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Synthesis and structure of $Fe[C_5(CH_2Ph)_5]_2$ and $Lu(C_8H_8)[C_5(CH_2Ph)_5]$ *

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Abstract

The crystal structures of decabenzylferrocene, $Fe[C_5(CH_2Ph)_5]_2$ (**1**), obtained from $FeCl_2$ and $LiC_5(CH_2Ph)_5$ at low temperature and (cyclooctatetraenyl)(pentabenzylcyclopentadienyl)lutetium, $Lu(C_8H_8)[C_5(CH_2Ph)_5]$ (**2**), obtained from $(C_8H_8)LuCl(thf)$ and $KC_5(CH_2Ph)_5$ (**3**), have been determined. **1** crystallizes in the space group $P2_1/c$ with a 1388.5(2), b 2213.1(6), c 2373.0(3) pm, β 103.50(1)°, and $V = 7.0905 \times 10^6$ pm^3. Solution of the structure led to final values of $R = 0.043$ (unit weights) for 11181 observed reflections with $F_o \geq 6\sigma(F_o)$. Crystals of **2** belong to the space group $P2_1/a$. The unit-cell parameters for **2** are a 1799.0(2), b 1030.2(1), c 1902.3(2) pm, β 97.41(1)°, $V = 3.4962 \times 10^6$ pm^3 with final values of $R = 0.021$ and $R_w = 0.030$ for 7453 observed reflections with $F_o \geq 3\sigma(F_o)$.

Introduction

The relatively "young" ligand $(PhCH_2)_5C_5^-$ was first used in the synthesis of decabenzyl-germanocene, -stannocene and -plumbocene, $E[C_5(CH_2Ph)_5]_2$ (E = Ge, Sn, Pb) which posess a bent structure [1,2].

Depending on the crystallization conditions, $TlC_5(CH_2Ph)_5$ forms two modifications, needles and parallelepipeds, which both consist of covalent, monomeric molecules. In the needles they are arranged in a linear chain [3], whereas in the parallelepipeds two molecules form a "quasi-dimeric" unit [4].

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* In memoriam Professor Dr. Jerold J. Zuckerman.

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Until now, pentabenzyl-transition-metal systems are limited to $M(CO)_2[C_5(CH_2Ph)_5]$ with M = Co and Rh [5]. All our previous efforts to prepare organolanthanoid derivatives were without success. The reactions between SmI_2, YbI_2 or $YbCl_2$ and $LiC_5(CH_2Ph)_5$ or $KC_5(CH_2Ph)_5$ in thf, between Yb and $C_5H(CH_2Ph)_5$ in liquid ammonia, or between Sm or Yb and $Sn[C_5(CH_2Ph)_5]_2$ or $TlC_5(CH_2Ph)_5$ as ligand carriers in thf or toluene did not afford the desired products.

Syntheses and properties

The synthesis of $Fe[C_5(CH_2Ph)_5]_2$ (**1**) proved to be quite dependent on the solvent and the reaction temperature. Thus, all efforts failed to obtain **1** from $FeCl_2$ and $LiC_5(CH_2Ph)_5$ [2] in thf at room-temperature. Reduction of $FeCl_2$ to metallic iron is the major process. When we used $TlC_5(CH_2Ph)_5$ as a possible ligand carrier, we only recovered the starting materials. However, if the reaction of $FeCl_2$ with $LiC_5(CH_2Ph)_5$ is conducted at −80 to −40 °C in thf or diethyl ether, **1** is isolated in yields of 45 or 70% respectively. Even under these conditions the reduction of $FeCl_2$ is observed as a side reaction.

$$FeCl_2 + 2\ LiC_5(CH_2Ph)_5 \xrightarrow[-80\text{ to }-40\,^\circ C]{\text{thf or ether}} \underset{(\mathbf{1})}{Fe[C_5(CH_2Ph)_5]_2} + 2\ LiCl$$

1 is isolated as yellow crystals of parallelepipedal form. They contain only weakly bonded solvent molecules (thf or toluene from the isolation process), which are easy to remove by washing (e.g. with hexane), by drying in vacuo, or by prolonged standing. Each procedure leaves powders, which melt at 368 to 369 °C without decomposition. **1** is stable in air, shows a good solubility in polar solvents like thf, di- or trichloromethane, but is only less soluble in cold toluene or benzene.

$Lu(C_8H_8)[C_5(CH_2Ph)_5]$, the first pentabenzylcyclopentadienyl complex of a lanthanoid, has been prepared by the reaction of $(C_8H_8)LuCl \cdot thf$ [7] with $KC_5(CH_2Ph)_5$ (**3**) in thf at room temperature. **3** is obtained by the reaction of $C_5H(CH_2Ph)_5$ with exactly the stoichiometric amount of potassium in toluene at 80 °C as an off-white, yellowish powder. When potassium is used in excess a deep-blue powder is formed the constitution of which is not yet clarified.

$$C_5H(CH_2Ph)_5 + K \xrightarrow[80\,^\circ C]{\text{toluene}} \underset{(\mathbf{3})}{KC_5(CH_2Ph)_5} + \tfrac{1}{2}H_2$$

$$\underset{(\mathbf{3})}{KC_5(CH_2Ph)_5} + (C_8H_8)LuCl \cdot thf \xrightarrow{\text{thf}} \underset{(\mathbf{2})}{Lu(C_8H_8)[C_5(CH_2Ph)_5]} + KCl$$

2, a colorless crystalline substance, is highly soluble in thf or toluene but only less in pentane. In contrast to $Lu(C_8H_8)(C_5Me_5)$ [8] it is neither dissolved nor attacked by 50% aqueous acetic acid within 30 min nor oxidized to Lu^{3+} by oxalic acid. However, on standing in air **2** decomposes within a few minutes.

Nuclear magnetic resonance

^{13}C NMR studies on **1** indicate a free rotation and equilibration of the phenyl or benzyl groups. Only six sets of signals according to the six sets of differently bonded carbon atoms (cyclopentadienyl-C, methylene-C, quarternary-, *ortho*-, *meta*, and *para*-phenyl-C) are observed. The room-temperature spectrum of **2** shows the same feature together with the additional signal for C_8H_8.

Molecular model studies for **1** based on the X-ray structural results (see below) suggest that only the phenyl ring but not the benzyl group as a whole can rotate. Steric hindrance caused by the opposite pentabenzylcyclopentadienyl ring should prevent the rotation of the benzyl moiety around the methylene–cyclopentadienyl carbon bond. The studies also suggest that the rotation of the phenyl rings may easily be frozen due to the obvious steric hindrance among them. However, low-temperature ^{13}C NMR studies down to $-45\,^\circ C$ did not show any sign of coalescence or splitting for the *ortho*- and *meta*-phenyl-carbon signals. Below that temperature the solubility of **1** in deutero-thf, -methylene chloride or -chloroform decreased dramatically, so that ^{13}C-NMR studies were no longer feasible. The interpretation of the splitting and the assignment of the $^nJ(C,H)$ coupling constants in the ^1H-coupled ^{13}C-NMR-spectrum of **1** is based on the assumption of a first-order coupling. The coupling constants are in good agreement with the one observed for benzene or toluene [9].

Compared with **1** and **2**, the ^1H and ^{13}C NMR spectrum of the potassium salt **3**, recorded in deutero-dimethylsulfoxide (DMSO-d_6) or deutero-thf, is more complex. Thirteen or eleven different carbon signals could be resolved, although the expected six signals have the major intensity.

X-ray crystal structure

Decabenzylferrocene (1)

The atom coordinates are listed in Table 1. Fig. 1 shows an ORTEP-plot of a molecule of **1** viewed parallel to the cyclopentadienyl-ring planes, and Fig. 2 gives a view perpendicular to the ring planes. The X-ray structure displays a parallel and staggered conformation of the cyclopentadienyl rings as expected for a ferrocene analogue [11–15]. Fe–C_{ring} distances (Table 2) show no differences to those observed in the unsubstituted [11,12] and decamethyl-substituted ferrocene [13–15]. The asymmetric unit consists of one molecule of **1** and two molecules of toluene.

The methylene groups are tilted out of the plane of the cyclopentadienyl ring, seven of them towards the iron center by 0.8–1.6° (deviation by 2.2(2)–4.2(2) pm from the Cp-ring plane), two of them away from the iron atom by 2.0–2.5° (deviation by 5.4(2)–6.6(2) pm), one methylene group lies in the plane of the Cp-ring. A similar inclination is seen in decamethylferrocene for the CH_3 groups [13,15].

More remarkable is the fact that all five phenyl groups of each ligand lie on the same side of the cyclopentadienyl ring, unexpected from previous studies on metal complexes of $C_5(CH_2Ph)_5^-$ [1–5]. However, this orientation can not be attributed to a missing metal–phenyl π-interaction, but to the steric situation caused by the opposite pentabenzylcyclopentadienyl moiety in conjunction with the small iron atom in between. Molecular model studies clearly demonstrate the inability of a benzyl group to rotate around the CH_2–C_5 carbon bond or to be oriented towards the iron, owing to lack of space. The repulsion and the steric crowding by the methylene groups of the opposite pentabenzylcyclopentadienyl ring are in their turn a consequence of the smallness of the iron center. Thus, the observed ordering of the five benzyl groups on the same side of the ring may not be a really satisfying but

Table 1

Fractional atomic coordinates of **1** with estimated standard deviations in parentheses and equivalent isotropic thermal parameters ($Å^2$)

Atom	x/a	y/b	z/c	B_{eq}
Fe	0.06036(2)	0.24244(1)	0.16244(1)	0.88
C1	0.1953(2)	0.2814(1)	0.1968(1)	1.11
C2	0.1993(2)	0.2178(1)	0.2091(1)	1.22
C3	0.1750(2)	0.1867(1)	0.1546(1)	1.23
C4	0.1564(2)	0.2306(1)	0.1089(1)	1.12
C5	0.1690(2)	0.2892(1)	0.1351(1)	1.07
C11	0.2202(2)	0.3313(1)	0.2406(1)	1.43
C12	0.3305(2)	0.3441(1)	0.2610(1)	1.35
C13	0.3981(2)	0.3277(1)	0.2289(1)	1.95
C14	0.4980(2)	0.3418(1)	0.2484(1)	2.40
C15	0.5312(2)	0.3723(1)	0.3004(1)	2.52
C16	0.4648(2)	0.3875(1)	0.3335(1)	2.22
C17	0.3652(2)	0.3734(1)	0.3141(1)	1.68
C21	0.2225(2)	0.1894(1)	0.2687(1)	1.66
C22	0.3283(2)	0.1678(1)	0.2910(1)	1.46
C23	0.3539(2)	0.1076(1)	0.2850(1)	2.08
C24	0.4507(2)	0.0879(1)	0.3055(1)	2.47
C25	0.5234(2)	0.1276(1)	0.3329(1)	2.14
C26	0.4987(2)	0.1875(1)	0.3399(1)	2.08
C27	0.4022(2)	0.2071(1)	0.3190(1)	1.71
C31	0.1737(2)	0.1190(1)	0.1462(1)	1.65
C32	0.2690(2)	0.0930(1)	0.1352(1)	1.53
C33	0.2659(2)	0.0377(1)	0.1068(1)	1.98
C34	0.3523(2)	0.0111(1)	0.0989(1)	2.73
C35	0.4432(2)	0.0397(1)	0.1189(1)	2.74
C36	0.4471(2)	0.0950(1)	0.1466(1)	2.32
C37	0.3602(2)	0.1213(1)	0.1547(1)	1.80
C41	0.1283(2)	0.2174(1)	0.0445(1)	1.50
C42	0.2077(2)	0.2352(1)	0.0131(1)	1.40
C43	0.3018(2)	0.2097(1)	0.0283(1)	1.72
C44	0.3747(2)	0.2265(1)	−0.0001(1)	2.21
C45	0.3537(2)	0.2685(1)	−0.0447(1)	2.42
C46	0.2598(2)	0.2937(1)	−0.0608(1)	2.41
C47	0.1875(2)	0.2773(1)	−0.0314(1)	1.81
C51	0.1553(2)	0.3493(1)	0.1035(1)	1.27
C52	0.2493(2)	0.3860(1)	0.1085(1)	1.31
C53	0.3272(2)	0.3651(1)	0.0859(1)	1.56
C54	0.4109(2)	0.4001(1)	0.0885(1)	1.91
C55	0.4179(2)	0.4572(1)	0.1140(1)	2.11
C56	0.3416(2)	0.4781(1)	0.1374(1)	2.21
C57	0.2578(2)	0.4428(1)	0.1346(1)	1.77
C6	−0.0364(1)	0.2555(1)	0.2154(1)	1.07
C7	−0.0478(2)	0.1960(1)	0.1904(1)	1.11
C8	−0.0741(2)	0.2026(1)	0.1285(1)	1.09
C9	−0.0785(2)	0.2659(1)	0.1153(1)	1.05
C10	−0.0553(2)	0.2985(1)	0.1690(1)	1.12
C61	−0.0069(2)	0.2703(1)	0.2794(1)	1.23
C62	−0.0829(2)	0.2529(1)	0.3134(1)	1.28
C63	−0.1772(2)	0.2783(1)	0.3016(1)	1.57
C64	−0.2450(2)	0.2619(1)	0.3337(1)	1.91
C65	−0.2191(2)	0.2203(1)	0.3786(1)	2.00
C66	−0.1255(2)	0.1944(1)	0.3905(1)	1.85
C67	−0.0582(2)	0.2106(1)	0.3579(1)	1.56

Table 1 (continued)

Atom	x/a	y/b	z/c	B_{eq}
C71	−0.0318(2)	0.1373(1)	0.2235(1)	1.29
C72	−0.1242(2)	0.1006(1)	0.2220(1)	1.27
C73	−0.1279(2)	0.0403(1)	0.2039(1)	1.77
C74	−0.2101(2)	0.0047(1)	0.2039(1)	2.43
C75	−0.2905(2)	0.0286(1)	0.2219(1)	2.54
C76	−0.2879(2)	0.0885(1)	0.2398(1)	2.25
C77	−0.2053(2)	0.1242(1)	0.2398(1)	1.76
C81	−0.0915(2)	0.1515(1)	0.0849(1)	1.29
C82	−0.1981(2)	0.1462(1)	0.0504(1)	1.30
C83	−0.2221(2)	0.1568(1)	−0.0094(1)	1.59
C84	−0.3196(2)	0.1537(1)	−0.0412(1)	1.91
C85	−0.3947(2)	0.1399(1)	−0.0138(1)	1.99
C86	−0.3719(2)	0.1284(1)	0.0456(1)	1.88
C87	−0.2743(2)	0.1318(1)	0.0774(1)	1.56
C91	−0.1015(2)	0.2941(1)	0.0555(1)	1.20
C92	−0.2022(2)	0.3241(1)	0.0366(1)	1.31
C93	−0.2888(2)	0.2950(1)	0.0420(1)	1.71
C94	−0.3804(2)	0.3221(1)	0.0213(1)	2.30
C95	−0.3873(2)	0.3781(1)	−0.0051(1)	2.65
C96	−0.3020(2)	0.4077(1)	−0.0099(1)	2.72
C97	−0.2096(2)	0.3811(1)	0.0112(1)	1.89
C101	−0.0499(2)	0.3668(1)	0.1751(1)	1.30
C102	−0.1286(2)	0.3945(1)	0.2021(1)	1.30
C103	−0.1008(2)	0.4261(1)	0.2544(1)	1.69
C104	−0.1715(2)	0.4536(1)	0.2787(1)	2.09
C105	−0.2713(2)	0.4499(1)	0.2511(1)	2.20
C106	−0.2999(2)	0.4185(1)	0.1990(1)	2.01
C107	−0.2289(2)	0.3911(1)	0.1746(1)	1.61
Toluene molecules C111–C117 and C118–C124				
C111	0.3156(3)	0.0551(2)	0.9482(2)	3.77
C112	0.2057(2)	0.0638(1)	0.9378(1)	2.54
C113	0.1610(3)	0.1187(1)	0.9182(1)	2.72
C114	0.0596(3)	0.1262(2)	0.9094(1)	3.62
C115	−0.0001(3)	0.0793(2)	0.9193(2)	4.11
C116	0.0433(3)	0.0242(2)	0.9384(2)	3.96
C117	0.1445(3)	0.0169(1)	0.9477(1)	3.30
C118	0.3128(3)	0.4585(2)	0.9232(2)	4.16
C119	0.2023(3)	0.4568(1)	0.9175(1)	2.98
C120	0.1633(3)	0.4487(1)	0.9662(1)	3.26
C121	0.0623(3)	0.4480(2)	0.9625(2)	4.05
C122	−0.0028(3)	0.4556(2)	0.9085(2)	4.67
C123	0.0359(4)	0.4639(2)	0.8596(2)	4.62
C124	0.1363(3)	0.4643(1)	0.8643(1)	3.61

apparently a local minimum resolution for the molecule, compromising steric constraints. The question if electronic or steric effects are the decisive factor for the orientation of the benzyl groups in main-group metallocenes still remains unanswered by this structural study.

The low solubility of **1** in toluene or benzene can be explained with the steric crowding of the phenyl groups leaving no space for the solvent arene to interact

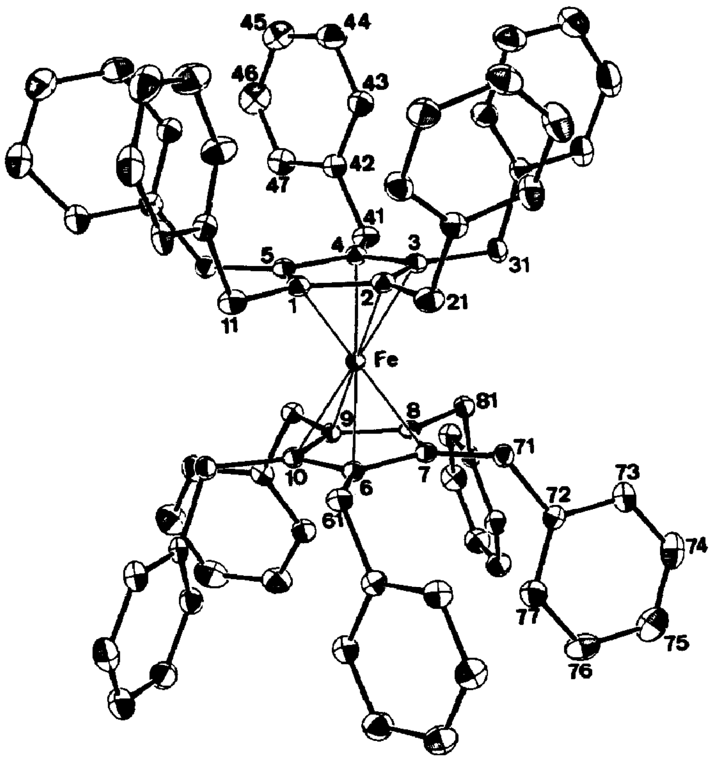

Fig. 1. ORTEP-drawing [10] of a molecule of decabenzylferrocene (1) viewed parallel to the cyclopentadienyl rings.

with the phenyls and subsequently to dissolve the molecule. In contrast the much more spacious situation in decabenzylgermanocene, stannocene, or plumbocene [1,2] as well as in **2** (see below) allows such an arene–arene interaction.

(Cyclooctatetraenyl)(pentabenzylcyclopentadienyl)lutetium (2)

The atom coordinates are listed in Table 3 and Fig. 3 shows an ORTEP-plot of a molecule of **2**, including the atomic numbering scheme. The X-ray structure shows the lutetium atom being octa-hapto bonded to the cyclooctatetraenyl- and penta-hapto bonded to the cyclopentadienyl ring-moiety, leaving no space for solvent coordination to the lutetium.

Relevant bond distances and angles are summarized in Table 4. The Lu–C_8H_8 carbon distances (range: 245.5–249.4 pm, average 246.9) compare well with corresponding Lu–C distances in $(C_8H_8)Lu[o\text{-}C_6H_4CH_2N(CH_3)_2](thf)$ (range: 252.9–257.0 pm, av.: 254.9) [16]. The Lu–cyclopentadienyl-carbon distances (average 256.3 pm) are slightly shorter than those found in pentamethylcyclopentadienyl- or cyclopentadienyl lutetium complexes, e.g. $[Li(tmed)_2][Me_5C_5Lu(CH_3)_3]$ (av. 270(2) pm) [17], $(Me_5C_5)_2Lu(\mu\text{-}CH_2)_2PMe_2$ (av. 271 pm) [18], $(Me_5C_5)_2LuCl(thf)$ (av. 263 pm) [19], $(Me_5C_5)_2Lu(\mu\text{-}S)\text{-}t\text{-}C_4H_9)_2Li(thf)_2$ (av. 266 pm) [20], and $(C_5H_5)_2Lu(\mu\text{-}SeC_6H_5)_2Li(thf)_2$ (av. 260 pm) [20].

The methylene groups show some displacement from the plane of the C_5-ring ranging from −10.5(2) (C14) to +3.8(2) pm (C19) (corresponding to −4.0° to +1.4°, respectively; a negative sign means opposite side from Lu). However, this

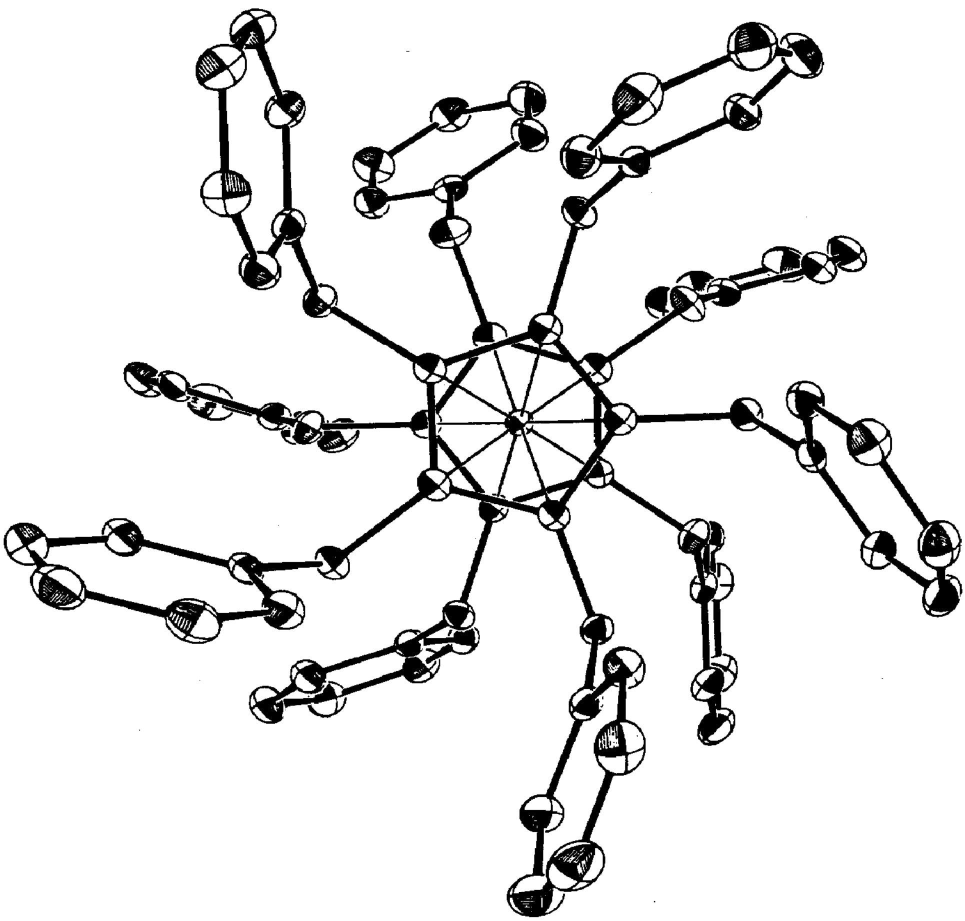

Fig. 2. ORTEP-drawing [10] of a molecule of decabenzylferrocene (1) viewed perpendicular to the C_5-ring planes.

Table 2

Relevant bond distances (pm) and angles (°) in 1 [a]

Fe–C1	205.2(2)	Fe–C6	206.1(2)
Fe–C2	206.2(2)	Fe–C7	205.2(2)
Fe–C3	205.7(2)	Fe–C8	205.0(2)
Fe–C4	206.3(2)	Fe–C9	205.7(2)
Fe–C5	205.7(2)	Fe–C10	206.3(2)
Fe–Cp1	165.8(2)	Fe–Cp2	165.5(2)
Cp1–Fe–Cp2	179.77(8)		
C1–C11–C12	114.1(2)	C6–C61–C62	114.8(2)
C2–C21–C22	115.7(2)	C7–C71–C72	115.4(2)
C3–C31–C32	114.5(2)	C8–C81–C82	113.9(2)
C4–C41–C42	113.5(2)	C9–C91–C92	115.8(2)
C5–C51–C52	115.0(2)	C10–C101–C102	114.8(2)

[a] Estimated standard deviations are given in parentheses. Cp denotes the center of the cyclopentadienyl ring. Distances and angles within the cyclopentadienyl (143.0(3)–143.5(3) pm, 107.3(2)–108.6(2)°) and the phenyl ring, and distances to the methylene group (150.2(3)–151.8(3) pm from the C_5-rings, 151.3(3)–152.1(3) pm from the Ph-rings) are normal. The deviation of the C_5-carbons out of their ring-plane is less than 0.1(2) pm.

Table 3

Fractional atomic coordinates of **2** with estimated standard deviations in parentheses and equivalent isotropic thermal parameters (Å^2)

Atom	x/a	y/b	z/c	B_{eq}
Lu	0.67313(0)	0.42588(1)	0.13453(0)	0.98
C1	0.6327(1)	0.3548(2)	0.0117(1)	2.38
C2	0.6981(1)	0.4298(2)	0.0091(1)	2.03
C3	0.7264(1)	0.5470(2)	0.0391(1)	1.98
C4	0.7025(1)	0.6397(2)	0.0857(1)	2.17
C5	0.6379(2)	0.6553(2)	0.1191(1)	2.60
C6	0.5701(2)	0.5841(3)	0.1186(1)	2.90
C7	0.5412(1)	0.4669(3)	0.0877(1)	2.95
C8	0.5676(1)	0.3711(3)	0.0440(1)	2.63
C9	0.7669(1)	0.3178(2)	0.2296(1)	0.96
C10	0.7140(1)	0.2197(2)	0.2040(1)	0.99
C11	0.6431(1)	0.2536(2)	0.2247(1)	1.07
C12	0.6518(1)	0.3734(2)	0.2622(1)	1.09
C13	0.7279(1)	0.4136(2)	0.2650(1)	1.07
C14	0.8499(1)	0.3136(2)	0.2237(1)	1.26
C15	0.8747(1)	0.3785(2)	0.1590(1)	1.31
C16	0.8991(1)	0.5072(2)	0.1627(1)	1.51
C17	0.9226(1)	0.5687(2)	0.1043(1)	1.94
C18	0.9221(1)	0.5015(2)	0.0409(1)	2.15
C19	0.9001(1)	0.3724(3)	0.0366(1)	2.18
C20	0.8768(1)	0.3111(2)	0.0954(1)	1.75
C21	0.7336(1)	0.0980(2)	0.1669(1)	1.18
C22	0.7810(1)	0.0030(2)	0.2156(1)	1.19
C23	0.8363(1)	−0.0716(2)	0.1900(1)	1.65
C24	0.8790(1)	−0.1593(2)	0.2337(1)	1.88
C25	0.8663(1)	−0.1746(2)	0.3036(1)	1.77
C26	0.8120(1)	−0.1002(2)	0.3301(1)	1.78
C27	0.7702(1)	−0.0115(2)	0.2860(1)	1.51
C28	0.5701(1)	0.1784(2)	0.2093(1)	1.24
C29	0.5633(1)	0.0598(2)	0.2557(1)	1.14
C30	0.5846(1)	−0.0620(2)	0.2340(1)	1.59
C31	0.5772(1)	−0.1715(2)	0.2754(1)	1.81
C32	0.5477(1)	−0.1617(2)	0.3382(1)	1.67
C33	0.5247(1)	−0.0422(2)	0.3602(1)	1.67
C34	0.5328(1)	0.0682(2)	0.3191(1)	1.44
C35	0.5911(1)	0.4492(2)	0.2922(1)	1.44
C36	0.5652(1)	0.3964(2)	0.3595(1)	1.29
C37	0.4903(1)	0.4112(2)	0.3691(1)	1.93
C38	0.4649(1)	0.3677(3)	0.4310(1)	2.74
C39	0.5138(1)	0.3083(3)	0.4829(1)	2.69
C40	0.5881(1)	0.2917(2)	0.4737(1)	2.05
C41	0.6136(1)	0.3357(2)	0.4121(1)	1.57
C42	0.7620(1)	0.5345(2)	0.3012(1)	1.32
C43	0.7751(1)	0.5226(2)	0.3815(1)	1.31
C44	0.8244(1)	0.4295(2)	0.4134(1)	1.64
C45	0.8372(1)	0.4180(2)	0.4866(1)	2.02
C46	0.8002(1)	0.4986(2)	0.5292(1)	2.10
C47	0.7508(1)	0.5899(2)	0.4982(1)	2.22
C48	0.7384(1)	0.6036(2)	0.4244(1)	1.76

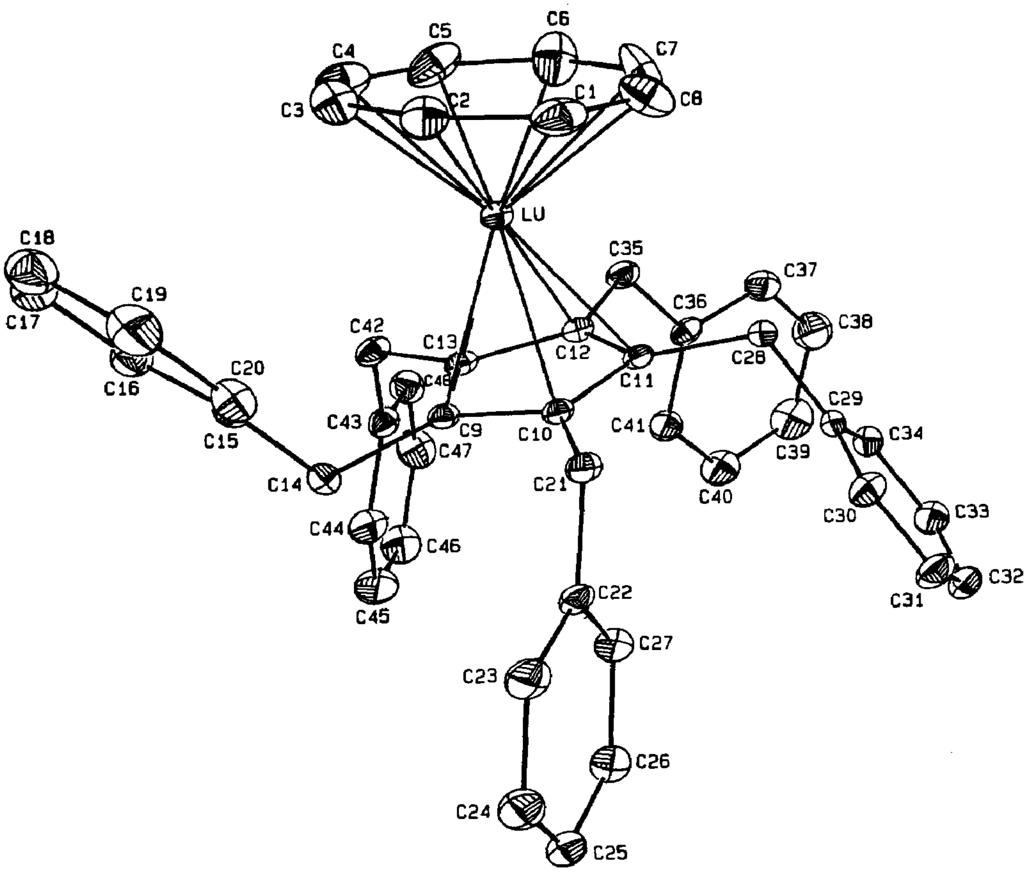

Fig. 3. ORTEP-drawing [10] of a molecule of (cyclooctatetraenyl)(pentabenzylcyclopentadienyl)lutetium (2).

deviation is small compared to out-of-plane displacements of up to 13° seen in $(Me_5C_5)_2LuCl(thf)$ [19].

The planes of the C_8- and the C_5-ring form an angle of 12.9° and the connection lines between the two ring-centroids and the lutetium enclose an angle of 167.7°. The non-parallelism of the ring planes together with the apparent lack of significant steric constraints by the C_8H_8-ring allows one phenyl group to be oriented towards the lutetium atom, just in the area of maximum opening between the two ligand ring-planes, the minimum $Lu-Ph_C$-distance being 362.9 pm (C15). The other four benzyl groups are still placed on the outside of the C_5-plane.

Since there are no lone-pair electrons at the lutetium metal center, it must be concluded that the ordering of the five benzyl groups is determined only by steric effects.

Experimental section

All manipulations were carried out in an inert gas atmosphere (nitrogen or argon) using standard Schlenk- and vacuum techniques and dried solvents.

Table 4

Relevant bond distances (pm) and angles (°) in **2** [a]

Lu–C1	246.7(2)	Lu–C9	256.3(2)
Lu–C2	248.4(2)	Lu–C10	255.9(2)
Lu–C3	249.4(2)	Lu–C11	257.3(2)
Lu–C4	247.4(2)	Lu–C12	256.5(2)
Lu–C5	245.5(2)	Lu–C13	255.3(2)
Lu–C6	245.8(2)		
Lu–C7	246.1(2)	Lu–Cp	225.7(5)
Lu–C8	245.9(2)	Lu–C_5-plane	225.70(1)
Lu–COT	164.5(5)		
Lu–C_8-plane	164.48(1)		
C1–C2	141.4(4)	C9–C10	143.0(2)
C2–C3	140.3(3)	C10–C11	142.6(3)
C3–C4	140.7(3)	C11–C12	142.4(3)
C4–C5	140.4(4)	C12–C13	142.4(3)
C5–C6	142.2(4)	C13–C9	142.9(3)
C6–C7	141.2(4)		
C7–C8	141.1(4)	C9–C14–C15	116.4(1)
C8–C1	140.1(4)	C10–C21–C22	113.3(2)
		C11–C28–C29	115.4(1)
COT–Lu–Cp	167.6(2)	C12–C35–C36	116.6(2)
C_8–C_5 plane-angle	12.9(2)	C13–C42–C43	113.1(2)

[a] Estimated standard deviations are given in parentheses. Cp and COT denote the center of gravity in the cyclopentadienyl and cyclooctatetraenyl ring, respectively. Distances and angles within the phenyl rings, angles within the cyclopentadienyl (107.7(2)–108.3(2)°) and the cyclooctatetraenyl ring (134.1(2)–135.8(2)°), and distances to the methylene groups (150.3(3)–152.1(3) pm from C_5-ring, 151.7(3)–152.9(3) pm from the Ph-rings) are normal. The C_8 carbons deviate less than 2.5(2) pm, the C_5 carbons less than 0.6(2) pm from their ring planes.

Decabenzylferrocene (1)

A solution of pentabenzylcyclopentadienyllithium, freshly prepared from $C_5H(CH_2Ph)_5$ (2.12 g, 4.10 mmol) and n-butyllithium (2.7 ml, 1.55 molar in hexane) in 10 ml of tetrahydrofuran [2] is added dropwise to a slurry of anhydrous $FeCl_2$ (0.26 g, 2.05 mmol) in 30 ml of diethyl ether at −78 °C. The first drops of the blood-red lithium salt solution are decolorized but eventually a violet-pink slurry is obtained which is allowed to warm up slowly with the cold-bath. At about −40 to −30 °C the color changes to black-green and a yellow crystalline precipitate is finally observed. When room temperature is reached stirring is continued for 5 more hours, then the solvent is removed in vacuo to give a black-green oil. Addition of toluene (40 ml) leads to the reprecipitation of the yellow crystalline solid which is flushed on a filter and extracted with the refluxing toluene in a continuous, Soxhlet-type process over the filter frit. Spontaneous crystallization occurs eventually when the toluene solution is allowed to cool, followed by ice-cooling to increase the yield. Since a fine grey metal precipitate was washed through the frit as well, a second continuous extraction with fresh toluene (25 ml) was carried out to give pure yellow crystals after cooling. The solvent is decanted and the crystals dried in vacuo overnight at 100 °C to remove coordinated solvent molecules for an unambiguous elemental analysis. 1.57 g (70%) of a yellow powdery solid (m.p. 368–369 °C, no decomposition observed) are obtained after drying.

1 can also be crystallized from thf by overlayering and slow diffusion with hexane. Substituting the ether for thf, i.e. carrying out the reaction solely in thf decreases the yield to 45% and a higher amount of reduced iron metal is observed.

IR [21*] (CsI): $\tilde{\nu}$ (cm^{-1}) 3085w, 3060m, 3025m, 3000vw, 2930sh, 2918m, 2835vw, 1950–1750vw, 1603m, 1584vw, 1495s, 1454m to s, 1445sh, 1430sh, 1180vw, 1155vw, 1075m, 1030m, 980w, 905w,br, 760sh, 730s, 694s, 610w, 500m, 461 w, 345w,br.

X-ray powder diffractogram [22 *]: 2θ(intensity $\geq 5\%$) = 6.70(100), 9.00(54), 10.00(62), 12.10(34), 13.15(24), 13.55(19), 16.05(14), 17.10(21), 17.30(38), 17.75(28), 19.10(18), 19.55(16), 19.85(29), 20.25(21), 20.50(19), 21.15(23), 21.50(40), 22.00(17), 22.70(7), 24.00(14), 24.75(11), 26.30(9), 27.30(7), 27.60(17), 29.40(5), 29.95(11), 30.35(9), 31.25(17).

^1H NMR [23*] ($CDCl_3$, conc. 90 mg/ml): δ (ppm) 4.21 (s, 10H, CH_2), 6.48–6.60 (m, 20H, Ph–H), 6.80–6.98 (m, 30H, Ph–H).

^{13}C NMR [24a*] (CD_2Cl_2, conc. 112 mg/ml): δ (ppm) [multiplicity, ^nJ(C,H), Hz] 32.95 (CH_2)[tt, ^1J(C,H) 125.5, ^3J(C,H) 4.0], 85.27 (C_5)[s], 126.01 (*para*-Ph-C)[dt, ^1J(C,H) 160.0, ^3J(C,H) 7.6], 128.16 (*meta*-Ph–C) [ddd, ^1J(C,H) 158.5, ^3J(C,H) 7.2, ^2J(C,H) 1.7], 129.61 (*ortho*-Ph-C)[d,quintet, not very good resolved, ^1J(C,H) 155.8, ^3J(C,H) 4.7], 140.62 (quarternary-Ph-C)[quintet, ^3J(C,H) 6.1].

MS [25*] (70 eV): m/e (%) = 1086 (100) $[Fe[C_5(CH_2Ph)_5]_2]^+ = M^+$, (the 200000 resolution spectrum shows the expected isotope pattern) 995 (3) $[M - PhCH_2(= 91)]^+$, 904 (25) $[M - 2PhCH_2]^+$, 813 (10) $[M - 3\ PhCH_2]^+$, 722 (5) $[M - 4\ PhCH_2]^+$, 571 (83) $[FeC_5(CH_2Ph)_5]^+$, 481/480 (19/12) $[FeC_5(CH_2Ph)_5 - PhCH_{1/2}]^+$, 390/388 (14/21) $[FeC_5(CH_2Ph)_5 - PhCH - PhCH_2/PhCH_2 - PhCH_3]$.

Analysis. Found: C, 88.14; H, 6.36. $C_{80}H_{70}Fe$ (1087.28): calc: C, 88.37; H, 6.49%.

(Cyclooctatetraenyl)(pentabenzylcyclopentadienyl)lutetium (2)

13 ml of a 0.19 molar solution of $KC_5(CH_2Ph)_5$ in thf (2.5 mmol) were added dropwise to a suspension of $(C_8H_8)LuCl(thf)$ (0.96 g, 2.6 mmol) in 100 ml of thf. After stirring for 24 h, the solvent was removed in vacuo. The remaining powder was extracted with 100 ml of toluene, the solution concentrated to 20 ml and cooled to −20 °C overnight. White crystals of **2** were isolated and dried in vacuo. Suitable crystals for X-ray analysis were grown by vapor diffusion of 25 ml of pentane into 5 ml of a concentrated solution of **2** in toluene over three days.

^1H NMR [23*] (toluene-d_8): δ (ppm) 3.65 (s, 10H, CH_2), 6.15 (s, 8H, C_8H_8), 6.6–6.8 (m, 10H, Ph-H), 6.8–7.0 (m, 15H, Ph-H).

^{13}C NMR [24b*] (toluene-d_8): δ (ppm) 32.12 (CH_2), 93.72 (C_8H_8), 120.92 (C_5), 126.06 (*para*-Ph-C), 128.28, 128.99 (*meta,ortho*-Ph-C), 141.07 (quarternary-Ph-C).

Analysis. Found: C, 72.39; H, 5.45. $C_{48}H_{43}Lu$ (794.83) calc.: C, 72.53; H, 5.45%.

Pentabenzylcyclopentadienylpotassium (3)

A suspension of potassium metal (0.42 g, 10.64 mmol) in a solution of $C_5H(CH_2Ph)_5$ (5.50 g, 10.64 mmol) in 30 ml of toluene is stirred at 80 °C for 24 h. After this time the metal has been almost completely consumed. Toluene is removed

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* Reference numbers with asterisks indicate notes in the list of references.

from the honey-yellow solution in vacuo at 50 °C. The honey-yellow, semi-solid residue is dissolved in ether (16 ml), the solution decanted, the ether again removed in vacuo and the residue stirred twice with 25 ml of hexane for 12 h each to achieve solidification. The hexane solution is decanted from the white, sticky, partly powdery residue and discarded. Drying of the residue in vacuo leaves a off-white, yellow powder (yield 3.50 g, 60%; m.p.: 129–132 °C).

^{1}H NMR [23*] (($(CD_3)_2SO$, conc. 130 mg/ml): δ (ppm) 3.64, 3.66 (s, 10H, CH_2), 7.01–7.10 (m, 25H, Ph-H); (thf-d_8): δ (ppm) 3.79, 3.82 (s, 10H, CH_2), 7.06–7.14 (m, 25H, Ph-H).

^{13}C NMR [24a*] (($(CD_3)_2SO$, conc. = 130 mg/ml): δ (ppm) 33.43*, 35.96 (CH_2), 110.21*, 110.90, 112.37 (C_2), 123.55* (splitted, *para*-Ph-C), 126.96*, 127.11 (*meta*-Ph-C), 128.41*, 128.59 (*ortho*-Ph-C), 146.75, 146.84, 147.01* (quarternary-Ph-C); (thf-d_8): δ (ppm) 34.00*, 36.54 (CH_2), 113.68*, 115.54 (C_5), 124.84 (*para*-Ph-C), 128.45 (*meta*-Ph-C), 129.03*, 129.14 (*ortho*-Ph-C), 147.30*, 147.39, 147.58 (quartenary-Ph-C); (the major signal observed for the respective carbons is indicated with an asterisk).

Analysis. Found: C, 86.08; H, 6.38. $C_{40}H_{35}K$ (554.82): calc.: C, 86.59; H, 6.36%.

X-ray structure determinations of 1 and 2

1 crystallizes as yellow cubes, crystal dimensions 0.25 × 0.29 × 0.79 mm^3; monoclinic, $P2_1/c$ from intensity statistics and structure refinement; cell parameters from 24 reflections ($20° \leq 2\theta \leq 40°$), Mo-$K_\alpha$-radiation; 17320 reflections in the 2θ range $2° \leq 2\theta \leq 55°$ with $0 \rightarrow h$, $0 \rightarrow k$ and $\bar{l} \rightarrow l$ were measured at 140(5) K with Mo-K_α-radiation (graphit monochromator), θ–2θ scan technique, variable scan width $(0.85 + 0.30 \tan\theta)°$; three standard reflections measured every hour of X-ray exposure, maximal fluctuation of 3.9%, 317 h total exposure time, no decay correction applied; no absorption correction (μ 2.23 cm^{-1}); raw data corrected for Lorentz and polarization effects and converted into structure factors; structure determination with heavy-atom technique and successive difference Fourier syntheses; refinement by block-diagonal least squares, nonhydrogen atoms anisotropically, hydrogen atoms found in the difference Fourier-map but placed on calculated positions (d(C–H) 108 pm, U_{iso} 0.4 Å^2) and added to the structure model; 14242 unique reflections; $R = 0.0434$ (unit weights) for 892 refined parameters and 11181 observed reflections ($F_o \geq 6\sigma(F_o)$); maximum shift to error ratio in the last refinement: 0.029; maximum electron density in the final difference map 0.70 e/Å^3.

2 crystallizes as white parallelepipeds, crystal dimensions 0.36 × 0.36 × 47 mm^3; monoclinic, $P2_1/a$ from intensity statistics and structure refinement; cell parameters from 56 reflections (2θ range 50–55°), Mo-K_α, 9112 unique reflections, $2\theta_{max}$ 56°, $-23 \leq h \leq 23$, $0 \leq k \leq 13$, $-25 \leq l \leq 0$, collected at 140(5) K, Mo-K_α (graphite monochromator), θ–2θ scan technique, variable scan width $(0.90 + 0.25 \tan\theta)°$, variable horizontal aperture 2.50 mm; three standard reflections measured every 1.5 h of X-ray exposure, maximal fluctuation 3.5%, 204 hours of total exposure time, decay correction; Lorentz and polarization correction, empirical absorbtion correction (μ 27.12 cm^{-1}, ψ scan method, max. transition 100%, min. transition 83%); 7453 observed data with $F_o \geq 3\sigma(F_o)$; structure determined by heavy-atom technique and succesive difference Fourier syntheses; refinement by block-diagonal least squares in which the quantity $\Sigma w(|F_o| - |F_c|)^2$ was minimized; non-hydrogen atoms refined anisotropically, all hydrogen atoms located and refined isotropically.

Table 5

Crystal and data collection parameters for **1** and **2** [a]

	1	**2**
Crystal dimensions, mm^3	0.25×0.29×0.79	0.36×0.36×0.47
Formula	$C_{80}H_{70}Fe \cdot C_{14}H_{16}$	$C_{48}H_{43}Lu$
Fw	1271.58	794.84
Space group	$P2_1/c$ [b]	$P2_1/a$ [c]
a, pm	1388.5(2)	1799.0(2)
b, pm	2213.1(6)	1036.2(1)
c, pm	2373.0(3)	1902.3(2)
β, °	103.50(1)	97.41(1)
V, $\times 10^{-30}$ m^3	7090.5	3496.2
Z	4	4
$\rho_{calc.}$, g/cm^3	1.19	1.52
μ, cm^{-1}	2.23	27.12
$F(000)$	2704	1608
Diffractometer	Enraf–Nonius CAD/4	Enraf–Nonius CAD/4
Radiation, λ, Å	Mo-K_α, 0.71069	Mo-K_α, 0.71069
Temperature, K	140(5)	140(5)
Scan technique	θ–2θ	θ–2θ
Data collected	$0 \to h, 0 \to k, \bar{l} \to l$, 17320	$\bar{h} \to h, 0 \to k, \bar{l} \to 0$
2θ limits	$2° \leq 2\theta \leq 55°$	$1° \leq 2\theta \leq 56°$
No. of unique data	14242	9112
No. of observed data	11181, $F_o \geq 6\sigma(F_o)$	7453, $F_o \geq 3\sigma(F_o)$
$R = \Sigma[\|\|F_o\| - \|F_c\|\|]/\Sigma\|F_o\|$	0.043 (unit weights)	0.021
$R_w = [\Sigma w\|\|F_o\| - \|F_c\|\|^2/\Sigma w\|F_o\|^2]^{1/2}$		0.030 $w = 1.936/[\sigma^2(F_o) + 0.0008(F_o)^2]$
No. of parameters	892	614
Corrections	Lorentz, polarization	Lorentz, polarization decay, absorption (emp.)

[a] Estimated standard deviations of the last significant digit are given in parantheses. [b] No. 14, International Tables for X-ray Crystallography. [c] Nonstandard setting of $P2_1/c$ (No. 14, International Tables for X-ray Crystallography).

$R = 0.021$, $R_w = 0.030$ for 614 parameters and 7453 observed reflections ($F_o > 3\sigma(F_o)$. $w = 1.936/[\sigma^2(F_o) + 0.0008(F_o)^2]$; maximum ratio of shift to error $(\Delta/\sigma) = 0.000$; maximum electron density in final difference map 0.96 e/Å^3 around Lu position.

All X-ray measurements on an Enraf–Nonius CAD-4 automatic diffractometer fitted with a liquid-nitrogen low temperature set-up. Scattering factors for H from Stewart, Davidson and Simpson [26]. The atomic scattering factors and anomalous-dispersion terms of Fe and Lu from International Tables for X-ray Crystallography [27]; all calculations with SHELX76 [28].

X-ray structural parameters for **1** and **2** are summarized in Table 5 [29*].

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21 Perkin–Elmer infrared spectrometer, 580B; vw = very weak, w = weak, m = medium, s = strong, sh = shoulder, br = broad; sample concentration 2–3 mg sample/300 mg CsI; against CsI as a reference.

22 Rigaku–Geigerflex diffractometer, room-temperature, Cu-K_{α}, λ 1.540562 Å.

23 Bruker WP 80 SY, 80 MHz, chemical shifts are given in the δ-scale against a TMS reference. The shifts were measured with respect to the chloroform (7.27 ppm), toluene (7.09 ppm), dimethylsulfoxide (2.49 ppm) or tetrahydrofuran (1.73 ppm) signals.

24 (a) Bruker WP 80 SY, 20.15 MHz, chemical shifts are given in the δ-scale against a TMS reference. The shifts were measured with respect to the chloroform (77.00 ppm), methylene chloride (53.80 ppm), toluene (20.40 ppm), dimethylsulfoxide (39.50 ppm) or tetrahydrofuran (25.30 ppm) signals; (b) Bruker AM 270, 67.93 MHz.

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