Pyridyl-Functionalised Cyclopentadienyl Ligands: Building Blocks for Oligonuclear Organometallic Assemblies

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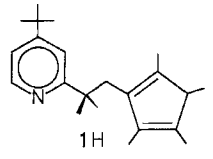
Lithiated 2-methylpyridine reacts with 2,3,4,5-tetramethylfulvene (TMF) to give 2-[2-(2,3,4,5-tetramethylcyclopenta-1,4-dien-1-yl)ethyl]pyridine (**2**H) after aqueous work-up. Similarly, a mixture of 2-methyl-6-[2-(2,3,4,5-tetramethylcyclopenta-1,4-dien-1-yl)ethyl]pyridine (**3**H) and 2,6-bis[2-(2,3,4,5-tetramethylcyclopenta-1,4-dien-1-yl)ethyl]pyridine ($\mathbf{4}H_2$) was obtained from monolithiated 2,6-dimethylpyridine and TMF. All three compounds were obtained as a roughly statistical mixture of double-bond isomers. 2-Lithiopyridine reacts with 2,3,4,5-tetramethylcyclopent-2-enone to yield 2-(2,3,4,5-tetramethylcyclopenta-1,3-dien-1-yl)pyridine (**5**H) after acidic work-up. This compound was obtained as a non-statistical mixture of double-bond isomers, which is presumably due to intramolecular hydrogen-bond interactions. The lithiated derivatives **2**Li, **3**Li and **5**Li react with iron(II) chloride to afford the respective ferrocenes $(\mathbf{2})_2$Fe (**8**), $(\mathbf{3})_2$Fe (**9**) and $(\mathbf{5})_2$Fe (**10**). The structure of **10** was determined by a single-crystal X-ray diffraction study. The cyclopentadienyl ligands adopt a staggered conformation; the pyridyl rings are arranged in a stacked fashion with the closest ring-ring contact being 3.16 Å. The distance between the iron atom and the cyclopentadienyl ring centroids is 1.66 Å.

We have recently described the first example of a pentamethylcyclopentadiene functionalised with a pendant pyridyl unit[1]; compound **1**H could be obtained in 60% yield by the addition of lithiated 4-*tert*-butyl-2-isopropylpyridine to tetramethylfulvene (TMF)[2] and subsequent aqueous work-up.



1H
(mixture of isomers)

Donor-functionalised cyclopentadienyl systems such as **1** are of great current interest[3]. They belong to the rapidly growing class of hemilabile ligands[3,4] and have, for example, proved useful for the "reversible" stabilisation of reactive metal–ligand fragments (serving, for example, as MOCVD precursors or molecular catalysts) and also for the construction of oligonuclear metal complexes[3,5].

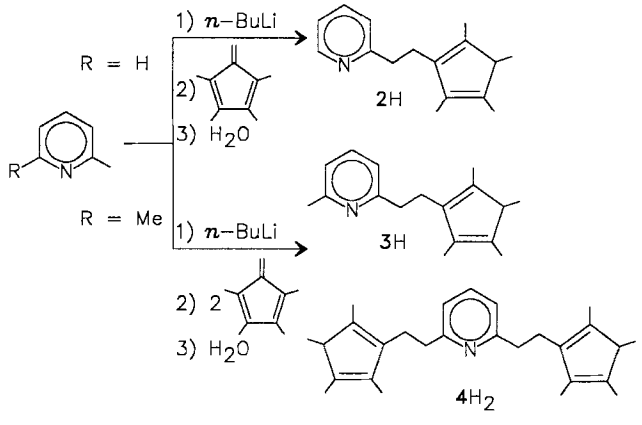
The steric and electronic properties of cyclopentadienyl ligands can be tailored by the introduction of methyl groups. However, when it comes to *hemilabile* cyclopentadienyl ligands, only very few examples of (oligo-)methyl-substituted systems are known in the literature[5g,h,n,6] with ligand **1** being one of them.

In this paper we report on further examples of such species, including first results from their coordination chemistry.

Results and Discussion

The strategy for the synthesis of **1**H, which is based on the use of TMF as synthetic equivalent for the cyclopentadienyl moiety, was extended to the preparation of compounds **2**H and **3**H. These cyclopentadienes were obtained as yellow oils in 38% (**2**H) and 45% (**3**H) yield, respectively, after vacuum distillation. Owing to deprotonation equilibria, the bis(cyclopentadiene) $\mathbf{4}H_2$ was obtained as a side product (11% yield) in the latter case (Scheme 1).

Scheme 1. Synthesis of the pyridyl-functionalised cyclopentadienes **2**H, **3**H and $\mathbf{4}H_2$ (only one isomer is shown in each case)



This strategy cannot be extended, however, to the preparation of pyridyl-functionalised cyclopentadienes containing a single methylene spacer group between the pyridine and cyclopentadiene ring: When 2-lithiopyridine (prepared

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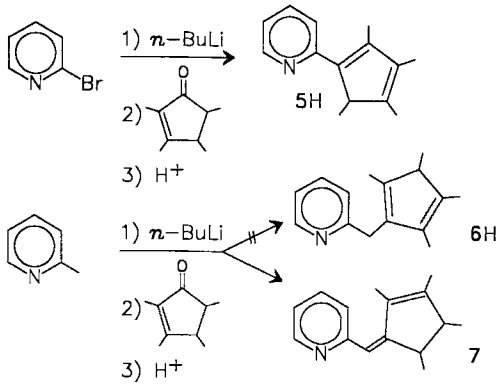
from 2-bromopyridine and *n*-butyllithium) was treated with TMF, an intractable mixture of products was obtained.

A second synthetic strategy is based on the use of 2,3,4,5-tetramethylcyclopent-2-enone as equivalent for the cyclopentadienyl moiety. 2-Lithiopyridine reacts smoothly with this reagent, and the desired cyclopentadiene **5H** was obtained as a yellow oil in 61% yield after acidic work-up and vacuum distillation. Again, this strategy failed with the monomethylene spacer group: 2-Picolyllithium does react with 2,3,4,5-tetramethylcyclopent-2-enone, but instead of the desired cyclopentadiene **6H**, a product mixture containing compound **7** as the main component as determined by ^{1}H-NMR spectroscopy was obtained (Scheme 2).

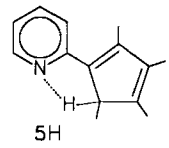
Scheme 2. Synthesis of compound **5H**; attempted synthesis of compound **6H** (only one isomer is shown in each case)



In order to prevent formation of the exocyclic double bond, lithiated 2-isopropylpyridine was treated with the cyclopentenone. However, in this case owing to the bulkiness of the carbanion only deprotonation of the ketone (i.e. enolate formation) takes place and both 2-isopropylpyridine and tetramethylcyclopentenone can be recovered after standard work-up.

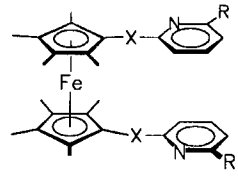
According to ^{1}H- and ^{13}C-NMR spectroscopic data, compounds **2H** and **3H** are formed as roughly statistical mixtures of the three possible regioisomers. For example, in their respective ^{13}C-NMR spectra three signals are observed for the allylic cyclopentadiene C atom in each case; the intensity of the two lowfield signals (detected at δ = 49.1 and 51.4 for **2H** and at δ = 49.3 and 51.3 for **3H**) is approximately twice that of the highfield signal (observed at δ = 55.7 for both compounds). Interestingly, for compound **5H**, one of the two possible isomers having the cyclopentadiene double bonds in conjugation with the pyridine unit is the major isomer (ca. 60%); the other one of these two isomers is by far the minor isomer (ca. 5%). The third isomer, whose cyclopentadiene double bonds are not in conjugation with the pyridine ring, is present in ca. 35% in the equilibrium mixture. A possible explanation for this unusual isomer distribution is the occurrence of a hydrogen-bond interaction between the nitrogen atom and the cyclopentadienyl CH unit in the two major isomers of **5H** as shown in Figure 1. We are currently investigating this effect and will report on our findings in due course.

Figure 1. Proposed intramolecular hydrogen-bond interaction in the main isomer of compound **5H**



Attempts to convert the cyclopentadienes **2H** and **3H** to the respective ferrocene-type iron(II) complexes by lithiation with *n*-butyllithium and subsequent reaction with iron(II) chloride gave unsatisfactory results. In the case of **2H**, 6% of the desired ferrocene **8** could be obtained; with **3H**, the corresponding ferrocene **9** could not be isolated. A much better way to prepare these ferrocenes proved to be the immediate use of the lithium cyclopentadienides **2Li** and **3Li** formed in situ from TMF and the respective lithiated methylpyridine. In this case, 36% of **8** and 38% of **9** could be isolated as yellow crystals (Figure 2). It is as yet unclear why the lithiation of the cyclopentadienes **2H** and **3H** with *n*-butyllithium was unsuccessful. Similar observations have been made by Kauffmann et al.[7]. In contrast to the behaviour of **2H** and **3H**, the cyclopentadiene **5H** can be cleanly deprotonated at the cyclopentadiene ring with *n*-butyllithium. The resultant lithio derivative **5Li** reacts swiftly with iron(II) chloride in THF to afford 75% of the desired ferrocene **10** as dark red crystals (Figure 2). A single-crystal X-ray diffraction study of this compound was performed (Figure 3).

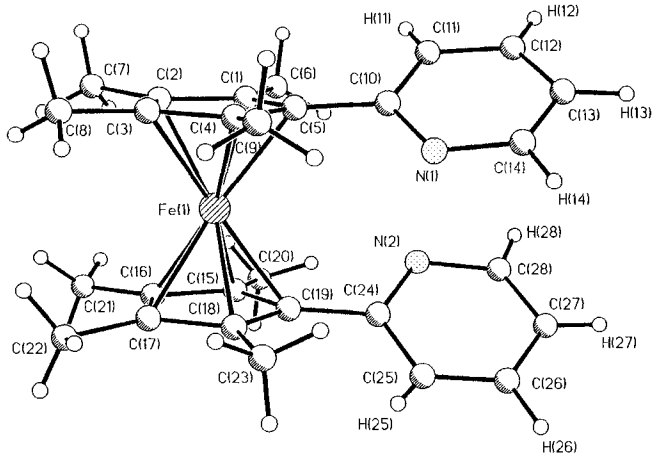
Figure 2. The pyridyl-functionalised ferrocenes **8**–**10**



8 (X = CH_2CH_2, R = H)
9 (X = CH_2CH_2, R = Me)
10 (X = /, R = H)

The cyclopentadienyl rings adopt an eclipsed conformation. Each iron–ring centroid distance is 1.66 Å, which is identical with the values observed for ferrocene and decamethyl ferrocene[8]. The pyridyl rings are arranged in an antiparallel fashion; their best planes intersect each other at an angle of 9.9°. The best planes for the pyridyl ring containing N(1) and for the cyclopentadienyl ring attached to it intersect each other forming an angle of 33.3°; the corresponding twist angle for the second pair of ring planes is 36.9°; these values are close to the value of 30° observed for 2-phenylpyridine in solution and can be rationalised by steric interactions between the nitrogen lone pairs and the respective cyclopentadienyl methyl groups at C(4) and C(15)[9]. The bond lengths between the cyclopentadienyl and the neighbouring pyridyl ring are 1.468(7) [C(5)–C(10)] and 1.457(7) Å [C(19)–C(24)], respectively, which is the value expected for a single bond between two sp^2-hybridised carbon atoms[10]. There seems to be a corre-

Figure 3. Crystal structure of **10**[a]



[a] Selected bond lenghts [Å]: C(1)–C(2) 1.440(8), C(2)–C(3) 1.419(8), C(3)–C(4) 1.442(7), C(4)–C(5) 1.436(7), C(1)–C(5) 1.432(7), C(5)–C(10) 1.468(7), C(10)–C(11) 1.376(8), C(11)–C(12) 1.383(9), C(12)–C(13) 1.372(9), C(13)–C(14) 1.354(9), N(1)–C(10) 1.367(7), N(1)–C(14) 1.347(7); the bond angles in this compound are unexceptional.

lation between the interannular bond length and the ring twist angle in such compounds: For the two independent molecules of crystalline 4-biphenylylferrocene the corresponding values are 1.56 Å/2.1° and 1.54 Å/9.7°[11]; for 4'-ferrocenyl-2,2':6',2''-terpyridine 1.47 Å/19.2°[12] (1.47 Å/19.0°[13]) is observed. Obviously, small twist angles lead to noticeable steric repulsion between the rings. The closest contact between the two pyridyl units in **10** is 3.16 Å [C(10)–N(2)], which is slightly less than the estimated van der Waals distance of 3.40 Å between two aromatic π systems and even less than the graphite layer distance of 3.35 Å[14]. It is also smaller than the mean distance between the cyclopentadienyl ring planes of 3.32 Å in this compound. This may be indicative of secondary intramolecular interactions responsible for the conformation of the molecule in the solid state (however, crystal packing effects cannot be ruled out[15]).

Investigations concerning the use of the ferrocenes **8**–**10** as bidentate redox-active ligands for transition-metal ions are currently under way. We are also extending the synthetic strategies described in this paper to the preparation of bipyridyl- and terpyridyl-functionalised tetramethylcyclopentadienyl ligands with a view to constructing stable redox-active sensitisers for light-induced water splitting.

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Experimental

Air- and/or moisture-sensitive compounds were handled under purified argon by using standard Schlenk techniques. Solvents and reagents were appropriately dried and purified by using standard procedures. – NMR: Bruker AM 300 (300.133 MHz, ^{1}H, ext. TMS; 75.453 MHz, ^{13}C, ext. TMS). – MS: VG Autospec (70 eV); only characteristic fragments are listed. – Elemental analyses: Microanalytical laboratory, Universität Bielefeld.

2-[2-(2,3,4,5-Tetramethylcyclopenta-1,4-dien-1-yl)ethyl]pyridine (**2**H): 31.5 ml of a 1.59 M solution of *n*-butyllithium in hexane (50.0 ml) was added dropwise with stirring to a solution of 4.66 g (50.0 mmol) of 2-methylpyridine in 50 ml of *n*-hexane cooled to 0°C. After 2 h a solution of 6.71 g (50.0 mmol) of 2,3,4,5-tetramethylfulvene in 10 ml of *n*-hexane was added dropwise to the orange suspension. The mixture was allowed to warm to room temp. and stirred for ca. 12 h. Then 20 ml of a saturated aqueous solution of ammonium chloride was added, the yellow organic layer was separated, washed with water (3 × 50 ml) and dried with sodium sulfate. Volatile products were removed in vacuo and the crude product was distilled to yield 4.26 g (38%) of a yellow oil, b.p. 100°C/0.001 mbar. – ^{1}H NMR ($CDCl_3$): δ = 0.96, 1.01 (2 d, ^3J = 7.7 Hz, 3H, allyl. CH_3); 1.73–1.79 (m, 9H, vinyl. CH_3); 2.10–2.83 (several superimposed m, 5H, CH_2, CH); 6.96–7.08 (m, 2H, 3-, 5-H); 7.46–7.53 (m, 1H, 4-H); 8.50–8.52 (m, 1H, 6-H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 10.8, 11.1, 11.4, 11.6, 13.9, 14.0 (CH_3); 26.0, 26.6, 27.4 [$(C_5H_4N)CH_2CH_2$]; 37.6, 38.2, 39.0 [$(C_5H_4N)CH_2CH_2$]; 49.1, 51.4, 55.7 (allyl. CH); 119.4, 120.4, 120.7, 122.5, 123.0 (C-3, C-5); 133.2, 133.8, 134.7, 135.2, 135.7, 135.9, 137.2, 138.3, 139.2, 141.0 (vinyl. ring C's and C-4); 148.9, 149.0 (C-6); 161.7, 161.9, 162.8 (C-2). – $C_{16}H_{21}N$ (227.3): calcd. C 84.52, H 9.31, N 6.16; found C 84.48, H 9.11, N 6.23.

2-Methyl-6-[2-(2,3,4,5-tetramethylcyclopenta-1,4-dien-1-yl)-ethyl]pyridine (**3**H) *and 2,6-Bis[2-(2,3,4,5-tetramethylcyclopenta-1,4-dien-1-yl)ethyl]pyridine* (**4**H_2): 31.5 ml of a 1.59 M solution of *n*-butyllithium in hexane (50.0 mmol) was added dropwise with stirring to a solution of 5.36 g (50.0 mmol) of 2,6-dimethylpyridine in 150 ml of THF cooled to 0°C. After 1 h a solution of 6.71 g (50.0 mmol) of 2,3,4,5-tetramethylfulvene in 25 ml of *n*-hexane was added dropwise to the red solution. The mixture was allowed to warm to room temp. and stirred overnight. After cooling to 0°C, a second equivalent of TMF was added dropwise to the brown solution. After stirring of the mixture at room temp. for 1 h, 50 ml of a saturated aqueous solution of ammonium chloride was added. The yellow organic layer was separated, washed with water (2 × 100 ml) and dried with magnesium sulfate. Volatile products were removed in vacuo and the remaining oil was distilled to yield 5.46 g (45%) of **3**H, b.p. 105°C/0.001 mbar, and 2.08 g (11%) of **4**H_2, b.p. 180°C/0.001 mbar, as yellow oils.

3H: ^{1}H NMR ($CDCl_3$): δ = 0.92, 1.01 (2 d, ^3J = 7.6 Hz, 3H, allyl. CH_3); 1.72–1.79 (m, 9H, vinyl. CH_3); 2.21–2.84 (several superimposed m, 5H, CH_2, CH); 2.50 (s, 3H, pyridyl CH_3); 6.73–6.93 (m, 2H, 3-, 5-H); 7.33–7.41 (m, 1H, 4-H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 10.7, 11.2, 11.5, 11.7, 14.0, 14.1 (cyclopentadienyl CH_3); 24.4 (pyridyl CH_3); 26.0, 26.6, 27.0 [$(H_3CC_5H_3N)CH_2CH_2$]; 32.1, 38.2, 39.1 [$(H_3CC_5H_3N)CH_2CH_2$]; 49.3, 51.3, 55.7 (allyl. CH); 119.1, 119.4, 120.0, 120.2 (C-3, C-5); 135.9, 136.0, 136.2 (C-4); 133.3, 133.9, 134.8, 135.1, 137.2, 138.1, 139.1, 139.3, 141.2 (vinyl. ring C's); 157.3, 157.5, 161.0, 161.3, 162.2 (C-2, C-6). – $C_{17}H_{23}N$ (241.4): calcd. C 84.59, H 9.60, N 5.80; found C 84.44, H 9.62, N 5.34.

4H_2: ^{1}H NMR ($CDCl_3$): δ = 0.93, 1.01 (2 m, 6H, allyl. CH_3); 1.54–1.82 (m, 18H, vinyl. CH_3); 2.08–2.85 (several superimposed m, 10H, CH_2, CH); 6.78–6.89 (m, 4H, 3-, 5-H); 7.35–7.42 (m, 2H, 4-H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 11.0, 11.3, 11.6, 11.8, 14.0, 14.2 (CH_3); 26.1, 26.7, 27.5 [$C_5H_3N(CH_2CH_2)_2$]; 32.2, 38.3, 39.2 [$C_5H_3N(CH_2CH_2)_2$]; 49.4, 51.5, 55.8 (allyl. CH); 119.2, 119.5, 119.7, 120.0 (C-3, C-5); 133.5, 134.0, 135.0, 135.1, 136.0, 137.5, 138.2, 138.3, 139.3, 141.4 (vinyl. ring C's); 160.9, 161.1, 161.3, 162.0, 162.2 (C-2, C-6). – $C_{27}H_{35}N$ (373.6): calcd. C 86.80, H 9.44, N 3.74; found C 86.60, H 9.51, N 3.99.

2-(2,3,4,5-Tetramethylcyclopenta-1,3-dien-1-yl)pyridine (**5H**): 31.5 ml of a 1.59 M solution of *n*-butyllithium in hexane (50.0 mmol) was added dropwise with stirring to a solution of 7.90 g (50.0 mmol) of 2-bromopyridine in 100 ml of diethyl ether cooled to −40°C. The brown solution was stirred for 1 h at this temperature. A solution of 6.90 g (50.0 mmol) of 2,3,4,5-tetramethylcyclopent-2-enone in 50 ml of diethyl ether was added dropwise and the mixture was stirred at −40°C for 1 h after which time the colour had turned dark green. The mixture was allowed to warm to room temp. (colour change to red) and subsequently hydrolysed with 50 ml of water. Subsequently, 50 ml of hydrochloric acid (37%) was added and the mixture was stirred vigorously for 10 min. The yellow organic layer was separated. The aqueous phase was neutralised with sodium hydroxide solution and then extracted with diethyl ether (3 × 30 ml). The combined organic layers were dried with sodium sulfate. Volatile products were removed in vacuo and the crude product was distilled to yield 6.03 g (61%) of a yellow oil, b.p. 80°C/0.01 mbar. – ^{1}H NMR ($CDCl_3$): δ = 1.01, 1.11 (2 d, ^3J = 7.6 Hz, 3H, allyl. CH_3); 1.67, 1.80, 1.83, 1.90, 2.16 (5 s, 5H, vinyl. CH_3); 3.36 (m, 1H, allyl. CH); 6.96–7.21 (m, 2H, 3-, 5-H); 7.45 (m, 1H, 4-H); 8.49–8.59 (m, 1H, 6-H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 10.7, 11.0, 11.4, 11.8, 12.3, 12.9, 13.3, 13.7, 14.5 (CH_3); 49.5, 52.1, 66.2 (allyl. CH); 119.3, 120.7, 121.0, 121.3, 122.5, 124.0 (C-3, C-5); 134.9, 136.3, 136.7, 138.8, 141.7, 142.8, 143.5 (vinyl. ring C's); 135.3, 136.2 (C-4); 149.0 (C-6); 155.4, 160.6 (C-2). – $C_{14}H_{17}N$ (199.3): calcd. C 84.37, H 8.59, N 7.02; found C 84.28, H 8.81, N 7.12.

Bis{1,2,3,4-tetramethyl-5-[2-(2-pyridyl)ethyl]cyclopenta-2,4-dien-1-yl}iron(II) (**8**): 31.5 ml of a 1.59 M solution of *n*-butyllithium in hexane (50.0 mmol) was added dropwise with stirring to a solution of 4.66 g (50.0 mmol) of 2-methylpyridine in 25 ml of THF cooled to −40°C. After 1 h, the mixture was allowed to warm to 0°C and a solution of 6.71 g (50.0 mmol) of 2,3,4,5-tetramethylfulvene in 25 ml of THF was added dropwise. After stirring of the mixture at room temp. for ca. 12 h, the resultant solution of **2**Li was added dropwise with stirring to a suspension of 3.17 g (25.0 mmol) of iron(II) chloride in 10 ml of THF cooled to 0°C. The mixture was stirred at room temperature for ca. 12 h. Volatile products were removed in vacuo and the dark, oily residue was extracted with 50 ml of dichloromethane. The extract was filtered through a short column of Florisil. The volume was reduced to ca. 20 ml. Cooling to −40°C afforded 4.60 g (36%) of yellow crystals. – ^{1}H NMR ($CDCl_3$): δ = 1.52, 1.58 (2 s, 24H, CH_3); 2.43, 2.68 (2 m, 8H, CH_2CH_2); 6.97 (d, ^3J = 7.8 Hz, 2H, 3-, 3'-H); 7.07 (m, 2H, 5-, 5'-H); 7.52 (m, 2H, 4-, 4'-H); 8.52 (m, 2H, 6-, 6'-H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 9.3, 9.4 (CH_3); 26.2 [$(C_5H_4N)CH_2CH_2$]; 39.7 [$(C_5H_4N)CH_2CH_2$]; 78.4, 79.0 (CCH_3); 82.0 (cyclopentadienyl CCH_2); 120.8, 122.9, 136.0, 149.3 (CH); 162.0 (pyridyl CCH_2). – MS (EI): *m/z* (%) = 508 (100) [M^+], 282 (47) [$M^+ - C_5H_4N(CH_2)_2C_5Me_4$], 226 (9) [$C_5H_4N(CH_2)_2C_5Me_4^+$]. – $C_{32}H_{40}FeN_2$ (508.5): calcd. C 75.58, H 7.92, N 5.50; found C 75.57, H 8.03, N 5.65.

Bis{1,2,3,4-tetramethyl-5-[2-(6-methyl-2-pyridyl)ethyl]cyclopenta-2,4-dien-1-yl}iron(II) (**9**): 15.7 ml of a 1.59 M solution of *n*-butyllithium in hexane (25.0 mmol) was added dropwise with stirring to a solution of 2.68 g (25.0 mmol) of 2,6-dimethylpyridine in 30 ml of THF cooled to 0°C. After 1 h, a solution of 3.36 g (25.0 mmol) of 2,3,4,5-tetramethylfulvene in 10 ml of THF was added dropwise with stirring. The mixture was heated to 40°C for 10 min and then immediately cooled again to room temp. The resultant solution of **3**Li was added dropwise with stirring to a suspension of 1.58 g (12.5 mmol) of iron(II) chloride in 10 ml of THF. After stirring of the mixture overnight it was heated to 40°C for 15 min. Volatile products were removed in vacuo and the dark solid was extracted with 70 ml of methylene chloride. The extract was passed three times through a short column of alumina (activity grade II). The solvent was removed in vacuo and the yellow solid was dissolved in a small amount of *n*-hexane. Cooling of the solution to −40°C afforded 2.55 g (38%) of a light yellow microcrystalline solid. – ^{1}H NMR ($CDCl_3$): δ = 1.53, 1.61 (2 s, 24H, cyclopentadienyl CH_3); 2.48, 2.65 (2 m, 8H, CH_2CH_2); 2.51 (s, 6H, pyridyl CH_3); 6.70–6.73 (m, 2H, 3-, 3'-H); 6.90–6.93 (m, 2H, 5-, 5'-H); 7.36–7.39 (m, 2H, 4-, 4'-H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 9.5 (cyclopentadienyl CH_3); 24.6 (pyridyl CH_3); 26.2 [$(H_3CC_5H_3N)CH_2CH_2$]; 39.6 [$(H_3CC_5H_3N)CH_2CH_2$]; 78.4, 78.9 (cyclopentadienyl CCH_3); 82.1 (cyclopentadienyl CCH_2); 199.9, 120.2, 136.1 (CH); 157.7, 161.4 (quart. pyridyl C's). – MS (EI): *m/z* (%) = 536 (100) [M^+], 296 (37) [$M^+ - H_3CC_5H_3N(CH_2)_2C_5Me_4$]. – $C_{34}H_{44}FeN_2$ (536.6): calcd. C 76.10, H 8.26, N 5.22; found C 75.81, H 8.26, N 4.92.

Bis[1,2,3,4-tetramethyl-5-(2-pyridyl)cyclopenta-2,4-dien-1-yl]iron(II) (**10**): 6.3 ml of a 1.59 M solution of *n*-butyllithium in hexane (10.0 mmol) was added dropwise with stirring to a solution of 1.99 g (10.0 mmol) of **5H** in 15 ml of THF cooled to 0°C. The mixture was allowed to warm to room temp. and then added dropwise with stirring to a suspension of 634 mg (5.00 mmol) of iron(II) chloride in 10 ml of THF. The mixture was stirred for ca. 12 h. Volatile products were removed in vacuo. The brown solid was extracted with 100 ml of *n*-hexane and insoluble material was removed by filtration. Cooling of the red solution afforded 1.81 g (75%) of red crystals. – ^{1}H NMR ($CDCl_3$): δ = 1.69, 1.88 (2 s, 24H, CH_3); 6.92–6.95 (m, 2H, 3-, 3'-H); 7.13–7.16 (m, 2H, 5-, 5'-H); 8.40–8.42 (m, 2H, 6-, 6'-H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 9.5, 10.8 (CH_3); 80.0, 81.7 (cyclopentadienyl CCH_3); 83.5 (CC_5H_4N); 119.4, 124.6, 134.3, 148.5 (CH); 159.0 (quart. pyridyl C). – MS (EI): *m/z* (%) = 452 (100) [M^+], 254 (12) [$M^+ - C_5H_4NC_5Me_4$], 198 (16) [$C_5H_4NC_5Me_4^+$]. – $C_{28}H_{32}FeN_2$ (452.2): calcd. C 74.33, H 7.12, N 6.19; found C 74.40, H 7.09, N 6.32.

Table 1. X-ray structural analysis of compound **10**

Empirical formula: $C_{28}H_{32}FeN_2$; molecular mass: 452.4; crystal size: 0.5 × 0.2 × 0.1 mm; crystal colour: red; crystal system: monoclinic; space group: $P2_1/c$; a = 17.525(5), b = 8.878(3), c = 14.749(4) Å; β = 97.03(2)°; V = 2277.5(12) Å^3; Z = 4; $d_{calcd.}$ = 1.319 gcm^{-3}; μ = 0.680 mm^{-1}; λ = 0.71073 Å; $F(000)$ = 960; diffractometer: Siemens $P2_1$; scan type: ω; temperature: 293 K; radiation: Mo-K_α; $2\Theta_{max}$ = 50.1°; reflections collected: 4217 (±h, −k, +l); independent reflections: 4041 (R_{int} = 0.0353); parameters refined: 312; structure solution: direct methods; R_F = 0.067, wR_{F2} = 0.114 for 2110 reflections [$I > 2\sigma(I)$]; largest difference peak and hole: 0.3 and −0.3 eÅ^{-3}.

Crystal-Structure Determination of **10**: Table 1 contains details concerning the crystal structure determination[16]. The hydrogen atoms of the pyridine rings were located by difference Fourier synthesis and were refined isotropically without constraints; all other hydrogen atoms were included in calculated positions. All non-hydrogen atoms were refined anisotropically. The programme packages Siemens SHELXTL PLUS (VMS) and SHELXL-93 were used. Atomic scattering factors were taken from the literature[17].

[1] U. Siemeling, B. Neumann, H.-G. Stammler, *Z. Naturforsch., B: Chem. Sci.* **1994**, *49*, 683–686.
[2] P. Jutzi, T. Heidemann, B. Neumann, H.-G. Stammler, *Synthesis* **1992**, 1096–1098.
[3] J. Okuda, *Comments Inorg. Chem.* **1994**, *16*, 185–205 and references cited therein.

[4] For recent reviews, see: [4a] T. A. Kaden, *Top. Curr. Chem.* **1984**, *121*, 157–179. – [4b] A. Bader, E. Lindner, *Coord. Chem. Rev.* **1991**, *108*, 27–110. – [4c] K. R. Dunbar, *Comments Inorg. Chem.* **1992**, *13*, 313–357.

[5] Recent publications not referenced in ref.[3]: [5a] D. Deng, C. Qian, G. Wu, P. Zheng, *J. Chem. Soc., Chem. Commun.* **1990**, 880–881. – [5b] G. Paolucci, R. D. Fischer, F. Benetollo, R. Seraglia, G. Bombieri, *J. Organomet. Chem.* **1991**, *412*, 327–342. – [5c] C. Qian, B. Wang, D. Deng, G. Wu, P. Zheng, *J. Organomet. Chem.* **1992**, *427*, C29–C32. – [5d] U. Siemeling, *J. Organomet. Chem.* **1992**, *429*, C14–C18. – [5e] Y. Qian, G. Li, *Polyhedron* **1993**, *12*, 967–970. – [5f] D. Deng, C. Qian, F. Song, Z. Wang, G. Wu, P. Zheng, S. Jin, Y. Lin, *J. Organomet. Chem.* **1993**, *458*, 83–88. – [5g] P. Jutzi, J. Dahlhaus, M. Bangel, *J. Organomet. Chem.* **1993**, *460*, C13–C15. – [5h] U. Siemeling, B. Neumann, H.-G. Stammler, *Chem. Ber.* **1993**, *126*, 1311–1316. – [5i] C. Qian, J. Guo, C. Ye, J. Sun, P. Zheng, *J. Chem. Soc., Dalton Trans.* **1993**, 3441–3445. – [5j] D. Deng, X. Zheng, C. Qian, J. Sun, L. Zheng, *J. Organomet. Chem.* **1994**, *466*, 95–100. – [5k] C. Qian, X. Zheng, B. Wang, D. Deng, J. Sun, *J. Organomet. Chem.* **1994**, *466*, 101–105. – [5l] G. Paolucci, R. D. D'Ippolito, C. Ye, C. Qian, J. Gräper, R. D. Fischer, *J. Organomet. Chem.* **1994**, *471*, 97–104. – [5m] J. R. van den Hende, P. B. Hitchcock, M. F. Lappert, T. A. Nile, *J. Organomet. Chem.* **1994**, *472*, 79–85. – [5n] U. Siemeling, G. Hüffmann, *J. Organomet. Chem.* **1994**, *475*, 229–232. – [5o] P. Jutzi, M. Bangel, *J. Organomet. Chem.* **1994**, *480*, C18–C19. – [5p] W. S. Rees, Jr., U. W. Lay, K. A. Dippel, *J. Organomet. Chem.* **1994**, *483*, 27–31. – [5q] C. Qian, B. Wang, D. Deng, J. Hu, J. Chen, G. Wu, P. Zheng, *Inorg. Chem.* **1994**, *33*, 3382–3388.

[6] For alkylated cyclopentadienyl ligands containing a pendant heteroatom donor group, see: [6a] J. W. Pattiasina, F. van Bolhuis, J. H. Teuben, *Angew. Chem.* **1987**, *99*, 342–343; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 330–331. – [6b] D. M. Bensley, Jr., E. A. Mintz, *J. Organomet. Chem.* **1988**, *353*, 93–102. – [6c] J. Szymoniak, J. Besonçon, A. Dormond, C. Moïse, *J. Org. Chem.* **1990**, *55*, 1429–1432. – [6d] J. A. Miguel-Garcia, P. M. Maitlis, *J. Chem. Soc., Chem. Commun.* **1990**, 1472–1473. – [6e] J. A. Miguel-Garcia, H. Adams, N. A. Bailey, P. M. Maitlis, *J. Organomet. Chem.* **1991**, *413*, 427–444. – [6f] M. Ogasa, D. T. Mallin, D. W. Macomber, M. D. Rausch, R. D. Rogers, A. N. Rollins, *J. Organomet. Chem.* **1991**, *405*, 41–52. – [6g] R. Fandos, A. Meetsma, J. H. Teuben, *Organometallics* **1991**, *10*, 59–60. – [6h] P. Jutzi, J. Dahlhaus, M. O. Kristen, *J. Organomet. Chem.* **1993**, *450*, C1–C3. – [6i] P. Jutzi, M. O. Kristen, J. Dahlhaus, B. Neumann, H.-G. Stammler, *Organometallics* **1993**, *12*, 2980–2985. For alkylated cyclopentadienyl ligands containing a pendant alkenyl or alkinyl donor group, see refs.[6c,f]. – [6j] J. F. Buzinkai, R. R. Schrock, *Organometallics* **1987**, *6*, 1447–1452. – [6k] K. H. Dötz, J. Rott, *J. Organomet. Chem.* **1988**, *338*, C11–C13. – [6k] J. Okuda, K. H. Zimmermann, *J. Organomet. Chem.* **1988**, *344*, C1–C4. – [6l] J. Okuda, K. H. Zimmermann, *Chem. Ber.* **1989**, *122*, 1645–1647. – [6m] J. Okuda, K. H. Zimmermann, *Chem. Ber.* **1990**, *123*, 1641–1648. – [6n] H. Lehmkuhl, J. Näser, G. Mehler, T. Keil, F. Danowski, R. Benn, R. Mynott, G. Schroth, B. Gabor, C. Krüger, P. Betz, *Chem. Ber.* **1991**, *124*, 441–452. – [6o] J. Okuda, K. H. Zimmermann, E. Herdtweck, *Angew. Chem.* **1991**, *103*, 446–447; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 430–431. – [6p] J. Okuda, K. H. Zimmermann, *Chem. Ber.* **1992**, *125*, 637–641. – [6q] K. H. Zimmermann, R. S. Pilato, I. T. Horváth, J. Okuda, *Organometallics* **1992**, *11*, 3935–3937. – [6r] F. Moulines, B. Gloaguen, D. Astruc, *Angew. Chem.* **1992**, *104*, 452–454; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 458–460.

[7] T. Kauffmann, J. Ennen, H. Lhotak, A. Rensing, F. Steinseifer, A. Woltermann, *Angew. Chem.* **1980**, *92*, 321–323; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 328–329.

[8] [8a] C. Elschenbroich, A. Salzer, *Organometallchemie*, 2nd ed., Teubner, Stuttgart, **1988**, p. 380. – [8b] D. P. Freyberg, J. L. Robbins, K. N. Raymond, J. L. Smart, *J. Am. Chem. Soc.* **1979**, *101*, 892–897.

[9] [9a] H. Günther, S. Castellano, *Ber. Bunsenges. Phys. Chem.* **1966**, *70*, 913–918. – [9b] H. H. Huang, *Chem. Commun.* **1969**, 815.

[10] F. A. Cotton, G. Wilkinson, P. L. Gaus, *Grundlagen der Anorganischen Chemie*, VCH, Weinheim, **1990**, p. 96.

[11] F. H. Allen, J. Trotter, C. S. Williston, *J. Chem. Soc. A* **1970**, 907–911.

[12] B. Farlow, T. A. Nile, J. L. Walsh, *Polyhedron* **1993**, *12*, 2891–2894.

[13] E. C. Constable, A. J. Edwards, R. Martínez-Máñez, P. R. Raithby, A. M. W. Cargill Thompson, *J. Chem. Soc., Dalton Trans.* **1994**, 645–650.

[14] E. Heilbronner, Z. Yang, *Top. Curr. Chem.* **1983**, *115*, 1–55.

[15] A. G. Orpen, *Chem. Rev.* **1993**, *22*, 191–197 and references cited therein.

[16] Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-58789, the names of the authors, and the journal citation.

[17] *International Tables for X-ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, England, **1974**.

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