A Pentamethylcyclopentadienyl Ligand Functionalized with a
Pendant Pyridyl Group; Crystal Structure of its Ferrocene-Type Iron Complex

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Hemilabile Cyclopentadienyl Ligands, Pyridyl-Functionalized Cyclopentadienes, Pyridyl-Functionalized Ferrocene. Crystal Structure

The novel cyclopentadiene $HMe_4C_5CH_2CMe_2py$ [py = 2-(4-tert-butyl)pyridyl] **2H** has been prepared from tetramethylfulvene and lithiated 2-isopropyl-4-tert-butylpyridine. Lithiation of **2H** with Bu^nLi and subsequent reaction with $FeCl_2$ yields the ferrocene $(2)_2Fe$, which crystallizes in the triclinic space group $P\bar{1}$ with $a = 8.368(1)$, $b = 8.468(1)$, $c = 14.313(1)$ Å, $\alpha = 80.64(1)$, $\beta = 86.67(1)$, $\gamma = 80.12(1)°$ and $V = 985.4(2)$ Å^3.

More than 80% of all organometallic compounds of the transition metals are cyclopentadienyl complexes with C_5H_5 (Cp) and C_5Me_5 (Cp*) as the most prominent cyclopentadienyl systems used [1]. However, during the past few years functionalized cyclopentadienyl systems that do not just act as innocent spectator ligands are also attracting considerable attention [2]. Among these, systems with a pendant nitrogen donor group form an important class of hemilabile cyclopentadienyl ligands, which have, for example, proved useful for the stabilization of reactive metal-ligand fragments serving as MOCVD precursors or molecular catalysts [3].

Very recently, the groups of Nile [4] and Lappert [5] have presented work on pyridyl-substituted cyclopentadienyl ligands $RC_5H_3-X-pyr$ **1** (pyr = o-pyridyl; **a:** R = H, X = CMe_2; **b:** R = H, X = CMe_2CH_2; **c:** R = $SiMe_3$, X = CMe_2; **d:** R = $SiMe_3$, X = CMe_2CH_2). The synthesis of one of the parent cyclopentadienes (**1aH**), which to date are the only examples of this type of compounds, had been described by Nile et al. [4].

We here report the synthesis and properties of the cyclopentadiene **2H**, which is related to **1bH** in the same way as CpH is related to Cp*H.

It is expected that the cyclopentadienyl moiety of **2** will have many of the well-known advantages of the Cp* ligand [6]; the pyridyl N atom of **2** is sterically shielded by the bulky ortho substituent

2H
(one of three isomers)
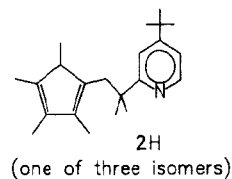
and will thus show intramolecular coordination to strong Lewis acid centres only [7]. This ligand design should prove useful for the "reversible" stabilization of 14 electron cationic alkyl complexes similar to those described by Jordan et al. [8].

The cyclopentadiene **2H** can be prepared in 52% yield by reaction of tetramethylfulvene with lithiated 2-isopropyl-4-tert-butylpyridine and subsequent aqueous work-up; the product is obtained as a mixture of regioisomers.

Reaction of **2H** with Bu^nLi yields the lithio derivative **2Li**. This can be reacted with iron(II) chloride (0.5 equiv.) to give the ferrocene $(2)_2Fe$ in 62% yield. The structure of this compound has been determined from single-crystal X-ray diffraction data (Fig. 1). Atomic coordinates and isotropic displacement parameters are given in Table I.

The centrosymmetric molecule is essentially unstrained. Bond distances and angles are unexceptional. The cyclopentadienyl rings are arranged in a staggered conformation; the iron-ring centroid distance is 166 pm, which is identical to the value observed for ferrocene and decamethyl ferrocene [9]. A slight distortion occurs only at C(10): the angle C(5)–C(10)–C(13) (116°) and the bond distance C(10)–C(11) (155.5 pm) are the largest observed for an sp^3 C atom in the molecule.

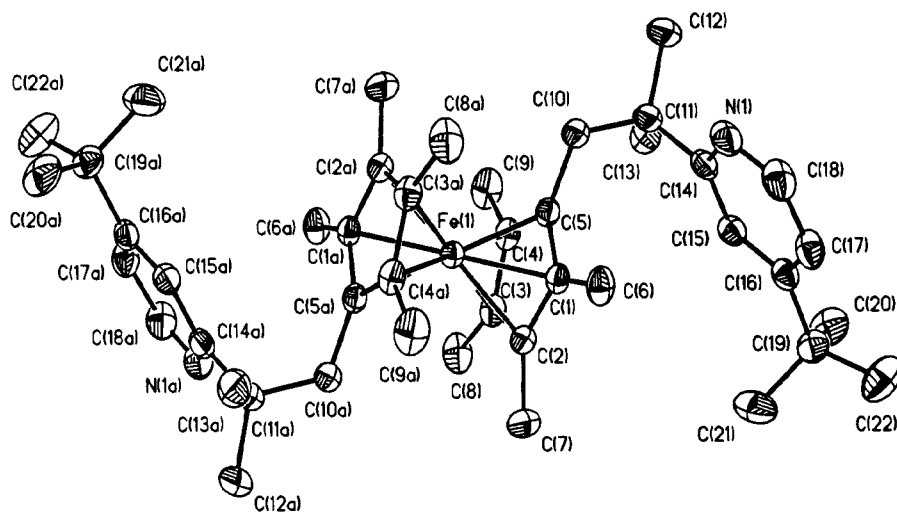* Reprint requests to Dr. U. Siemeling.

Fig. 1. Molecular structure of $(2)_2$Fe. Selected bond distances [Å] and angles [°]: N(1)–C(14) 1.344(2), N(1)–C(18) 1.324(2), C(1)–C(2) 1.425(2), C(1)–C(5) 1.431(2), C(1)–C(6) 1.499(2), C(2)–C(3) 1.425(2), C(2)–C(7) 1.502(2), C(3)–C(4) 1.428(2), C(3)–C(8) 1.505(2), C(4)–C(5) 1.430(2), C(4)–C(9) 1.499(2), C(5)–C(10) 1.506(2), C(10)–C(11) 1.555(2), C(11)–C(14) 1.527(2), C(11)–C(13) 1.530(2), C(11)–C(12) 1.545(2); C(2)–C(1)–C(5) 108.09(12), C(1)–C(2)–C(3) 108.24(12), C(2)–C(3)–C(4) 107.85(12), C(3)–C(4)–C(5) 108.22(12), C(4)–C(5)–C(1) 107.59(12), C(5)–C(10)–C(11) 116.04(12), C(14)–C(11)–C(10) 108.95(12), C(13)–C(11)–C(12) 108.64(14).

Table I. Atomic coordinates $(\times 10^4)$ and isotropic displacement parameters U_{iso} or U_{eq}^a $[Å^2 \times 10^3]$ for $(2)_2$Fe.

Atom	x	y	z	U_{eq}
Fe(1)	0	0	0	21(1)
N(1)	–999(2)	–137(2)	3883(1)	40(1)
C(1)	–1335(2)	986(2)	1074(1)	25(1)
C(2)	–2150(2)	1521(2)	204(1)	27(1)
C(3)	–2455(2)	129(2)	–154(1)	29(1)
C(4)	–1829(2)	–1273(2)	499(1)	28(1)
C(5)	–1145(2)	–747(2)	1264(1)	25(1)
C(6)	–825(2)	2087(2)	1679(1)	34(1)
C(7)	–2691(2)	3252(2)	–234(1)	42(1)
C(8)	–3353(2)	141(2)	–1036(1)	44(1)
C(9)	–1954(2)	–2977(2)	387(1)	44(1)
C(10)	–377(2)	–1833(2)	2115(1)	32(1)
C(11)	–1530(2)	–2187(2)	2987(1)	35(1)
C(12)	–534(2)	–3433(2)	3735(1)	54(1)
C(13)	–2954(2)	–2923(2)	2719(1)	43(1)
C(14)	–2104(2)	–620(2)	3395(1)	31(1)
C(15)	–3645(2)	286(2)	3255(1)	29(1)
C(16)	–4111(2)	1720(2)	3632(1)	29(1)
C(17)	–2957(2)	2185(2)	4141(1)	36(1)
C(18)	–1439(2)	1223(2)	4242(1)	42(1)
C(19)	–5792(2)	2733(2)	3458(1)	35(1)
C(20)	–7092(2)	1650(2)	3667(2)	51(1)
C(21)	–5852(2)	3529(2)	2420(1)	53(1)
C(22)	–6147(2)	4056(3)	4089(2)	58(1)

^{a} U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Studies concerning ligands of type **2** with sterically less congested pyridyl units and possible applications of these ligands for single-component Ziegler-Natta initiators are currently underway.

Our preliminary results and those obtained by Nile and Lappert suggest the development of a rich chemistry of pyridyl-substituted cyclopentadienyl ligands, akin to that of the pyridylphosphanes [10].

Experimental

The experiments were carried out with rigorous exclusion of oxygen and moisture under purified argon using standard Schlenk techniques. Solvents and reagents were dried and purified prior to use. – NMR: Bruker AM 300 (300.133 MHz, ^{1}H, external TMS; 75.453 MHz, ^{13}C, external TMS); where necessary, assignments of ^{13}C NMR signals were made by using *J*-modulated spectra. – Elemental analyses: microanalytical laboratory of the Universität Bielefeld.

2-Isopropyl-4-tert-butylpyridine

This compound was synthesized by a Ziegler reaction [11] of 4-*tert*-butylpyridine with isopropyllithium [12]: Isopropyllithium (415 ml, 1.65 M in *n*-hexane, 685 mmol) is added dropwise with stirring to a solution of 4-*tert*-butylpyridine (92.3 g.

683 mmol) in n-hexane (300 ml) cooled to -80 °C. After warming to room temperature the mixture is refluxed for 36 h. After standard aqueous work-up, vacuum distillation yields 119 g (98%) of 2-isopropyl-4-tert-butylpyridine as a colourless liquid; b.p.$_5$ 77-80 °C. - ^{1}H NMR (CDCl$_3$): δ = 1.27 (d, ^3J = 7.0 Hz, 6H; CH$\underline{Me}_2$); 1.28 (s, 9H; Bu^t); 3.00 (sept, ^3J = 7.0 Hz, 1H; C$\underline{H}$Me$_2$); 7.05, 7.10, 8.42 (all m, 3H, aromatic CH).

Compound 2H (mixture of isomers)

Tetramethylfulvene [3f] (6.00 g, 44.7 mmol) in THF (30 ml) is added dropwise to a stirred solution of lithiated 2-isopropyl-4-tert-butylpyridine [prepared from 2-isopropyl-4-tert-butylpyridine (8.33 g, 47.0 mmol) and Bu^{n}Li (30 ml, 1.57 M in hexane, 47.1 mmol) in THF (100 ml)]. After standard aqueous work-up and subsequent vacuum distillation 2H (7.20 g, 52%) is obtained as a viscous yellow oil; b.p.$_{0.05}$ 110-118 °C. - ^{1}H NMR (CDCl$_3$): δ = 0.67, 0.96 (both d, ^3J = 7.6 Hz, 3H, allylic Me); 1.21, 1.25 (both s, 9H, Bu^t); 1.30, 1.38 (both s, 6H, CH$_2$C$\underline{Me}_2$); 1.63, 1.64, 1.69 (all s, 9H, vinylic Me); 2.48-2.65 (m, 3H, CH$_2$ and allylic ring H); 7.05-7.17 (m, 2H, pyridyl H); 8.45-8.47 (m, 1H, pyridyl H). - ^{13}C NMR (CDCl$_3$): δ = 10.9, 11.0, 11.6, 11.7, 12.6, 14.3, 14.6 (cyclopentadienyl Me); 26.3, 27.9, 28.0, 29.5 (C$\underline{Me}_2$); 30.5 (C$\underline{Me}_3$); 34.7 (C$\underline{Me}_3$); 39.1, 40.0 (CH$_2$); 42.4, 42.6 (C$\underline{Me}_2$); 50.2, 51.6, (allylic CH); 117.1, 117.7, 117.8, 117.9 (pyridyl CH); 133.4, 134.9, 136.0, 137.3, 139.0, 140.0, 142.0 (vinylic cyclopentadienyl C); 148.3 (pyridyl CH); 159.2, 159.3, 167.5, 167.9 (pyridyl C).

Analysis for C$_{22}$H$_{33}$N (311.5)

Calcd	C 84.83	H 10.68	N 4.50%,
Found	C 84.69	H 10.67	N 4.49%.

(2)$_2$Fe

Bu^{n}Li (5.00 ml, 1.58 M in hexane, 7.90 mmol) is added dropwise to a stirred solution of 2H (2.65 g, 7.90 mmol) in THF (15 ml). The resultant solution of 2Li is added dropwise to a stirred suspension of FeCl$_2$ (500 mg, 3.95 mmol) in THF (30 ml) at

0 °C. The mixture is stirred at room temperature overnight. Volatiles are removed in vacuo. The resultant brown solid is extracted with n-hexane (50 ml). After filtration through Florisil and crystallization, (2)$_2$Fe (1.67 g, 62%) is obtained as yellow crystals. - ^{1}H NMR (CDCl$_3$): δ = 1.07 (s, 12H, cyclopentadienyl Me); 1.16 (s, 18H, Bu^t); 1.29 (s, 12H, CMe$_2$); 1.41 (s, 12H, cyclopentadienyl Me); 2.31 (s, 4H, CH$_2$); 6.91, 6.99, 8.41 (all m, 6H, pyridyl H). - ^{13}C NMR (CDCl$_3$): δ = 9.5, 10.5 (cyclopentadienyl Me); 28.1 (C$\underline{Me}_2$); 30.4 (C$\underline{Me}_3$); 34.6 (C$\underline{Me}_2$); 39.7 (CH$_2$); 43.0 (C$\underline{Me}_3$); 78.8, 78.9, 80.1 (cyclopentadienyl C); 117.6, 118.1, 148.1 (pyridyl CH); 158.9, 167.6 (pyridyl C).

Analysis for C$_{44}$H$_{64}$FeN$_2$ (676.9)

Calcd	C 78.08	H 9.53	N 4.14%,
Found	C 78.01	H 9.28	N 4.14%.

Crystal structure determination of compound (2)$_2$Fe

Siemens P2$_1$ four-circle diffractometer, graphite-monochromated Mo-K$_\alpha$ radiation (λ = 0.71073 Å). Structure solution by direct methods; full-matrix least-squares refinement on F^2 (Siemens SHELXTL plus. SHELXL-93). R values: $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^2)^{1/2}$. C$_{44}H_{64}FeN_2$: triclinic space group P$\bar{1}$, a = 8.368(1), b = 8.468(1), c = 14.313(1) Å, α = 80.64(1), β = 86.67(1), γ = 80.12(1)°, V = 985.4(2), Z = 1, d_{calcd} = 1.141 mg cm^{-3}, μ = 0.414 mm^{-1}, F(000) = 368. The integrated intensities of 9651 reflections were measured at 173 K, 4498 of which were unique (R_{int} = 0.029). The non-hydrogen atoms were refined anisotropically; all hydrogen atoms were located by difference Fourier syntheses and were refined isotropically without constraints. All unique structure factors were used in the final refinement cycles. Final $R1$ = 0.044, $wR2$ = 0.097. Residual electron density: +0.3/ -0.2 e/Å^3. [13].

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