

meso-Bis{ η^5 -1-[1-(dimethylamino)ethenyl]-3-(trimethylsilyl)cyclopentadienyl}iron(II) and the cobalt(II) analogue

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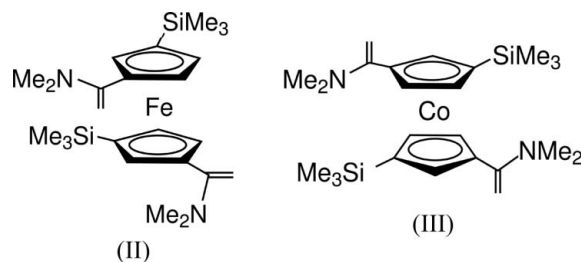
The two title crystalline compounds, *viz.* *meso*-bis{ η^5 -1-[1-(dimethylamino)ethenyl]-3-(trimethylsilyl)cyclopentadienyl}iron(II), [Fe(C₁₂H₂₀NSi)₂], (II), and *meso*-bis{ η^5 -1-[1-(dimethylamino)ethenyl]-3-(trimethylsilyl)cyclopentadienyl}cobalt(II), [Co(C₁₂H₂₀NSi)₂], (III), were obtained by the reaction of lithium 1-[1-(dimethylamino)ethenyl]-3-(trimethylsilyl)cyclopentadienide with FeCl₂ and CoCl₂, respectively. For (II), the trimethylsilyl- and dimethylaminoethenyl-substituted cyclopentadienyl (Cp) rings present a nearly eclipsed conformation, and the two pairs of trimethylsilyl and dimethylaminoethenyl substituents on the Cp rings are arranged in an interlocked fashion. In the case of (III), the same substituted Cp rings are perfectly staggered leading to a crystallographically centrosymmetric molecular structure, and the two trimethylsilyl and two dimethylaminoethenyl substituents are oriented in opposite directions, respectively, with the trimethylsilyl group of one Cp ring and the dimethylaminoethenyl group of the other Cp ring arranged more closely than in (II).

Comment

Group 4 *ansa*-metallocenes have played a significant role in organometallic chemistry and homogeneous Ziegler–Natta olefin polymerization catalysis. Over the years, Erker and co-workers have contributed to these and related aspects of metallocene chemistry (Erker, 2011; Knüppel *et al.*, 2005). The reaction of (enamino-Cp)Li reagents (Cp = cyclopentadienyl) prepared from the deprotonation of various 6-(dialkylamino)fulvenes with the group 4 metal tetrahalides MCl₄ (M = Ti, Zr or Hf) in a 2:1 stoichiometry gave first the nonbridged bis(enamino-Cp)MCl₂ complexes, which then readily underwent an intramolecular Mannich coupling reaction and thus

led to the synthesis of the corresponding C₃-bridged *ansa*-metallocenes (Tumay *et al.*, 2009; Venne-Dunker *et al.*, 2003).

Using an analogous route, Erker has also reported the preparation of several similar C₃-bridged *ansa*-ferrocenes from the reaction of FeCl₂ with (enamino-Cp)Li reagents that bear different substituents at the enamino N atom, such as dimethyl, diethyl and piperidine (Liptau *et al.*, 2001; Knüppel *et al.*, 1999). In contrast, we now report the noncoupling reaction between FeCl₂ and two molar equivalents of lithium 1-[1-(dimethylamino)ethenyl]-3-(trimethylsilyl)cyclopentadienide, which results in the formation of the title nonbridged tetrasubstituted ferrocene compound *meso*-bis{ η^5 -1-[1-(dimethylamino)ethenyl]-3-(trimethylsilyl)cyclopentadienyl}iron(II), (II). For comparison, the reaction of the same lithium cyclopentadienide with CoCl₂ was also undertaken and the similar nonbridged tetrasubstituted cobaltocene compound was isolated, the title compound, *meso*-bis{ η^5 -1-[1-(dimethylamino)ethenyl]-3-(trimethylsilyl)cyclopentadienyl}cobalt(II), (III). The noncoupling reaction between lithium [1-(dimethylamino)ethyl]cyclopentadienide and CoCl₂ has been reported by our group previously (Bai *et al.*, 2001), but to the best of our knowledge the nonbridged enamino-substituted ferrocene system prepared *via* the fulvene route has not been reported before. It is proposed that the introduction of the sterically bulky trimethylsilyl substituent into the dimethylaminoethyl-substituted Cp ring might exert an important effect on the formation of the nonbridged enamino-substituted ferrocene system.



In the molecule of the tetrasubstituted ferrocene, (II), the Fe^{II} cation is nearly symmetrically located between the two substituted Cp rings, with distances of 1.6492 (17) and 1.6517 (19) Å (*PLATON*; Spek, 2009) to the centroids of the Cp rings [Cp_{1centr} and Cp_{2centr} refer to the centroids of Cp rings C1–C5 and C13–C17, respectively]. The dihedral angle between the two planes of the Cp rings is small [3.41 (2)°] (Fig. 1*a*). As shown in Fig. 1*b*), the two Cp rings adopt an almost eclipsed conformation, with an average torsion angle of 13.7° [mean of the five torsion angles: C1–Cp_{1centr}–Cp_{2centr}–C14 = 13.29°, C2–Cp_{1centr}–Cp_{2centr}–C15 = 13.36°, C3–Cp_{1centr}–Cp_{2centr}–C16 = 13.63°, C4–Cp_{1centr}–Cp_{2centr}–C17 = 13.90° and C5–Cp_{1centr}–Cp_{2centr}–C13 = 14.19° (*Mercury*; Macrae *et al.*, 2008)], and two pairs of substituents (two trimethylsilyl and two dimethylaminoethenyl) are interlocked to reduce interannular repulsive interactions. The two pairs of substituents are held at varying C_{sub}–Cp_{1centr}–Cp_{2centr}–C_{sub} torsion angle and the smallest such angle is C1–Cp_{1centr}–Cp_{2centr}–C15 of 59.10° (Macrae *et al.*, 2008), where C_{sub} refers to the C atom of the Cp ring at which the substi-

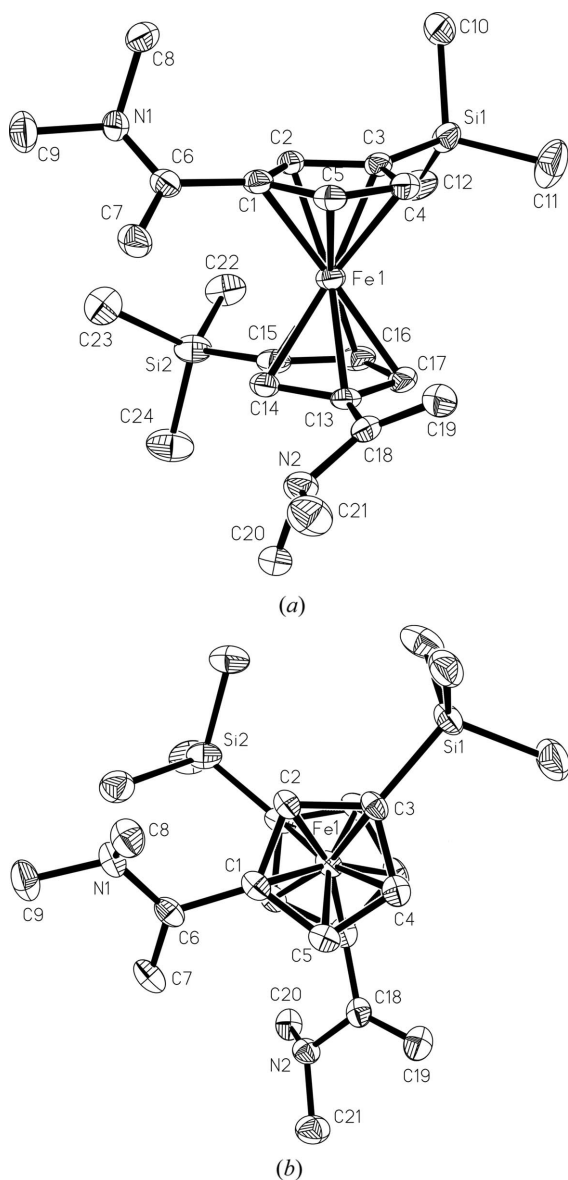


Figure 1
 (a) Side view and (b) top view of the molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

tuents are attached. The conformations of the two Cp rings and the orientations of the four substituents in (II) are similar to those of 1,1',3,3'-tetra(trimethylsilyl)ferrocene (Okuda & Herdtweck, 1989) and 1,1',3,3'-tetra-*tert*-butylferrocene (Abel *et al.*, 1991), respectively. Atoms Si1, Si2, C6 and C18 are bent away from the planes of the Cp rings to which they are directly attached, with their perpendicular distances to the ring plane being 0.150 (1), 0.155 (1), 0.061 (4) and 0.036 (4) Å, respectively (Macrae *et al.*, 2008), and away from the Fe^{II} cation. Obviously, the bulky trimethylsilyl substituents are bent out of the Cp ring planes more than the dimethylaminoethyl substituents. The Fe–C_{Cp} bond lengths of the substituted C atoms (C1, C3, C13 and C15) exceed those of the unsubstituted C atoms, and the average Fe–C bond length in (II) of 2.046 (3) Å compares well with that in ferrocene (2.052 Å for

triclinic ferrocene and 2.045 Å for orthorhombic ferrocene; Okuda & Herdtweck, 1989). Both the C7/C6/N1/C9 and C19/C18/N2/C21 frameworks lie approximately in a plane (with corresponding mean deviations of 0.0119 and 0.0134 Å) and display small angles of 32.76 (2) and 32.54 (11)°, respectively, with the Cp ring plane to which they are attached. The C6=C7 [1.327 (5) Å] and C18=C19 [1.329 (5) Å] bond lengths are typical for normal C=C double bonds in nonbridged bis(enamino-Cp)ZrCl₂ complexes (1.325–1.332 Å; Tumay *et al.*, 2009); the shorter bond lengths for C6–N1 [1.398 (5) Å] and C18–N2 [1.391 (5) Å] indicate electronic delocalization between the N atoms (N1 and N2) and the double bonds attached to them.

The molecule of the tetrasubstituted cobaltocene, (III), displays a rigorously planar sandwich geometry and the Co^{II} cation occupies a crystallographic inversion centre at (−*x* + 1, −*y*, −*z* + 2), affording a staggered conformation of the Cp ligands with the same distance of 1.7315 (4) Å from the Co^{II} cation to the centroids of the two Cp rings (C_{pcentr}), defined by C1–C5 and its symmetry-related counterpart (Fig. 2). The conformation of the Cp rings in (III) is different from those found in (II) and in 1,1',3,3'-tetra(*tert*-butyl)cobaltocene

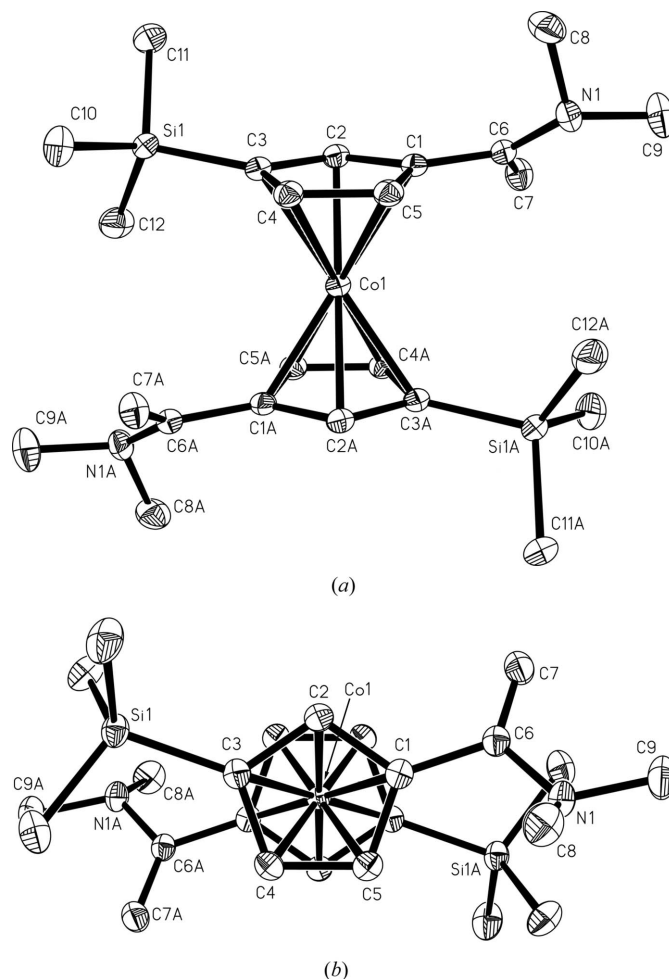


Figure 2
 (a) Side view and (b) top view of the molecular structure of (III), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (A) −*x* + 1, −*y*, −*z* + 2.]

(Schneider *et al.*, 1997) so as to meet the steric demands in (III). Just as observed in (II), the Co—C_{sub} (substituted C atoms of the Cp rings) bond lengths exceed those of the unsubstituted C atoms; the average Co—C(ring) distance of 2.112 (3) Å is comparable with the average metal–carbon distances in Cp₂Co (2.096 Å) and Cp*₂Co (2.105 Å; Cp* is pentamethylcyclopentadienyl). The slightly longer M—C(ring) bonds in (III) than in (II) are favourable to reduce the transannular steric repulsive interactions. As shown in Fig. 2(b), the two trimethylsilyl and two dimethylaminoethenyl substituents are oriented in opposite directions, respectively, and the trimethylsilyl group of one Cp ring and the dimethylaminoethenyl group of the other Cp ring are arranged more closely (torsion angle C1—Cp_{1centr}—Cp_{2centr}—C3A = 35.06°; Macrae *et al.*, 2008) than in (II). Furthermore, the trimethylsilyl and dimethylaminoethenyl substituents are bent away from the Co centre to reduce the transannular steric repulsion interactions from neighbouring substituents; the perpendicular distances from atoms Si1 and C6 to the attached Cp ring plane are 0.243 (1) and 0.077 (3) Å, respectively (Macrae *et al.*, 2008). The planar C7/C6/N/C9 skeleton (mean deviation = 0.0223 Å) forms a dihedral angle of 35.51 (2)° with the Cp ring plane to which it is attached. The bond distances and angles involving the trimethylsilyl and dimethylaminoethenyl substituents are as expected and are well within the corresponding range observed in (II).

Although previous studies of the eclipsed and staggered forms of metallocenes have already shown that the eclipsed conformation is energetically more favourable than the staggered one (Swart, 2007; Zlatar *et al.*, 2009), no systematics for the adoption of a certain conformation in multiply ring-substituted metallocenes can be deduced so far. Conformational preferences appear to be even more delicately balanced by the interannular repulsive interactions, metal–ring distances, substituents on the Cp rings *etc.* (Okuda, 1991; Phillips *et al.*, 2010).

Experimental

6-Dimethylamino-6-methyl-3-(trimethylsilyl)fulvene, (I), was prepared as a pale-yellow solid in high yield by the successive reaction of 6-dimethylamino-6-methylfulvene, which was prepared as described in the literature (Bai *et al.*, 1999; Duan *et al.*, 2007), with equal equivalents of lithium diisopropylamide (LDA) and Me₃SiCl. Crystallization from hexane yielded yellow needles of (I) (yield 78%; m.p. 369–371 K). ¹H NMR (300 MHz, CDCl₃): δ 6.73–6.33 (*m*, 3H, Cp-H), 3.27, 3.25 [*d*, 6H, N(CH₃)₂], 2.41, 2.38 (*d*, 3H, CH₃), 0.09 [*s*, 9H, Si(CH₃)₃].

LDA (0.802 g, 7.48 mmol) was added to a diethyl ether solution (30 ml) of (I) (1.552 g, 7.48 mmol) at 273 K. The reaction mixture was warmed to room temperature and stirred for 12 h to give a diethyl ether solution of lithium 1-[1-(dimethylamino)ethenyl]-3-(trimethylsilyl)cyclopentadienide, which was used *in situ* in the subsequent reactions with FeCl₂ or CoCl₂.

To a diethyl ether solution (30 ml) of lithium 1-[1-(dimethylamino)ethenyl]-3-(trimethylsilyl)cyclopentadienide (7.48 mmol), solid iron dichloride (0.475 g, 3.74 mmol) was added at 195 K. The reaction mixture was warmed to room temperature and stirred for 12 h. After

removal of the volatiles *in vacuo*, the resulting orange residue was extracted with hexane and filtered. The orange filtrate was concentrated *in vacuo* to ca 5 ml, from which orange single crystals of (II) (yield 0.656 g, 37.4%; m.p. 350–353 K) were isolated after storage at 253 K for several days. Compound (II) is a slightly air-sensitive crystalline solid. ¹H NMR (300 MHz, CDCl₃): δ 4.69, 4.17–3.81 (*m*, 10H, Cp-H and CH₂), 2.59, 2.45 [*d*, 12H, N(CH₃)₂], 0.08 [*s*, 18H, Si(CH₃)₃].

Solid CoCl₂ (0.485 g, 3.74 mmol) was added to a diethyl ether solution (30 ml) of lithium 1-[1-(dimethylamino)ethenyl]-3-(trimethylsilyl)cyclopentadienide (7.48 mmol) at 195 K. The reaction mixture was warmed to room temperature and stirred for 12 h. After remove of the volatiles *in vacuo*, the resultant brown residue was extracted into hexane. Concentration of the extract *in vacuo* and storage at 253 K for 3 d yielded brown single crystals of (III) (yield 0.624 g, 35.4%; m.p. 353–355 K). Compound (III) is paramagnetic and air sensitive.

Compound (II)

Crystal data

[Fe(C ₁₂ H ₂₀ NSi) ₂]	<i>V</i> = 2602.6 (9) Å ³
<i>M_r</i> = 468.61	<i>Z</i> = 4
Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Mo <i>K</i> α radiation
<i>a</i> = 10.186 (2) Å	<i>μ</i> = 0.68 mm ⁻¹
<i>b</i> = 11.736 (3) Å	<i>T</i> = 213 K
<i>c</i> = 22.341 (5) Å	0.30 × 0.20 × 0.20 mm
<i>β</i> = 102.978 (3)°	

Data collection

Siemens SMART CCD area-detector diffractometer	10503 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	4563 independent reflections
<i>T</i> _{min} = 0.821, <i>T</i> _{max} = 0.875	3637 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.042

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.062	272 parameters
<i>wR</i> (<i>F</i> ²) = 0.136	H-atom parameters constrained
<i>S</i> = 1.09	Δ <i>ρ</i> _{max} = 0.44 e Å ⁻³
4563 reflections	Δ <i>ρ</i> _{min} = -0.25 e Å ⁻³

Compound (III)

Crystal data

[Co(C ₁₂ H ₂₀ NSi) ₂]	<i>γ</i> = 102.658 (3)°
<i>M_r</i> = 471.69	<i>V</i> = 649.2 (3) Å ³
Triclinic, <i>P</i> $\bar{1}$	<i>Z</i> = 1
<i>a</i> = 7.891 (2) Å	Mo <i>K</i> α radiation
<i>b</i> = 9.363 (3) Å	<i>μ</i> = 0.77 mm ⁻¹
<i>c</i> = 10.440 (3) Å	<i>T</i> = 213 K
<i>α</i> = 105.531 (3)°	0.30 × 0.20 × 0.20 mm
<i>β</i> = 111.101 (3)°	

Data collection

Siemens SMART CCD area-detector diffractometer	3180 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	2240 independent reflections
<i>T</i> _{min} = 0.803, <i>T</i> _{max} = 0.862	2076 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.017

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.037	138 parameters
<i>wR</i> (<i>F</i> ²) = 0.093	H-atom parameters constrained
<i>S</i> = 1.08	Δ <i>ρ</i> _{max} = 0.24 e Å ⁻³
2240 reflections	Δ <i>ρ</i> _{min} = -0.38 e Å ⁻³

All H atoms were placed in calculated positions, with C–H = 0.94 [aromatic in (III) and vinyl in both structures], 0.97 (methyl) and 0.99 Å [aromatic in (II)], and allowed to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for the methyl groups and $1.2U_{\text{eq}}(\text{C})$ otherwise.

For both compounds, data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3173). Services for accessing these data are described at the back of the journal.

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