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An Efficient Access to Organocerium(IV) Complexes: Synthesis and Structure of Bis[1,3,6-tris(trimethylsilyl)cyclo-octatetraene]cerium(IV)**

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Dedicated to Professor Wolfgang Lüttke on the occasion of his 75th birthday

The synthesis of stable organometallic compounds containing tetravalent cerium is one of the challenges in the field of preparative organo-f-element chemistry.^[1] The main reason why numerous attempts at the synthesis of organocerium(IV) complexes have failed is the strong oxidizing effect of the cerium(IV) ion (E^0 for Ce^{3+}/Ce^{4+} in HCl: +1.28 V; in 8 M HClO₄: +1.87 V^[2]). Thus, in reactions with organometallic reagents such as NaC₅H₅, the cerium(IV) reagents (NH₄)₂[Ce(NO₃)₆] or [pyH]₂[CeCl₆] (pyH = pyridinium cation) are reduced without exception to cerium(III) products. A series of complexes of the type [(C₅H₅)₃CeX] and [(C₆H₇)₂CeX₂] (X = H, BH₄, Cl, N₃, CN, NCO, NO₂, NO₃, OR, O₂CR, SR, NH₂, alkyl, aryl) described in the 1970s^[3–6] were all found to have been wrongly characterized.^[1] Also, for “[C₅H₅)₄Ce]”^[3] it was demonstrated that this compound was in fact [(C₅H₅)₃Ce(thf)].^[7] Bis(cyclo-octatetraene)cerium(IV) (**1**), also known as bis([8]annulene)-

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cerium(IV) or “cerocene”, which is of considerable theoretical interest,^[8, 9] and its 1,1'-dimethyl derivative [Ce(C₈H₇Me)₂]^[10] are among the few fully characterized organocerium(IV) complexes. Complex **1** was discovered in 1976 by Cesca et al.;^[11] however, because of its pyrophoric nature and its poor solubility in organic solvents, unsubstituted **1** is not very attractive for reactivity studies. We describe here an efficient entry to soluble bis(cyclooctatetraene)cerium(IV) complexes, which for the first time allows an extensive study of this interesting class of compounds.

For the reasons mentioned above the controlled oxidation of cerium(III) precursors appeared to be a more suitable route for the synthesis of new cerium(IV) complexes than starting from (NH₄)₂[Ce(NO₃)₆] or [pyH]₂[CeCl₆]. In our synthesis concept substituted cyclooctatetraene ligands should sterically shield the cerium atom and thus protect it from decomposition reactions. As in many cyclopentadienyl complexes, for example those with 1,3-bis(trimethylsilyl)cyclopentadienyl ligands,^[12, 13] bulky trimethylsilyl substituents should be particularly suitable for this purpose.

Following a suggestion by Cloke et al.,^[14] initially the dianion of 1,4-bis(trimethylsilyl)cyclooctatetraene was prepared. Its lithium salt **3** is readily accessible by metalation of 1,4-bis(trimethylsilyl)cyclooctatriene (**2**) with *n*-butyllithium.^[13] The starting material **2** can be obtained in a one-pot reaction from 1,5-cyclooctadiene.^[15] The reaction of **3** with anhydrous cerium trichloride in a molar ratio of 2:1 leads to the bright green anionic sandwich complex **4**, which because of its extreme sensitivity to oxidation was not isolated but immediately converted to the neutral cerium(IV) derivative. The desired oxidation to yield **5** occurs smoothly and under mild conditions with

an excess of silver iodide as oxidizing agent. Bis[1,4-bis(trimethylsilyl)cyclooctatetraene]cerium(IV) (**5**) is the first readily accessible derivative of **1**, which is sufficiently soluble to allow reactivity studies. Spectroscopically pure, diamagnetic **5** is obtained as a deep purple oil, which thermally decomposes only above 226 °C. In contrast to the pyrophoric parent compound **1**,^[11] compound **5** can be handled in air for short periods of time. In the EI mass spectrum the molecular ion appears as the highest mass peak with 6% relative intensity.

The synthesis of a crystalline derivative of **1** was achieved by using the new sterically demanding ligand 1,3,6-(Me₃Si)₃C₈H₅²⁻. Compound **3** prepared in situ reacted with two

equivalents of chlorotrimethylsilane in Et₂O/THF selectively to give 1,3,6,6-tetrakis(trimethylsilyl)cyclooctatriene (**6**),^[15] which can be isolated as colorless, sublimable needles in 52% yield. The substitution pattern of **6** is confirmed unequivocally by the NMR data. The presence of two trimethylsilyl groups on one carbon atom of the cycle initially made the desired derivatization to give the substituted cyclooctatetraene dianion appear impossible (1,2,4-tetrakis(trimethylsilyl)cyclopentadiene cannot be metalated at the cyclopentadiene ring^[16]).

Indeed, **6** proved to be completely inert towards *n*-butyllithium. Surprisingly, the metalation was achieved with potassium hydride; however, a notable reaction was only observed in boiling THF. In addition to the expected deprotonation, a trimethylsilyl group is eliminated in the form of trimethylsilane. This leads to the dipotassium salt of the 1,3,6-tris(trimethylsilyl)cyclooctatetraene dianion **7** (37%). The latter is isolated as a colorless, microcrystalline powder of the composition $[\text{K}_2(\text{thf})_3][\text{C}_8\text{H}_5(\text{SiMe}_3)_3]$ and spectroscopically characterized. Subsequent reaction with cerium triflate (molar ratio 2:1) led to the extremely air-sensitive dark green anionic complex **8**, which was oxidized *in situ* with silver iodide to give bis[1,3,6-tris(trimethylsilyl)cyclooctatetraene]cerium(IV) (**9**). This forms permanganate-colored crystals with a low melting point (m.p. = 38 °C), which are stable in air for a short period of time and very soluble in nonpolar solvents such as pentane, hexane, or toluene. Complex **9** can be vaporized without decomposition; in the EI mass spectrum it exhibits the molecular peak with 14% relative intensity.

Deep purple single crystals of **9** were obtained from acetonitrile. The single-crystal X-ray structure analysis^[17] confirms the presence of a neutral cerium(IV) complex (Fig. 1). The two annulene rings are η^8 -coordinated to the cerium atom. The Ce–C distances range from 267.0 to 275.1 pm and are comparable with those of related complexes.^[10] The two C₈ rings in **9** are not coplanar. The ring centroid–Ce–ring centroid angle is

Fig. 1. Side view (left) and top view (right) of **9**; mean bond lengths [pm] and bond angles [°]: Ce1–C (mean) 270.4(7) (267.0(6)–275.1(7)), Ce1–ring centroid 197.6(6) and 197.7(6); ring centroid–Ce–ring centroid 176.1(3).

176.1° and is thus almost identical with the corresponding value in the anionic Yb^{II} derivative $[\text{Yb}(\text{C}_8\text{H}_8)_2]^{2-}$ (177°).^[18] The nonlinear coordination of the metal atom in **9** is probably due to steric reasons. The more open side of **9** is the one at which the Me₃Si groups of Si1 and Si3 (Fig. 1 right) are closest to each other (521.4 pm). In comparison, for example, the Si2⋯Si4 distance on the closed side is 30 pm longer. All other Si⋯Si distances range from 570 to 590 pm.

The high solubility of **9** can be attributed to the Me₃Si groups, which interlock like a set of cog wheels (Fig. 2) and surround the metal atom with an organic shell.

Fig. 2. Space-filling model of **9**.

In order to determine the rotation barrier in sandwich complexes with the 1,3,6-(Me₃Si)₃C₈H₅²⁻ ligand, the uranium complex **10**, analogous to **9**, was synthesized and its variable-temperature ¹H NMR spectra were analyzed. Dark green **10** is readily obtained from the reaction of anhydrous uranium tetrachloride with two equivalents of **7**. This complex is also stable in air for a short period of time, whereas the unsubstituted parent compound $[\text{U}(\text{C}_8\text{H}_8)_2]$ is highly pyrophoric.^[19] In the EI mass spectrum of **10** the molecular peak appears with 100% relative intensity. The energy barrier for the rotation of the two sub-

stituted cyclooctatetraene rings can be determined ($\Delta G^\ddagger = 18 \text{ kJ mol}^{-1}$) from the coalescence of the SiMe_3 signals in the temperature-dependent ^1H NMR spectrum of **10**.

This value seems surprisingly low when compared with the rotation barrier of 34.7 kJ mol^{-1} , which was determined by Streit-

wieser et al. for bis[1,4-bis(*tert*-butyl)cyclooctatetraene]-uranium.^[20] Our explanation for this difference is that the substituted cyclooctatetraene ligands in **10** do not undergo a complete rotation but only oscillate. The same phenomenon was already detected by NMR spectroscopy by Okuda for 1,1',2,2',4,4'-hexakis(trimethylsilyl)ferrocene.^[21,22] The rotation barrier here is as high as that for 1,1',3,3'-tetrakis(trimethylsilyl)ferrocene (11.0 kJ mol^{-1}), which contains only four silyl groups.

The ready availability of soluble cerium(IV) complexes opens up very promising perspectives for novel electron transfer reactions. The redox reaction of **5** with cobaltocene serves as a first example. This reduction leads to the saltlike Ce^{III} compound **11**, in which both the cation and the anion are sandwich complexes. The green cobaltocenium salt **11** can be characterized spectroscopically without any problems.

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The further development of the redox chemistry of **5** and **9** as well as possible applications of these complexes as soluble oxidizing agents in organic synthesis are currently under investigation.

Experimental Procedure

Synthesis and characterization: All work was carried out under a purified N_2 atmosphere.

5: **2** (6.1 g, 24.4 mmol) [**14**] in THF (50 mL) was treated dropwise with *n*BuLi (48.8 mmol) at -30°C . The mixture was allowed to warm to room temperature and stirred for 1 h. To the resulting brown solution was added a suspension of CeCl_3 (3.0 g, 12.2 mmol) [**23**] in THF (30 mL) at 0°C . This led to a dark green solution which was again allowed to warm to room temperature, stirred for two days, filtered through a layer of Celite, and the filtrate was treated with AgI (5.6 g, 24.0 mmol). In addition to the formation of elemental Ag, the solution immediately turned deep purple. The reaction mixture was stirred for 12 h with exclusion of light, and evaporated. The residue was treated with hexane (50 mL), and carefully filtered. Removal of the solvent under vacuum afforded **5** (3.1 g, 40%) as a deep purple, oily product. Correct elemental analysis: m.p. 226°C (decomp); ^1H NMR (250.1 MHz, C_6D_6): $\delta = 6.13$ (m, $^3J(\text{H,H}) = 7 \text{ Hz}$, 2H, ring-H), 5.98 (m, 2H, ring-H), 5.92 (m, $^3J(\text{H,H}) = 11 \text{ Hz}$, $^4J(\text{H,H}) = 3 \text{ Hz}$, 2H, ring-H), 5.88 (m, $^3J(\text{H,H}) = 7 \text{ Hz}$, 2H, ring-H), 5.83 (m, 2H, ring-H), 5.72 (m, $^3J(\text{H,H}) = 11 \text{ Hz}$, $^4J(\text{H,H}) = 3 \text{ Hz}$, 2H, ring-H), 0.08 (s, 18H, SiMe_3), 0.07 (s, 18H, SiMe_3); ^{29}Si NMR (49.7 MHz, $[\text{D}_8]\text{toluene}$): $\delta = -5.44$ (s), -5.43 (s); MS (EI): m/z : 636 ($[\text{M}^+]$, 6%), 388 ($[\text{Ce}(\text{C}_8\text{H}_6(1,4\text{-SiMe}_3)_2)]$, 52%), 249 ($[\text{C}_8\text{H}_6(1,4\text{-SiMe}_3)_2]^+$, 4%), 73 ($[\text{SiMe}_3]^+$, 100%); IR (KBr, pure substance): $\tilde{\nu}(\text{cm}^{-1}) = 1578 \text{ m}$, 1310 m, 1249 vs, 1102 s, 1080 m, 1004 m, 975 m, 929 s, 880 s, 839 vs, 751 s, 715 m, 633 s, 565 m, 511 m, 447 m, 372 m.

pure substance): $\tilde{\nu}(\text{cm}^{-1}) = 1578 \text{ m}$, 1310 m, 1249 vs, 1102 s, 1080 m, 1004 m, 975 m, 929 s, 880 s, 839 vs, 751 s, 715 m, 633 s, 565 m, 511 m, 447 m, 372 m.

6: *n*BuLi (239.6 mmol) was added dropwise to a solution of **2** (30 g, 119.8 mmol) [**14**] in THF (200 mL) at -30°C . Subsequently the solution was allowed to warm to room temperature and stirred for a further 12 h. The resulting deep brown solution was added dropwise to a solution of Me_3SiCl (26.0 g, 239.6 mmol) in Et_2O (150 mL) at -10°C . The mixture was allowed to react at -10°C for 10 min, then for 12 h at room temperature, filtered carefully, and the filtrate was evaporated to dryness under vacuum. The crude product was treated with dry MeOH (250 mL) and filtered while hot to remove the insoluble material. Cooling to -20°C afforded pale yellow, needlelike crystals of **6** (24.7 g, 52%), m.p. 87°C , correct elemental analysis: ^1H NMR (CDCl_3 , 400.1 MHz): $\delta = 6.15$ (ddd, $^3J(\text{H,H}) = 9 \text{ Hz}$, $^4J(\text{H,H}) = 1 \text{ Hz}$, $^4J(\text{H,H}) = 1 \text{ Hz}$, 1H, ring-H), 5.51 (dd, $^3J(\text{H,H}) = 11 \text{ Hz}$, $^3J(\text{H,H}) = 9 \text{ Hz}$, 1H, ring-H), 5.43 (dd, $^3J(\text{H,H}) = 13 \text{ Hz}$, $^4J(\text{H,H}) = 1 \text{ Hz}$, 1H, ring-H), 5.22 (ddd, $^3J(\text{H,H}) = 11 \text{ Hz}$, $^4J(\text{H,H}) = 1 \text{ Hz}$, $^4J(\text{H,H}) = 1 \text{ Hz}$, 1H, ring-H), 5.18 (ddd, $^3J(\text{H,H}) = 13 \text{ Hz}$, $^4J(\text{H,H}) = 1 \text{ Hz}$, $^5J(\text{H,H}) = 1 \text{ Hz}$, 1H, ring-H), 4.27 (ddd, $^3J(\text{H,H}) = 9 \text{ Hz}$, $^3J(\text{H,H}) = 9 \text{ Hz}$, $^4J(\text{H,H}) = 1 \text{ Hz}$, 1H, ring-H), 0.10 (s, 9H, SiMe_3), 0.04 (s, 9H, SiMe_3), 0.03 (s, 9H, SiMe_3), -0.03 (s, 9H, SiMe_3); ^{13}C NMR (CDCl_3): $\delta = 145.6$ (s, ring-C), 143.1 (t, $^1J(^{13}\text{C},^{29}\text{Si}) = 66 \text{ Hz}$, ring-C), 133.1 (s, ring-C), 131.0 (s, ring-C), 129.0 (s, ring-C), 126.2 (s, ring-C), 37.4 (t, $^1J(^{13}\text{C},^{29}\text{Si}) = 43 \text{ Hz}$, ring-C), 29.9 (t, $^1J(^{13}\text{C},^{29}\text{Si}) = 53 \text{ Hz}$, ring-C), -1.3 (t, $^1J(^{13}\text{C},^{29}\text{Si}) = 52 \text{ Hz}$, SiMe_3C), -1.4 (t, $^1J(^{13}\text{C},^{29}\text{Si}) = 52 \text{ Hz}$, SiMe_3C), -1.5 (t, $^1J(^{13}\text{C},^{29}\text{Si}) = 52 \text{ Hz}$, SiMe_3C), -3.1 (t, $^1J(^{13}\text{C},^{29}\text{Si}) = 51 \text{ Hz}$, SiMe_3C); ^{29}Si NMR (CDCl_3): $\delta = -5.3$ (s, SiMe_3), 2.0 (s, SiMe_3), 2.4 (s, SiMe_3), 2.6 (s, SiMe_3); MS (EI): m/z : 394 ($[\text{M}^+]$, 34%), 321 ($[\text{M}-\text{SiMe}_3]^+$, 60%), 233 ($[\text{M}-2\text{SiMe}_3\text{CH}_3]^+$, 54%), 73 ($[\text{SiMe}_3]^+$, 100%); IR (KBr, Nujol): $\tilde{\nu}(\text{cm}^{-1}) = 1578 \text{ m}$, 1310 m, 1249 vs, 1102 s, 1080 s, 1004 m, 975 m, 929 s, 880 s, 839 vs, 751 s, 715 s, 686 s, 633 s, 565 m, 511 m, 447 m, 372 m.

7: **6** (2.5 g, 6.3 mmol) and KH (0.8 g, 20.0 mmol) were heated under reflux in THF (50 mL) for 2 days. Subsequently, excess KH was filtered off, the orange solution evaporated to dryness, and the residue taken up in hexane (40 mL) and stirred for 3 h. The solid precipitate was separated and dried under vacuum. A white, microcrystalline powder **7** (1.57 g, 37%) was obtained. Correct elemental analysis: m.p. 247°C (decomp); ^1H NMR (250.1 MHz, $[\text{D}_8]\text{THF}$): $\delta = 6.39$ (m, 1H, ring-H), 6.34 (m, 1H, ring-H), 6.30 (m, 1H, ring-H), 6.23 (m, 1H, ring-H), 6.18 (m, 1H, ring-H), 3.62 (m, 12H, THF), 1.79 (m, 12H, THF), 0.32 (s, 18H, SiMe_3), 0.27 (s, 9H, SiMe_3); ^{29}Si NMR ($[\text{D}_8]\text{THF}$): $\delta = -2.3$ (s), -3.2 (s, half intensity); MS (EI): m/z : 320 ($[\text{C}_8\text{H}_6(\text{SiMe}_3)_2]^+$, 8%), 247 ($[\text{C}_8\text{H}_6(\text{SiMe}_3)_2]^+$, 42%), 73 ($[\text{SiMe}_3]^+$, 100%); IR (KBr, Nujol): $\tilde{\nu}(\text{cm}^{-1}) = 1734 \text{ m}$, 1532 m, 1304, 1240 vs, 1216 m, 1081 vs, 1046 vs, 975 s, 924 m, 889 m, 870 s, 824 vs, 740 vs, 672 m, 633 m, 567 m, 511 m.

9: **7** (2.5 g, 3.6 mmol) in THF (50 mL) was treated with a suspension of $\text{Ce}(\text{O}_3\text{SCF}_3)_3$ (1.1 g, 1.8 mmol) [**24**] in THF (30 mL) at 0°C and stirred. The solution turned bright green. Subsequently, the mixture was allowed to react for a further 12 h under reflux, then AgI (0.9 g, 3.8 mmol) was added at room temperature, which caused an immediate color change to purple. After stirring the mixture for 1 h with exclusion of light, the solvent was evaporated, the residue taken up in hexane (50 mL) and filtered. The filtrate was evaporated to dryness and the residue was treated with MeCN (50 mL). Crystallization at room temperature afforded **9** (0.5 g, 33%) as a microcrystalline, deep purple solid. Correct elemental analysis: m.p. 38°C ; ^1H NMR (250.1 MHz, C_6D_6): $\delta = 6.43$ (d, $^3J(\text{H,H}) = 12 \text{ Hz}$, 4H, ring-H), 6.00 (d, $^3J(\text{H,H}) = 12 \text{ Hz}$, 4H, ring-H), 5.61 (s, 2H, ring-H), 1.11 (s, 18 H, SiMe_3), 0.99 (s, 36H, SiMe_3); ^{29}Si NMR (C_6D_6): $\delta = -1.74$ (s), -3.09 (s, half intensity); MS (EI): m/z : 780 ($[\text{M}^+]$, 14%), 708 ($[\text{M}-\text{SiMe}_3]^+$, 2%), 460 ($[\text{Ce}(\text{C}_8\text{H}_6(\text{SiMe}_3)_2)]$, 100%), 386 ($[\text{Ce}(\text{C}_8\text{H}_6(\text{SiMe}_3)_2)]$, 8%), 73 ($[\text{SiMe}_3]^+$, 38%).

10: UCl_4 (0.7 g, 1.8 mmol) [**25**] in THF (30 mL) was added to a solution of **7** (2.5 g, 3.6 mmol) in THF (50 mL) at 0°C . The solution was then stirred for 3 h at room temperature, concentrated, treated with hexane (30 mL), and stirred for a further 12 h. Subsequently, the mixture was filtered while hot and concentrated to 10 mL. Cooling to -20°C afforded green crystals of **10** (0.4 g, 28%). Correct elemental analysis: m.p. 110°C (decomp); ^1H NMR (250.1 MHz, $[\text{D}_8]\text{THF}$): $\delta = 0.03$ (m, 10H, ring-H), -7.30 (br. s, 36H, SiMe_3), -9.10 (s, 18H, SiMe_3); ^{29}Si NMR ($[\text{D}_8]\text{THF}$): $\delta = -120.7$ (s); MS (EI): m/z : 878 ($[\text{M}^+]$, 100%), 806 ($[\text{M}^+-\text{SiMe}_3]$, 3%), 732 ($[\text{M}^+-2\text{SiMe}_3]$, 5%), 558 ($[\text{U}(\text{C}_8\text{H}_6(\text{SiMe}_3)_2)]$, 51%), 73 ($[\text{SiMe}_3]^+$, 44%); IR (KBr, Nujol): $\tilde{\nu}(\text{cm}^{-1}) = 1260 \text{ vs}$, 1249 s, 1090 vs, 1019 vs, 836 s, 801 vs, 747 m, 638 m.

11: **5** (2.0 g, 3.1 mmol) and Cp_2Co (0.6 g, 3.1 mmol) [**26**] were dissolved in THF (40 mL) and stirred for 3 h. The initially purple solution turned red-brown. The mixture was filtered over a thin layer of Celite and the filtrate was evaporated to dryness. The residue taken up in hexane (50 mL), and the green precipitate was isolated and dried. Compound **11** (0.2 g, 7%) was obtained as a pyrophoric, extremely air-sensitive solid. Correct elemental analysis: m.p. 142°C (decomp); ^1H NMR (250.1 MHz, $[\text{D}_8]\text{THF}$): $\delta = 6.21-5.79$ (m, 12H, ring-H), 1.30 (s, 5H, C_5H_5), 1.05 (s, 18H, SiMe_3), 0.90 (s, 5H, C_5H_5), 0.08 (s, 18H, SiMe_3); ^{29}Si NMR ($[\text{D}_8]\text{THF}$): $\delta = -2.4$ (s), -5.3 (s); MS (EI): m/z : 248 ($[\text{C}_8\text{H}_6(1,4\text{-SiMe}_3)_2]^+$, 16%), 189 ($[\text{Co}(\text{C}_5\text{H}_5)_2]^+$, 50%), 124 ($[\text{Co}(\text{C}_5\text{H}_5)_2]^+$, 11%), 73 ($[\text{SiMe}_3]^+$, 100%); IR (KBr, Nujol): $\tilde{\nu}(\text{cm}^{-1}) = 1413 \text{ m}$, 1306 m, 1261 vs, 1248 m, 1092 vs, 1037 vs, 980 m, 937 m, 861 m, 836 s, 800 vs, 750 m, 688 m, 637 m, 436 m.

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Mixed-Valence, Tetranuclear Iron Chelate Complexes as Endoreceptors: Charge Compensation Through Inclusion of Cations**

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Dedicated to Professor Helmut Ringsdorf on the occasion of his 65th birthday

An essential prerequisite for the rapid development of endohedral chemistry, that is chemistry within cages, is easy access to host molecules of variable internal diameter.^[1] In this context we have recently reported the tetranuclear adamantanoid Fe^{III} spacer-complex $[\text{Fe}_4\text{L}^1_6]$ **1**.^[1] Complex **1** is endowed with a substantial cavity, which should, in principle, be suitable for the uptake of guest molecules. Our attempts to obtain the spacer-free metallospherand core unit $[\text{Fe}_4\text{L}^2_6]$ in analogous manner have thus far given rise to products which could not be characterized unambiguously.

In contrast, we have obtained for the first time, the tetranuclear, mixed-valence ammonium inclusion complexes $[\text{NH}_4^+ \text{Fe}_4\text{L}^2_6]$ **2** and $[\text{NH}_4^+ \text{Fe}_4\text{L}^3_6]$ **3** in a one-pot reaction.^[3] Complexes **2** and **3** are formed by spontaneous self-assembly^[1, 4–7] from the reaction of dialkyl malonates with methyl-lithium/iron(II) chloride and oxalyl chloride at -78°C in tetrahydrofuran, followed by workup with aqueous ammonium

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[+++] Mössbauer spectra.

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