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Tetra- and Pentacyclopropylcyclopentadiene—Two New Donor-Substituted Ligands for Metal Complexes**

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Jörg Magull, and Armin de Meijere*

*Dedicated to Professor Oskar Glemser
on the occasion of his 90th birthday*

Ligand tuning undoubtedly is one of the most important tools to modify the properties of metal complexes, for example to enhance the catalytic activity and stereoselectivity in metal-catalyzed reactions. Both the electronic and steric factors play an important role in this context. Among the most frequently used ligands are cyclopentadiene and its substituted analogues.[1] Although a great variety of substituted cyclopentadienes have been prepared, very little is known about cyclopropyl-substituted derivatives. Yet the cyclopropyl group has unique electronic properties[2, 3] in that it is a particularly good donor for electron-deficient centers, and sterically it is closer to an ethyl than to an isopropyl group.[4] We here report on the first synthesis of tetra- and pentacyclopropylcyclopentadiene[5] and some of their metal complexes.

Applying the protocol of Sato et al. for the hydromagnesation of alkynes,[6] the easily accessible dicyclopropylacetylene (**1**),[7] by treatment with isobutylmagnesium bromide in the presence of titanocene dichloride (1 mol%) in diethyl ether, was transformed to 1,2-dicyclopropylethenylmagnesium bromide (**2**) which, when added to a solution of *n*-butyl formate in tetrahydrofuran, gave 1,2,4,5-tetracyclopropylcyclopentadiene (**3**) right away in 56% yield (Scheme 1). The expected 1,2,4,5-tetracyclopropylpenta-1,4-dien-3-ol (**10**, R = H) was isolated in poor yield along with an isomer and a lot of polymeric material only when the *n*-butyl formate was added to the solution of the Grignard reagent **2**. In fact, the dienol **10** could not be converted to the cyclopentadiene **3** under the conditions that have been established for the conversion of

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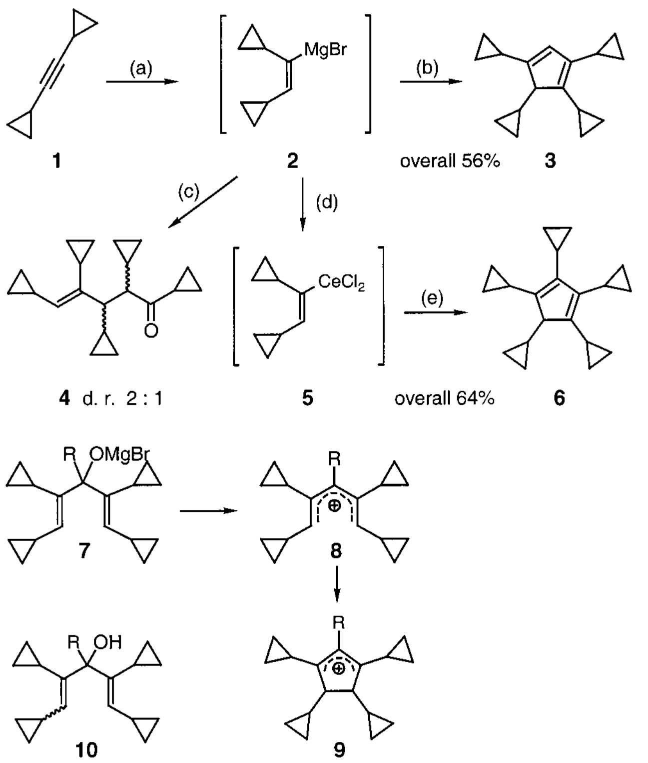
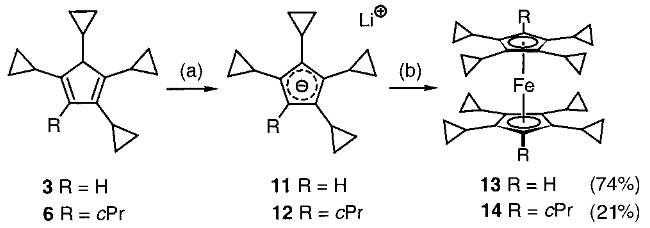


Scheme 1. a) *i*BuMgBr (1 equiv), [Cp_2TiCl_2] (1–2 mol%), Et_2O, 20°C, 30 min. b) Add inversely to HCO_2nBu (0.9 equiv) in THF, 20°C, 1 h. c) Add inversely to $cPrCO_2Me$ in THF, 20°C, 1 h. d) Add inversely to a suspension of $CeCl_3$ (1.5 equiv) in THF, 20°C, 1 h. e) 1) Add $cPrCO_2Me$ (0.48 equiv) in THF, 20°C, 1 h; 2) H_2O/HOAc (6:1).

the corresponding tetramethyl-substituted pentadienol to tetramethylcyclopentadiene.[8] Thus, **3** must have been formed from the magnesium alkoxide **7** (R = H) prior to hydrolysis. Owing to its drastically enhanced stability (by way of the four cyclopropyl substituents) the pentadienyl cation **8** (R = H) is probably formed from **7** (R = H) under the action of the Lewis acidic magnesium halide in the solution, and **8** then undergoes the well-known conrotatory 4π-electrocyclization.[9] Subsequent deprotonation of the resulting cyclopentenyl cation **9** (R = H), which also enjoys enhanced stability due to its cyclopropyl substituents, leads to the cyclopentadiene **3**.

To access 1,2,3,4,5-pentacyclopropylcyclopentadiene (**6**), the obvious next experiment was to add the Grignard reagent **2** to methyl cyclopropanecarboxylate (Scheme 1). However, the only isolated product was the pentacyclopropylpentenone **4** (58% yield), which apparently was formed by 1,4-addition of the second molecule of **2** onto the first formed enone intermediate from cyclopropanecarboxylate and **2**. To prevent this reaction mode, the solution of **2** in diethyl ether was first combined with a slurry of cerium(III) chloride in tetrahydrofuran,[10] then methyl cyclopropanecarboxylate was added at ambient temperature. After optimization of all parameters, work-up of this reaction mixture with aqueous acetic acid (6:1) gave the cyclopentadiene **6** in 64% yield.[11] Thus, the pentacyclopropylpentadienyl cation **8** (R = *c*Pr) also must be formed easily and undergo cyclization to **9** (R = *c*Pr) readily.

Upon treatment with an ethereal solution of methyllithium, both cyclopropyl-substituted cyclopentadienes **3** and **6** in tetrahydrofuran were quantitatively deprotonated to the corresponding cyclopentadienides **11** and **12**, respectively (Scheme 2), which were characterized by their ^1H and ^{13}C NMR spectra (Table 1). Treatment of the solutions of **11** and **12** with solutions of iron(II) chloride in tetrahydrofuran yielded the 1,1′,2,2′,3,3′,4,4′-octacyclopropyl- (**13**) (74%) and the decacyclopropylferrocene (**14**) (21%). After crystallization of **13** (from hexane) and **14** (from pentane/dichloromethane), the structures of both ferrocenes were established by X-ray crystal structure analysis (Figure 1).[12]



Scheme 2. a) MeLi (1 equiv) in Et_2O, THF, −78→20°C, 45 min. b) Add to $FeCl_2 \cdot 2THF$ in THF, 0→20°C, reflux, 5 h.

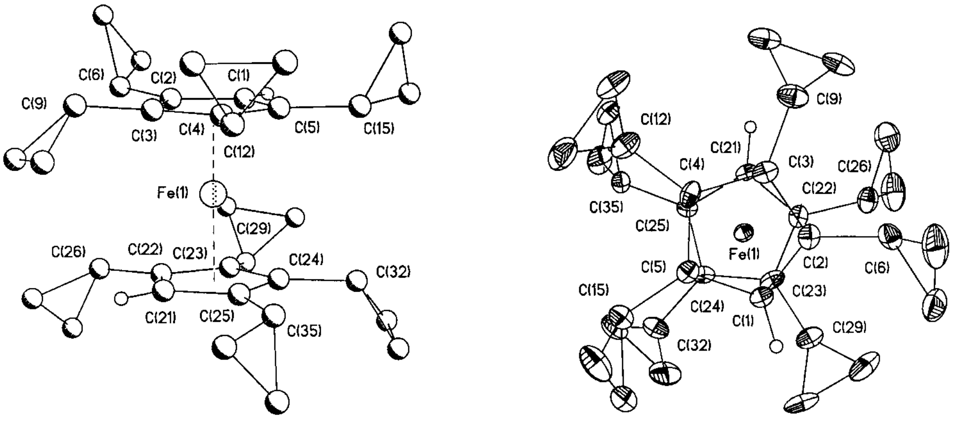
Table 1. ^{13}C NMR spectroscopic data (δ_{TMS}) of various cyclopentadienyl anions and ferrocenes as well as oxidation potentials ($E_{1/2}$ versus SCE) of ferrocenes (see Scheme 2).

Entry	Compound	$\delta(^{13}C)$[a] (Solvent)	$E_{1/2}$ [V][b]	Ref.
1	C_5H_5Li	103.2 ([D_8]THF)	–	[13]
2	C_5Me_5Na	105.1 ([D_8]THF)	–	[14]
3	$C_5(iPr)_4HNa$	120.2 ([D_8]THF)	–	[15]
4	$C_5(iPr)_5Na$	112.4 ([D_8]THF)	–	[16]
5	$C_5(cPr)_4HLi$ **11**	117.4, 116.2, 92.8 ([D_8]THF)	–	this work
6	$C_5(cPr)_5Li$ **12**	116.5 ([D_8]THF)	–	this work
7	$(C_5H_5)_2Fe$	68.2 (C_6D_6)	+0.48	[17]
8	$(C_5Me_5)_2Fe$	78.4 (C_6D_6)	−0.07	[14]
9	$[C_5(iPr)_4H]_2Fe$[c]	92.3, 89.7, 59.4 (C_6D_6)	[d]	[15]
10	$[C_5(cPr)_4H]_2Fe$ **13**	87.3, 87.0, 62.9 (C_6D_6)	−0.01	this work
11	$[C_5(cPr)_5]_2Fe$ **14**	85.1 (C_6D_6)	−0.13	this work

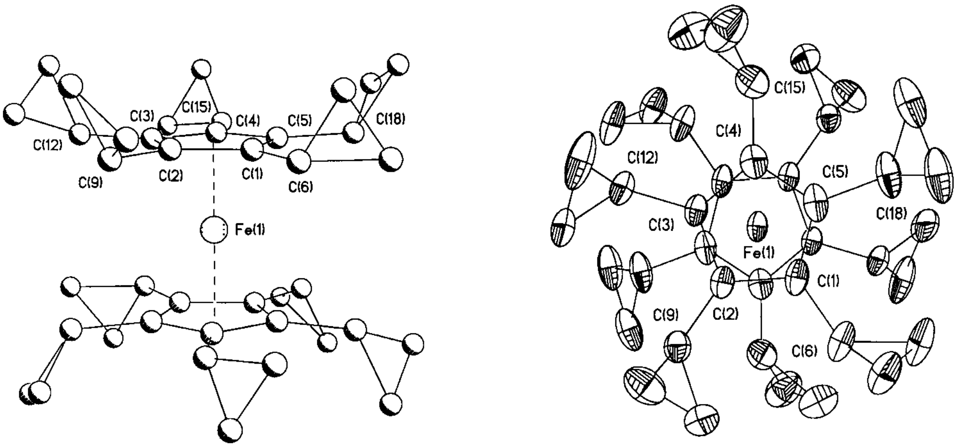
[a] Only for the central five-membered ring. [b] Scan rate: 0.1 $V s^{-1}$; 0.1 M nBu_4NPF_6 in CH_2Cl_2; versus SCE; $E^0 \sim E_{1/2} = (E_{PA} + E_{PC})/2$. [c] Decaisopropylferrocene could not be prepared, as sodium pentaisopropylcyclopentadienide was oxidized to the persistent pentaisopropylcyclopentadienyl radical upon treatment with $FeCl_2$.[18] [d] Not reported.

Interestingly, none of the cyclopropyl substituents on the two parallel orientated cyclopentadienyl rings in **13** and **14** are in the proper bisected orientation in which they would donate electron density[2, 3] to the central cyclopentadienide fragments. The dihedral angles, for example, in **14** alternate from closer to bisected to closer to perpendicular (39.8, 70.7, 20.1, 63.4, 61.1°), all cyclopropyl groups pointing away from the metal center. Of course, crystal packing effects may play an important role, and in solution the average orientation of all cyclopropyl groups may well be closer to the bisected conformation. The average distance between the iron and the cyclopentadienyl carbon atoms in **14** is slightly longer (206.8(5) pm) than that in the parent ferrocene (204(2) pm),[19] and so is the average C–C bond length in the ring (144.2(8) versus 140(2) pm).

To probe for the electronic properties of the new cyclopropyl-substituted ligands, the oxidation potentials of ferro-



13



14

Figure 1. Structures of **13** and **14** in the crystal.[12]

cenes **13** and **14** were determined by cyclic voltammetry. While this value for **13** of $E_{1/2} = -0.01$ V is slightly higher than that for decamethylferrocene ($E_{1/2} = -0.07$ V), the oxidation of **14** occurs at a slightly lower potential ($E_{1/2} = -0.13$ V). Both oxidations are fully reversible which indicates that the cyclopropyl groups in the ferrocenium ions stay intact.

In view of their easy accessibilities (one step each from dicyclopropylacetylene,[7] three steps from commercially available starting materials),[20] it is well conceivable that cyclopentadienes **3** and **6** with their fine-tuned steric demand and electronic features will establish themselves as new ligands in organometallic chemistry.

Experimental Section

6: Cerium(III) chloride heptahydrate (6.71 g, 18.0 mmol) was dried for 5 h at 180 °C (0.05 mbar). After cooling down to room temperature the anhydrous $CeCl_3$ was suspended in THF (150 mL) by stirring for 1 h. Meanwhile a solution of dicyclopropylethyne (**1**) (2.68 g, 25.2 mmol) and *i*BuMgBr in Et_2O (35.8 mL, 24.0 mmol, 0.67 M) was treated with $[Cp_2TiCl_2]$ (74.7 mg, 300 μmol, 1.25 mol%), stirred for 30 min at room temperature and was added to the $CeCl_3$ suspension. After 1 h at room temperature, the reaction mixture was treated with *c*$PrCO_2Me$ (1.22 g, 12.0 mmol) and was stirred for an additional 1 h at 20 °C, then aqueous acetic acid (6:1, 70 mL) was added. The phases were separated after 30 min, the organic layer was washed with water (2 × 50 mL) and 1 M $NaHCO_3$ (2 × 50 mL), and the combined aqueous layers were extracted with pentane (2 × 50 mL), dried over $MgSO_4$, and the solvents were removed in vacuo. Chromatography on silica gel (elution with pentane) yielded **6** (2.14 g; 64%, based on **1**; $R_f = 0.5$ in pentane) as a colorless oil. IR (film): $\tilde{\nu} = 3079$ (C-H), 3003 (C-H), 2869 (C-H), 1636 (C=C), 1457, 1427, 1264, 1021, 943, 889, 819 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.20-0.85$ (m, 21 H; *c*Pr-H), 1.42 (m_c, 2 H; *c*Pr-H), 1.55 (m_c, 2 H; *c*Pr-H), 1.84 (d, $^3J = 9.55$ Hz, 1 H; 5-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = 4.1$ (−, 2 C; *c*Pr-C), 6.1 (−, 2 C; *c*Pr-C), 6.2 (−, 2 C; *c*Pr-C), 6.5 (−, 2 C; *c*Pr-C), 7.8 (−, 2 C; *c*Pr-C), 8.8 (+, 2 C; *c*Pr-C), 9.8 (+, 2 C; *c*Pr-C), 12.5 (+, 1 C; *c*Pr-C), 58.5 (+; C-5), 142.2, 143.9 (C_{quat}, C-1(4), C-2(3)); MS (70 eV): *m/z* (%): 266 (100) [M^+], 237 (90) [$M^+ - C_2H_5$], 225 (75) [$M^+ - C_3H_5$], 209 (61), 195 (42), 181 (60), 167 (66), 155 (44), 141 (39), 128 (24), 115 (29), 91 (26), 41 (18) [$C_3H_5^+$]; elemental analysis (%) calcd for $C_{20}H_{26}$ (266.4): C 90.16, H 9.84; found: C 90.09, H 9.71.

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[11] In this case, the cyclopentadiene **6** could not be detected in the crude reaction mixture before H_2O/HOAc (6:1) had been added. Addition of aqueous hydrochloric acid gave **6** in much lower yield (22%), addition of pure water gave no **6** at all.

[12] Crystal structure analyses: **13** ($C_{34}H_{42}Fe$): $Z = 4$, $M_r = 506.56$, crystal dimensions: $0.50 \times 0.40 \times 0.40$ mm, monoclinic, space group $P2_1$, $a = 876.8(2)$, $b = 3494.8(7)$, $c = 897.2(2)$ pm, $\beta = 102.34(3)°$, $V = 2.6859(9)$ nm^3, $\rho_{\mathrm{calcd}} = 1.253$ Mg m^{-3}, $F(000) = 1088$, $\lambda = 71.073$ pm, $T = 133(2)$ K, $\mu(\mathrm{Mo_{K\alpha}}) = 0.582$ mm^{-1}. $2.32° \leq 2\theta \leq 25.02°$; out of 33365 collected reflections, 9498 are independent and were used for structure refinement of 632 parameters. The R values are $R_1 = 0.0370$ ($I > 2\sigma(I)$) and $wR_2 = 0.0716$ (all data); min./max. residual electron density: $-345/189$ e nm^{-3}. **14** ($C_{40}H_{50}Fe$): $Z = 1$, $M_r = 586.65$, crystal dimensions: $0.60 \times 0.40 \times 0.50$ mm, triclinic, space group $P\bar{1}$, $a = 911.2(2)$, $b = 982.6(2)$, $c = 1043.6(2)$ pm, $\alpha = 117.56(1)°$, $\beta = 107.35(1)$, $\gamma = 90.38(1)°$, $V = 0.7790(2)$ nm^3, $\rho_{\mathrm{calcd}} = 1.251$ Mg m^{-3}, $F(000) = 316$, $\lambda = 71.073$ pm, $T = 133(2)$ K, $\mu(\mathrm{Mo_{K\alpha}}) = 0.511$ mm^{-1}. $2.38° \leq 2\theta \leq 24.74°$; out of 6373 collected reflections, 2606 are independent and were used for structure refinement of 175 parameters. The R values are $R_1 = 0.0666$ ($I > 2\sigma(I)$) and $wR_2 = 0.1926$ (all data); min./max. residual electron density: $-581/1142$ e nm^{-3}. CCDC-172568 (**13**) and CCDC-172569 (**14**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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Spinel Sialons**

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In the system Si–Al–O–N and related multinary systems a large variety of crystalline and vitreous phases is known. These so called sialons are of technological importance, especially for applications as structural ceramics.[1] The term "classical sialons" refers to the solid solutions of Al_2O_3, (AlN), and Si_3N_4, known as β-sialons because of their close structural relationship to β-Si_3N_4.[2] By analogy, α-sialons can be derived from α-Si_3N_4, but they also incorporate metal ions such as Li, Ca, and Y and most rare earth metals.[1, 2] These Si–Al–O–N systems have been extensively studied. Haviar et al. reported their behavior at high temperature (up to 1800 °C) and high pressure (up to 6 GPa).[3]

Here we report the synthesis and structure determination of a high-pressure sialon phase with spinel structure (space group *Fd3m*) by conversion of β-Si_2AlON_3 at 13 GPa/1800 °C. Its hardness of 27.5 GPa significantly exceeds those of β- and α-sialons.

This work extends the recent discovery of binary spinel nitrides γ-E_3N_4 (E = Si, Ge, Sn),[4] in which both octahedral and tetrahedral lattice sites are occupied by cations with a

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