radii (4.0 Å).[20]

Neither **I** nor **II** reacts with $PPh_3$ or $C_2H_4$ at atmospheric pressure, yet both readily react with $PMe_3$ to give crystalline adducts ($\delta$ $^{31}$P NMR$_{(C_6D_6)}$ = −10.5 (Cr); −10.7 (Fe); cf. −60.5 for free $PMe_3$).[21] Both compounds also react with CO at room temperature (1 atm) to give mixtures of products whose exact nature is under investigation.

In summary, use of the bulky $C_3(SiMe_3)_2H_3$ ligand has allowed the synthesis, isolation, and structural authentication of the first monomeric homoleptic bis($\pi$-allyl) complexes of Cr and Fe. In contrast to other bis- and tris($\pi$-allyl) complexes of the 3*d* metals, the present compounds display remarkable thermal stability. The straightforward expedient of employing sterically demanding substituents promises to make previously unexplored areas of $\pi$-allyl transition metal chemistry synthetically and structurally accessible.

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**Supporting Information Available:** An X-ray crystallographic file in CIF format for $[C_3(SiMe_3)_2H_3]_2Cr$ and $[C_3(SiMe_3)_2H_3]_2Fe$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Crystals of $[C_3(SiMe_3)_2H_3]_2Fe$ are monoclinic, space group *C*2/*c*, with $a = 16.6387(11)$ Å, $b = 12.3896(8)$°, $c = 12.7749(8)$ Å, $\beta = 91.031(1)$°, $V = 2633.1(2)$ Å$^3$, $Z = 4$, and $\rho_{calc} = 1.076$ g cm$^{-3}$ for fw = 426.73. Refinement of 1822 reflections collected at the University of Minnesota at 173 ± 2 K with $I > 2.0\sigma(I)$ led to residuals of $R(F^2) = 0.0364$ and $R_w(F^2) = 0.0899$.

(17) DFT calculations on the staggered and eclipsed forms of the model compound $(C_3H_5)_2Fe$ were performed under $C_2$ symmetry with *Gaussian* 98W using the B3PW91 functional, the 6-31+G(d) basis set for geometry optimization and the 6-311+G(2d,2p) basis set for final energy calculations ($N_{imag} = 0$ for both conformations). There is a 4.9 kcal mol$^{-1}$ preference for the eclipsed form; thus, the ligand arrangement in **II** possibly reflects subtle electronic rather than steric effects. Similar calculations on $(C_3H_5)_2Cr$ ($C_1$ symmetry, $N_{imag} = 0$ for either conformation) indicate that the two arrangements are essentially equienergetic (0.3 kcal mol$^{-1}$ preference for the staggered form).

(18) Simon, F. E.; Lauher, J. W. *Inorg. Chem.* **1980**, *19*, 2338−2343.

(19) Hermes, A. R.; Girolami, G. S. *Organometallics* **1987**, *6*, 763−768.

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

(21) Krannich, L. K.; Watkins, C. L.; Kanjola, R. K. *Magn. Reson. Chem.* **1987**, *25*, 320−324.