Organometallics 1989, *8*, 396–401

Reactive π-Complexes of the Electron-Rich Transition Metals. 3.[†] (η^4-Methylnaphthalene)iron(0) Complexes. X-ray Crystal Structure of (5–8-η-1,4-Dimethylnaphthalene)tris(trimethyl phosphite)iron

Hartmut Schäufele, Donggi Hu, Hans Pritzkow, and Ulrich Zenneck*

Anorganisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 270, D-6900 Heidelberg, FRG

Received April 29, 1988

Bis(toluene)iron (1) reacts at about −50 °C with 1-methylnaphthalene to form (η^4-1-methylnaphthalene)(η^6-toluene)iron (2). Compound 2 consists of a mixture of two isomers, in which the metal is bound either to the unsubstituted (**2a**) or to the substituted ring (**2b**) of the naphthalene derivative. A three-component reaction of iron vapor, *p*-xylene, and 1,4-dimethylnaphthalene yields (5–8-η-1,4-dimethylnaphthalene)(η^6-*p*-xylene)iron (**4a**), (1–4-η-1,4-dimethylnaphthalene)(η^6-*p*-xylene)iron (**4b**), and an uncharacterized product, 5. Compounds **2a** and **4a** are the favored isomers. Substitution reactions of 2 and 4 with phosphites allow the synthesis of new or known complexes of the type (η^6-arene)FeL$_2$ in good yields (arene = toluene or *p*-xylene) below room temperature. Compound 5 and trimethyl phosphite or Fe vapor/1,4-dimethylnaphthalene/triethyl phosphite form (5–8-η-1,4-dimethylnaphthalene)Fe[P(OR)$_3$]$_3$ [R = Me (**7a**), Et (**7b**)]. An X-ray determination of the molecular structure of **7a** proves the η^4-bonding mode of the 1,4-dimethylnaphthalene ligand which is bent 41° along C5–C8 away from the metal. The two halves of the 1,4-dimethylnaphthalene are planar. ^{1}H and ^{13}C NMR studies on the series of compounds described in this paper give clear evidence for the (η^4-methylnaphthalene)Fe units in all cases.

Introduction

Examples of structurally characterized η^4-bonding of aromatic rings to transition metals remain rare.[2] On the other hand, matrix-isolation studies clearly point out that η^4-bonding is a quite common feature of low-temperature π-arene species. The cocondensation of iron vapor with arenes around 100 K for example yields (η^4-arene)(η^6-arene)iron,[3] which is an excellent starting material for the synthesis of many stable complexes of the type (η^6-arene)FeL$_n$.[1,4] The use of naphthalene and its derviatives instead of monocyclic arenes offers an additional route to the η^4-coordination of arenes at a metal center. The retention of the aromaticity in the uncomplexed ring may provide some stabilization to the complex. However, until now only two η^4-naphthalene complexes have been characterized structurally: (η^4-octamethylnaphthalene)(η^6-benzene)ruthenium[5] and (η^4-naphthalene)(dmpe)$_2$TaCl.[6]

For iron, the UV–visible spectrum of matrix-isolated bis(η^4-naphthalene)iron is the only evidence for η^4-bonding of naphthalene derivatives.[3d] Earlier reports on (η^4-naphthalene)Fe(CO)$_3$[7] have been questioned strongly.[8] We are interested in compounds of the type (η^6-arene)(η^4-naphthalene)iron, as they are potential precursors for (η^6-arene)iron fragments under mild conditions. These fragments are useful educts for organometallic syntheses as it was shown for (η^6-toluene)bis(ethene)iron.[1]

Experimental Section

General Information. All work was carried out in an atmosphere of dry and purified nitrogen in Schlenk-type glassware. The solvents and the ligands were dried and saturated with nitrogen according to standard procedures. The handling of the thermolabile compounds requires consequent cooling of all apparatus which comes into contact with the material. Instruments used: NMR spectra, JEOL FX 90, Bruker AC 200; UV–vis spectra, Varian Cary 17; mass spectra, Finnigan MAT CH7 [EI mode (70 eV)]. Elemental analyses were performed at the analytical laboratory of the Chemische Institute, Universität Heidelberg, Heidelberg, FRG.

Cocondensation reactions are carried out in locally constructed metal-atom reactors,[9] which use resistively heated alumina crucibles in tungsten baskets as metal evaporators. Static (V = 10 L) and rotating (V = 6 L) glass reactors are used. The constructions follow published designs.[10] The reactors allow low-temperature reactions of the cocondensation products and the transfer of cold solutions under exclusion of air and moisture. Workup is done by chromatography, either at −30 °C or at room temperature, on alumina which is desactivated with 5% water.

(η^4-1-Methylnaphthalane)(η^6-toluene)iron (2) (Mixture of Two Isomers, 2a and 2b). Iron (9.05 g, 162 mmol) and toluene (300 g, 3.25 mol) are cocondensed within 100 min at 10^{-2} Pa in a static glass reactor cooled by a liquid-nitrogen bath. At −80 °C, 30 g of 1-methylnaphthalene (211 mmol) in 50 g of toluene is added. The mixture is stirred while the temperature rises slowly to a maximum of −30 °C within 2 h. The product may be purified at −30 °C by chromatography with petroleum ether. After the

---

[†] For part 2 of this series see ref 1.

(1) Zenneck, U.; Frank, W. *Angew. Chem.* **1986**, *98*, 806; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 831.

(2) Muetterties, E. L.; Bleake, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499.

(3) (a) Ozin, G. A.; Francis, C. G.; Huber, H. X.; Andrews, M.; Nazar, L. *J. Am. Chem. Soc.* **1981**, *103*, 2453. (b) Parker, S. F.; Peden, C. H. F. *J. Organomet. Chem.* **1984**, *272*, 411. (c) Shobert, A. L.; Hisatsune, I. C.; Skell, P. S. *Spectrochim. Acta, Part A* **1984**, *40A*, 609. (d) Morand, P. D.; Francis, C. G. *Organometallics* **1985**, *4*, 1653.

(4) (a) Timms, P. L. *J. Chem. Soc., Chem. Commun.* **1969**, 1033. (b) Williams-Smith, D. L.; Wolf, L. R.; Skell, P. S. *J. Am. Chem. Soc.* **1972**, *94*, 4042. (c) Middleton, R.; Hull, J. R.; Simpson, S. R.; Tomlinson, C. H.; Timms, P. L. *J. Chem. Soc., Dalton Trans.* **1973**, 120. (d) Ittel, S. D.; Tolman, C. A. *J. Organomet. Chem.* **1979**, *172*, C47; *Organometallics* **1982**, *1*, 1432. (e) Beard, L. K., Jr.; Silvon, M. P.; Skell, P. S. *J. Organomet. Chem.* **1981**, *209*, 245. (f) Radonovich, L. J.; Eyring, M. W.; Groshens, T. J.; Klabunde, K. J. *J. Am. Chem. Soc.* **1982**, *104*, 2816. (g) Green, M. L. H.; Wong, L.-L. *J. Chem. Soc., Chem. Commun.* **1984**, 1442; *J. Chem. Soc., Dalton Trans.* **1987**, 411. Green, M. L. H.; O'Hare, D.; Wong, L.-L. *J. Chem. Soc., Dalton Trans.* **1987**, 2031.

(5) Gladfelter, W. L.; Hull, J. W. *Organometallics* **1984**, *3*, 605.

(6) Albright, J. O.; Brown, L. D.; Datta, S.; Kouba, J. K.; Wreford, S. S.; Foxman, B. M. *J. Am. Chem. Soc.* **1977**, *99*, 5518. Albright, J. O.; Datta, S.; Dezube, B.; Kouba, J. K.; Marynick, D. S.; Wreford, S. S.; Foxman, B. M. *J. Am. Chem. Soc.* **1979**, *101*, 611.

(7) Harper, R. J. U.S. Patent 3073855, 1963 (assigned to the Ethyl Corp.).

(8) Manuel, T. A. *Inorg. Chem.* **1964**, *3*, 1794.

(9) Zenneck, U.; Suber, L.; Pritzkow, H.; Siebert, W. *Chem. Ber.* **1986**, *119*, 971.

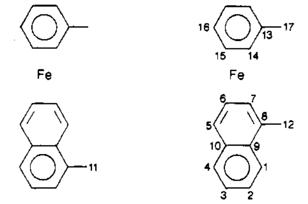
(10) Timms, P. L. *Adv. Inorg. Chem. Radiochem.* **1972**, *14*, 121. Timms, P. L.; Turney, T. W. *Adv. Metallorg. Chem.* **1977**, *15*, 53. Klabunde, K. J. *Chemistry of Free Atoms and Particles*; Academic: New York, 1980; and literature cited therein.

0276-7333/89/2308-0396$01.50/0

Table I. ^{1}H NMR Chemical Shifts of 2, 4, 7, and Related Compounds[a]

	1,4[b]	2,3	5,8	6,7	11	12	14,15	16	17	P(OR)$_3$	ref
2a	6.3–6.5[c]		2.0–2.1[c]	5.6–5.8[c]	1.98[e]	...	3.9–4.9[c]		1.88[e]	...	*d*
2b	6.3–6.5[c]		2.0–2.1[c]	5.6–5.8[c]	...	0.84[e]	3.9–4.9[c]		1.82[e]	...	*d*
4a	...	6.29	2.15	5.73	2.00	...	4.59	...	1.71	...	*d*
4b	6.52	6.30	...	5.59	...	0.77	3.90	...	2.10	...	*d*
7a	...	6.30	3.00	6.18	2.20	...	...	...	...	3.47	*d*
7b	...	6.41	2.89	6.10	2.21	...	...	...	...	3.95, 1.20	*d*
[(η^4-naphthalene)Cr(CO)$_3$]$^{2-}$ (**8**$^{2-}$)	5.6–5.7		2.00	5.23	...	...	...	...	...	...	24
(η^4-naphthalene)(DMPE)$_2$TaH (**9**)	6.59	6.39	1.50	4.47	...	...	...	...	...	...	6
(η^6-1,4-dimethylnaphthalene)$_2$Cr (**10a**)	...	6.70	5.33	4.45	2.15	...	...	...	...	...	21

[a] 200 MHz, toluene-d_8, T = −20 °C (**2**, **4**); benzene-d_6, T = 20 °C (**7**); δ vs TMS. [b] Numbering according to



[c] Assigned only as groups of multiplets. [d] This work. [e] Relative intensity is 5 (**2a**):3 (**2b**).

Table II. ^{13}C NMR Chemical Shifts of 2, 4, 7, and Related Compounds[a]

	1,4[b]	2,3	5,8	6,7	9,10	11	12	13,16	14,15	17	L	ref
2a	*c*	*c*	48.5–50.5[d]	*c*	145.5, 146[d]	17.5–19.9[d]		*c*	*c*	17.5–19.9[d]	...	*e*
2b	*c*	*c*	48.5–50.5[d]	*c*	145.5, 146[d]	17.5–19.9[d]		*c*	*c*	17.5–19.9[d]	...	*e*
4a	*c*	*c*	49.6	81.0	149	18.1	...	97.8	82.7	20.0	...	*e*
4b	*c*	*c*	49.6	77.3	144.9	...	17.9	93.1	83.2	20.0	...	*e*
7a	126.4	124.0	49.8	82.2	144.9	18.4	...	...	...	...	51.3	*e*
7b	126.1	123.8	49.5	82.5	144.7	18.5	...	...	...	...	59.6, 16.7	*e*
[(η^4-naphthalene)-Cr(CO)$_3$]$^{2-}$ (**8**$^{2-}$)	*c*	*c*	56.2	84.0	151.3	...	...	...	...	...	247.0	24
(η^6-naphthalene)$_2$Cr (**10b**)	133.9	123.0	74.9	77.7	89.2	...	...	...	...	...	...	18, 19

[a] 50.3 MHz, toluene-d_8, T = −20 °C (**2**, **4**); benzene-d_6, T = 20 °C (**7**); δ vs TMS. [b] Numbering as shown in Table I. [c] Not assigned, partly obstructed by the solvent. [d] Not assigned to a particular isomer, four lines for C5,8 and C11,12,17, respectively, two lines for C9,10. [e] This work.

solvent is pumped off at −20 °C (1 Pa), **2** is isolated as an orange-brown oil: yield, 16.3 g (56 mmol, 35%); T_{dec}(**2a** and **2b**) ≈ 0 °C. Spectroscopic data are given in Tables I, II, and V.

(η^6-Toluene)Fe[P(OPh)$_3$]$_2$ (3c). To 20 mL of a toluene solution containing 2.0 mmol of **2** is added 1.24 g (4 mmol) of P(OPh)$_3$ at −20 °C. The temperature is allowed to rise slowly. Around 0 °C, the color changes from orange to red and the reaction mixture is stirred 1 h at room temperature. Chromatography with petroleum ether and toluene followed by recrystallization from pentane yields 1.13 g (1.47 mmol, 73.5%) of red crystals, **3c**: mp 142 °C; ^{1}H NMR (C$_6$D$_6$, 90 MHz) δ 1.8 (s, 3 H), 4.4 (m, 4 H), 4.95 (m, 1 H), 7.1 (m, 30 H); ^{31}P NMR (C$_6$D$_6$, 36.4 MHz) δ 153.4. Anal. Calcd for $C_{43}H_{38}O_6P_2Fe$: C, 67.19; H, 4.95; P, 8.07. Found: C, 67.10; H, 5.07; P, 8.23.

(5–8-η-1,4-Dimethylnaphthalene)(η^6-*p*-xylene)iron (4a) and (1–4-η-1,4-Dimethylnaphthalene)(η^6-xylene)iron (4b). In a rotating reactor, 6.0 g (107 mmol) of iron is evaporated into a solution of 31 g (292 mmol) of *p*-xylene and 8.0 g (52 mmol) of 1,4-dimethylnaphthalene in 200 mL of methylcyclohexane at −120 °C (1 Pa). The reaction mixture turns dark brown. After complete evaporation of the metal, the temperature is raised to −30 °C and the mixture is filtered through alumina/5% H$_2$O yielding a brown solution which may be stored at −78 °C indefinetely. Aliquots of the solution are worked up by column chromatography at −30 °C with petroleum ether and toluene. In a typical example, 35 mL of a solution out of a total of 230 mL yields 790 mg of brown **4a**, 600 mg of brown **4b**, and 250 mg of dark brown **5** as solids after the removal of the solvent in vacuo. Converted on the basis of the whole run the yields are 5.2 g (16 mmol, 14.9%) of **4a**, 3.9 g (12.2 mmol, 11.2%) of **4b**, and 1.6 g (6.0 mmol Fe, 5.6%) of **5**. T_{dec}(**4a** and **4b**) ≈ 0 °C; T_{dec}(**5**) ≈ 10 °C. Spectroscopic data of **4a** and **4b** are given in Tables I, II, and V. **5** has not been characterized.

(η^6-*p*-Xylene)Fe[P(OEt)$_3$]$_2$ (6b). To 150 mg (0.47 mmol) of mixed crystals **4b**/**4a** (2:1) are added 10 mL of toluene, and the resulting solution is stirred with 0.5 g (3 mmol) of P(OEt)$_3$ at −10 °C. The temperature is increased slowly, and around 0 °C, the color changes from brown to red. After 1 h of stirring at room temperature, the solvent is removed and the residue is taken up in toluene. Chromatography with THF yields 190 mg (0.38 mmol, 81.4%) of **6b** as a red oil: ^{1}H NMR (C$_6$D$_6$, 90 MHz) δ 1.2 (m, 18 H), 2.4 (s, 6 H), 3.9 (m, 12 H), 4.7 (m, 4 H); ^{31}P NMR (C$_6$D$_6$, 36.4 MHz) δ 171.0. Anal. Calcd for $C_{20}H_{40}O_6P_2Fe$: C, 48.59; H, 8.16; P, 12.54. Found: C, 48.87; H, 8.45; P, 12.87.

(5–8-η-1,4-Dimethylnaphthalene)Fe[P(OMe)$_3$]$_3$ (7a). To 210 mg (0.44 mmol of Fe) of **5** in 10 mL toluene is added with stirring 1.0 g (8.0 mmol) of P(OMe)$_3$ at −10 °C. The temperature is increased slowly, and the color changes from dark brown to red around 10 °C. After 5 h of stirring at room temperature, the solvent is removed and the residue is taken up in toluene. Chromatography yields 65 mg (0.15 mmol, 33.8%) of red (η^6-*p*-xylene)Fe[P(OMe)$_3$]$_2$ (**6a**) and 125 mg (0.21 mmol, 47.4%) of orange **7a**. The analytical and spectroscopic data of **6a** are in agreement with literature values.[4d] Compound **7a** was recrystallized from pentane: mp 105 °C; MS, *m*/*e* (relative intensity) 554 (0.3, [M − 2Me]$^+$), 460 (0.2, [M − P(OMe)$_3$]$^+$), 428 (1.1, [M − 1,4-dimethylnaphthalene]$^+$); ^{31}P NMR (36.4 MHz) δ 176.5. Additional spectroscopic data are given in Tables I, II, and V. Anal. Calcd for $C_{21}H_{39}O_9P_3Fe$: C, 43,18; H, 6.73; P, 15.92. Found: C, 42.90; H, 6.74; P, 15.71.

(5–8-η-1,4-Dimethylnaphthalene)Fe[P(OEt)$_3$]$_3$ (7b). In a rotating reactor, 10.9 g (195 mmol) of iron is evaporated into a solution of 32 g (192 mmol) of P(OEt)$_3$ and 10 g (64 mmol) of 1,4-dimethylnaphthalene in 300 mL of methylenecyclohexane at −120 °C (1 Pa). The reaction mixture turns orange-brown. After the end of the reaction, the temperature is raised to 20 °C and the mixture is filtered through alumina/5% H$_2$O yielding an orange solution. Chromatography and recrystallization from pentane yield 15.5 g (21.8 mmol, 34%) of orange **7b**: mp 131 °C; ^{31}P NMR (36.4 MHz) δ 173.0. Additional spectroscopic data are given in Tables I, II, and V. Anal. Calcd for $C_{30}H_{57}O_9P_3Fe$: C, 50.71; H, 8.09; P, 13.08. Found: C, 50.70; H, 8.11; P, 13.19.

Table III. Atomic Parameters for $[C_{10}H_6(CH_3)_2]Fe[P(OCH_3)_3]_3$ (7a)

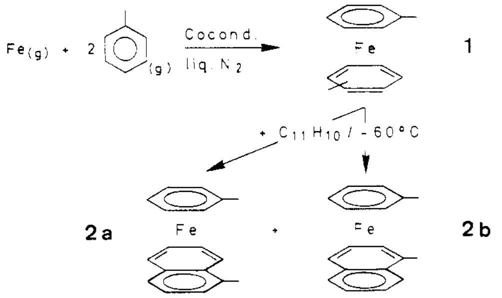
atom	x	y	z	$\bar{U}$,[a] Å^2
Fe	0.45277 (4)	0.21481 (6)	0.73776 (3)	0.040
C1	0.2852 (3)	−0.0437 (5)	0.5901 (3)	0.061
C2	0.2308 (4)	−0.0022 (7)	0.5276 (3)	0.075
C3	0.2078 (3)	0.1373 (7)	0.5146 (3)	0.075
C4	0.2385 (3)	0.2416 (5)	0.5652 (3)	0.064
C5	0.3301 (3)	0.2995 (5)	0.6867 (2)	0.053
C6	0.3299 (3)	0.2546 (5)	0.7586 (3)	0.058
C7	0.3520 (3)	0.1127 (6)	0.7723 (2)	0.061
C8	0.3718 (3)	0.0353 (4)	0.7108 (2)	0.053
C9	0.2923 (3)	0.2018 (5)	0.6275 (2)	0.052
C10	0.3155 (3)	0.0592 (5)	0.6414 (2)	0.051
C11	0.3132 (4)	−0.1971 (5)	0.6020 (4)	0.084
C12	0.2149 (5)	0.3932 (7)	0.5480 (4)	0.111
P1	0.50479 (7)	0.24583 (11)	0.64130 (6)	0.045
P2	0.50043 (8)	0.40010 (12)	0.79476 (6)	0.051
P3	0.55206 (8)	0.08644 (12)	0.79700 (7)	0.053
O1	0.6100 (2)	0.2459 (4)	0.65238 (18)	0.068
O2	0.4804 (2)	0.1320 (3)	0.57840 (15)	0.061
O3	0.4810 (2)	0.3810 (3)	0.58997 (17)	0.069
O4	0.5167 (2)	0.4106 (3)	0.88048 (16)	0.065
O5	0.4431 (4)	0.5364 (4)	0.7745 (2)	0.132
O6	0.5948 (3)	0.4557 (4)	0.7827 (2)	0.107
O7	0.5154 (3)	−0.0040 (4)	0.8582 (2)	0.108
O8	0.6361 (2)	0.1485 (4)	0.8466 (3)	0.104
O9	0.5993 (3)	−0.0371 (4)	0.7625 (2)	0.116
C13	0.6548 (4)	0.2602 (8)	0.5912 (4)	0.099
C14	0.4426 (4)	0.1544 (6)	0.5052 (3)	0.075
C15	0.4907 (6)	0.5201 (6)	0.6118 (4)	0.128
C16	0.4740 (4)	0.3290 (6)	0.9262 (3)	0.076
C17	0.4052 (4)	0.6312 (7)	0.8095 (4)	0.097
C18	0.6502 (5)	0.5426 (8)	0.8198 (4)	0.125
C19	0.5595 (5)	−0.1011 (7)	0.9043 (4)	0.120
C20	0.7175 (5)	0.1627 (10)	0.8309 (4)	0.131
C21	0.5753 (4)	−0.1039 (6)	0.6981 (3)	0.086
H1	0.218	−0.084	0.480	0.112
H2	0.158	0.162	0.470	0.084
H3	0.315	0.404	0.666	0.138
H4	0.314	0.322	0.802	0.075
H5	0.354	0.081	0.822	0.067
H6	0.395	−0.060	0.719	0.073

[a] $\bar{U}$ is defined as one-third of the trace of the orthogonalized **U** tensor.

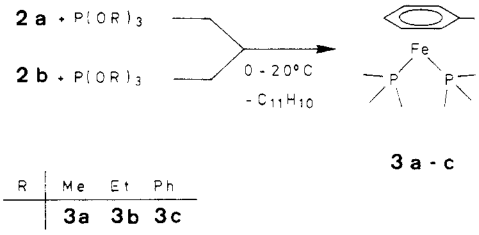
X-ray Structure Determination of 7a. Compound **7a** crystallizes in the monoclinic space group $P2_1/n$ with the cell parameters a = 15.543 (2) Å, b = 9.523 (3) Å, c = 18.864 (9) Å, β = 99.63 (3)°, V = 2752 Å^3, and Z = 4 molecules per unit cell. The cell parameters were determined by precession photographs and refined with the indexed lines of a Guinier photograph (Cu Kα_1 radiation, λ = 1.54051 Å). Intensity data were measured in the 2θ range 6.7–50.0° with a STOE Weissenberg diffractometer (Mo Kα radiation, λ = 0.7107 Å, graphite monochromator) using the ω-scan technique (scan speed 1.2° min^{-1}, with varying scan ranges $\Delta\omega = A + B \sin \mu/\tan \theta'$, A = 1.1–1.4°, B = 0.6–0.7°). Lp and a numerical absorption correction (μ(Mo Kα) = 7.4 cm^{-1}; crystal size 0.3 × 0.6 × 0.7 mm^3) were applied. A total of 4256 reflections of $I > \sigma_I$ of all 4903 measured were considered observed and used in the refinement.

The structure was solved by the heavy-atom method and refined by the least-squared method with weights $w = 1/\sigma_F^2$. Non-hydrogen atoms were refined anisotropically. The hydrogens directly bound to the naphthalene ring were located in a difference Fourier map, but only the isotropic temperature factor was refined. The methyl groups were refined as rigid groups (C–H = 0.95 Å) with one common temperature factor for the methyl groups on the naphthalene and one for those of the phosphite. The final refinement yielded R = 0.063 and R_w = 0.069. A difference Fourier map showed some additional peaks of about 1 e/Å^3 around the phosphorus atoms in distances of 1.5–1.7 Å. This may be caused by a disorder of the methoxy groups, and the peaks may be assigned to disordered positions of the oxygens. No attempt was made to refine a model with additional disordered methoxy groups. The final atomic parameters are listed in Table III and selected bond lengths and angles in Table IV. The SHELX-76[11] program system was used. Atomic scattering factors were those given by Cromer and Mann;[12] anomalous dispersion factors were taken from ref 13.

Scheme I



Scheme II



Results

(η^4-1-Methylnaphthalene)(η^6-toluene)iron (2). Bis(toluene)iron (**1**) is prepared in situ by the cocondensation of Fe vapor with toluene at a liquid-nitrogen-cooled surface.[4] Around −60 °C it is allowed to react with 1-methylnaphthalene to yield orange-brown (η^4-1-methylnaphthalene)(η^6-toluene)iron (**2**) in 35% yield (Scheme I). The same type of reaction has been carried out with the combinations bis(benzene)iron/1-methylnaphthalene, bis(p-xylene)iron/1-methylnaphthalene, **1**/naphthalene, and **1**/1,4-dimethylnaphthalene, too. In all these cases, the yields of the reactions were poor; thus workup was not attempted.

According to the ^{1}H and ^{13}C NMR spectra (Tables I and II), **2** consists of a mixture of two isomers, where the iron is bound either to the unsubstituted ring of the naphthalene (**2a**) or to the substituted ring (**2b**). As **2b** shows a very characteristic signal for the methyl group of the naphthalene at δ 0.84 (compare **4a** and **4b**), we have been able to determine the relative yields of the two isomers in spite of the fact that we did not assign the very complex spectra of **2a**/**2b** in detail. The ratio of **2a**/**2b** is 5/3, and this is confirmed throughout the spectrum, as the groupwise integration of the multiplets is always in good agreement with it.

The properties of **2a** and **2b** are very much the same; thus we cannot find any differences apart from the spectra, and attempts to separate them by chromatography failed. They decompose at 0 °C to form toluene and 1-methylnaphthalene in the ratio 1/1 and metallic iron. Exposure to air deliberates the ligands, too. Solutions of **2** may be stored at −78 °C for months without decomposition.

Reactions with ligands such as phosphites (L = trimethyl phosphite, triethyl phosphite, and triphenyl phosphite) easily form complexes (η^6-toluene)FeL$_2$ (**3**) at 0–20 °C in

---

(11) Sheldrick, G. M. SHELX76, A Program for Crystal Structure Determination; University of Cambridge: Cambridge, 1976.

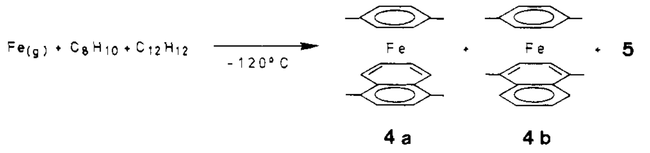
(12) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 321.

(13) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, 1974; Vol. IV, p 149.

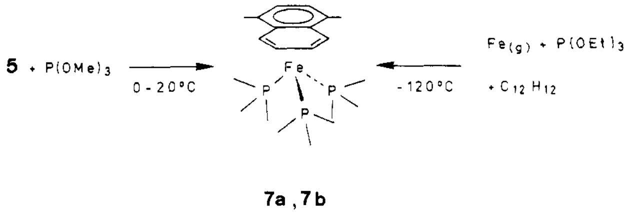
Table IV. Distances (Å) and Angles (deg) for $[C_{10}H_6(CH_3)_2]Fe[P(OCH_3)_3]_3$ (7a)

Fe–C5	2.145 (4)	C1–C2	1.388 (7)	C5–C6	1.422 (7)
Fe–C6	2.049 (5)	C1–C9	1.401 (7)	C5–C10	1.497 (6)
Fe–C7	2.040 (5)	C1–C11	1.531 (7)	C6–C7	1.407 (7)
Fe–C8	2.133 (4)	C2–C3	1.387 (9)	C7–C8	1.450 (7)
Fe–P1	2.132 (1)	C3–C4	1.405 (7)	C8–C9	1.466 (6)
Fe–P2	2.133 (1)	C4–C10	1.376 (6)	C9–C10	1.418 (6)
Fe–P3	2.133 (1)	C4–C12	1.511 (8)		
C9–C1–C2	118.3 (4)	C12–C4–C3	119.1 (4)	C5–C10–C4	124.9 (4)
C11–C1–C2	120.9 (4)	C12–C4–C10	122.5 (4)	C9–C10–C4	121.4 (4)
C11–C1–C9	120.8 (4)	C10–C5–C6	117.5 (4)	C9–C10–C5	113.7 (3)
C3–C2–C1	121.7 (5)	C7–C6–C5	115.1 (4)	C8–C9–C1	126.1 (4)
C4–C3–C2	120.6 (4)	C8–C7–C6	114.8 (4)	C10–C9–C1	119.8 (3)
C10–C4–C3	118.3 (4)	C9–C8–C7	117.4 (3)	C10–C9–C8	114.1 (3)

Scheme III



Scheme IV



good yields. The reaction with $P(OMe)_3$, which yields the known (η^6-toluene)$Fe[P(OMe)_3]_2$ (**3a**),[4d] is nearly quantitative. We use this to determine the concentration of **2** in solutions. Several other reactions of **2** have already demonstrated the use of this highly reactive, but easy to handle complex. Alkynes are catalytically cyclotrimerized by **2** below room temperature,[14] bis(trimethylsilyl)acetylene and **2** form the novel cluster tetrakis[bis(trimethylsilyl)-acetylene]diiron in up to 98% yield,[15] and *tert*-butylphosphaacetylene is cyclodimerized or transformed to five-membered rings in a pentaphosphaferrocene derivative by **2**.[16]

(η^4-1,4-Dimethylnaphthalene)(η^6-*p*-xylene)iron (4). Compound **4** is obtained best in a three-component reaction where iron is evaporated into a solution of *p*-xylene and 1,4-dimethylnaphthalene in methylcyclohexane at −120 °C. Chromatography at −30 °C yields three main fractions. The first two, which are close to each other, are the desired products **4a** (brown, 15%, first zone) and **4b** (brown, 11%). Well-separated from these two, a product, **5** (dark brown, 5.6% in respect to the iron content), is eluted from the column (Scheme III).

According to the NMR spectra the separation of **4a** and **4b** is not complete, but they are enriched by a factor of 2/1 in each of the fractions, respectively. The spectra are in good agreement with those of the proposed structures (Tables I and II) and will be discussed separately. At the moment, the structure of **5** is unknown. Oxidative decomposition yields, 1,4-dimethylnaphthalene/*p*-xylene in an approximate 2:1 ratio, and the diamagnetic NMR spectra with their many lines are in agreement with those of a mixture of compounds as well as with those of a complex structure. Properties and reactivities of **4a** and **4b** are closely related and do not differ significantly from **2a** and **2b**. Compounds **4a** and **4b** decompose around 0 °C and are air-sensitive, too. In both cases *p*-xylene and 1,4-dimethylnaphthalene are liberated in the ratio 1/1. The reaction of **4a** and **4b** with phosphites proceeds rapidly at 0–20 °C to form the known (η^6-*p*-xylene)$Fe[P(OMe)_3]_2$ (**6a**)[4d] or the new (η^6-*p*-xylene)$Fe[P(OEt)_3]_2$ (**6b**) in high yields. Thus again the naphthalene ligand is substituted exclusively, and the η^6-arene ligand remains bound to the iron.

(5–8-η-1,4-Dimethylnaphthalene)$Fe[P(OR)_3]_3$ (7). The uncharacterized product **5** of the *p*-xylene/1,4-dimethylnaphthalene/Fe reaction reacts with $P(OMe)_3$ to form **6a** (34%) and (5–8-η-1,4-dimethylnaphthalene)Fe-$[P(OMe)_3]_3$ (**7a**; 47%) (Scheme IV). There is no hint of the other isomer in which the metal is bound to the methylated ring. Separation of both products is easily achieved by column chromatography. Compound **7a** is very air-sensitive but stable to approximately 150 °C. It melts without decomposition.

An alternative route to complexes of the type **7** is the three-component reaction of the Fe vapor with triethyl phosphite and 1,4-dimethylnaphthalene in methylcyclohexane at −120 °C, which yields (5–8-η-1,4-dimethylnaphthalene)$Fe[P(OR)_3]_3$ (**7b**; 34%) (Scheme IV). The properties of **7b** and **7a** are nearly identical, and again there is no sign of the 1–4-η-isomer of **7b**. The NMR spectra of **7a** and **7b** confirm the proposed structures (vide infra), and X-ray structure determination of **7a** reveals the details in the solid state.

Molecular Structure of 7a. The main feature of **7a** (Figure 1) is the bending of the 1,4-dimethylnaphthalene ligand along C5–C8 by 41° away from the metal. Both halves of the naphthalene are nearly planar; the largest deviations from planarity are ±0.01 Å. The bonding distances Fe–C5(C8) and Fe–C6(C7) are nearly the same and do not differ much from Fe(0)–C(olefin) or Fe(0)–C(arene) distances found in (η^6-toluene)$Fe(C_2H_4)_2$, for example.[1] The distances Fe–C9(C10) are 2.96 and 2.97 (1) Å and thus are easily qualified as nonbonding interactions. By comparison of our data with the data of the two other complexes with η^4-naphthalene ligands the general features are the same:[5,6] The metal is situated above the trapezoid formed by four carbon atoms (here C5–C8). The dihedral angles between the planes through the four metal-bonded carbons and the six nonbonded ring carbons differ only by 2° in these structures. In all three cases C6–C7 is shortened in respect to C5–C6 and C7–C8 which is a common feature in coordinating conjugated dienes.[17] The distances C8–C9 and C5–C10 are the longest intra-ring

---

[14] Funhoff, A.; Schäufele, H.; Zenneck, U. *J. Organomet. Chem.* **1988**, *245*, 331.

[15] Schäufele, H.; Pritzkow, H.; Zenneck, U. *Angew. Chem.* **1988**, *100*, in press; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, in press.

[16] Drieß, M.; Hu, D.; Pritzkow, H.; Schäufele, H.; Zenneck, U.; Regitz, M.; Rösch, W. *J. Organomet. Chem.* **1987**, *334*, C35.

[17] Elschenbroich, Ch.; Salzer, A. *Organometallchemie*; Teubner, B. G., Ed.; Stuttgart: FRG, 1986.

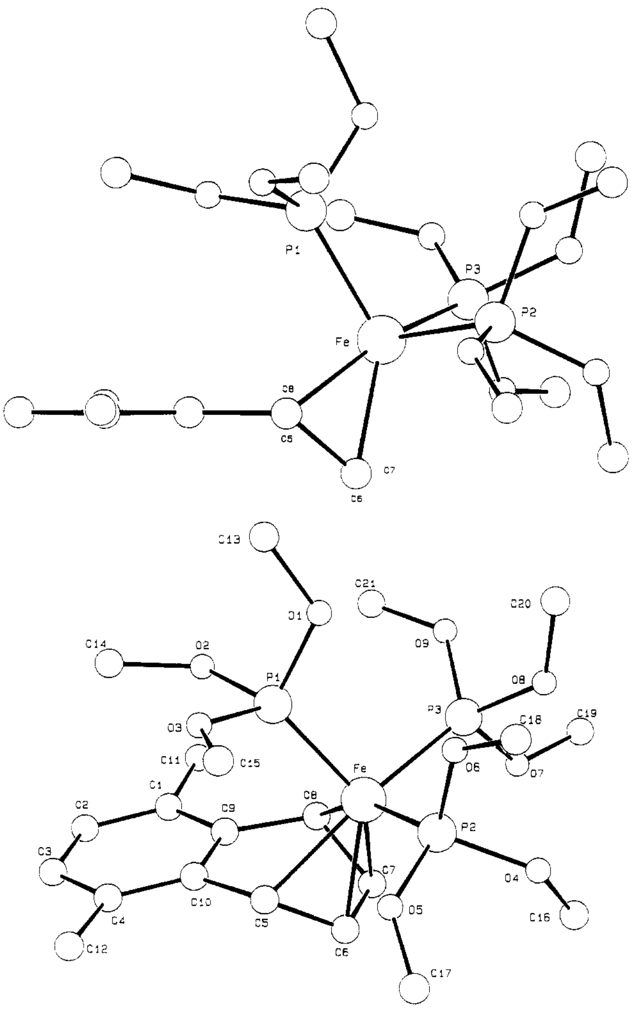


Figure 1. Two views of the molecular structure of **7a**.

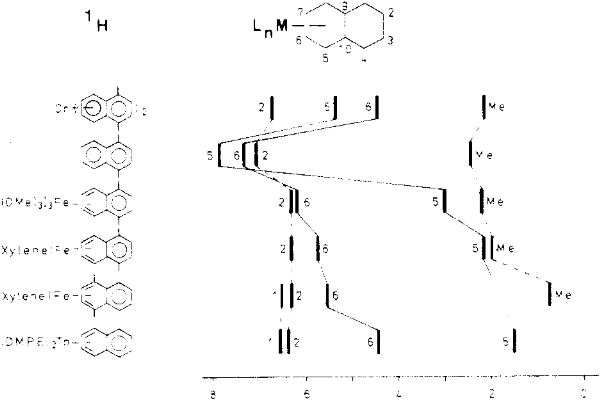


Figure 2. Schematic representations of naphthalene ^1H NMR shifts in π-complexes (δ vs TMS; for data see Table I): –, coordinated ring; - - -, free ring.

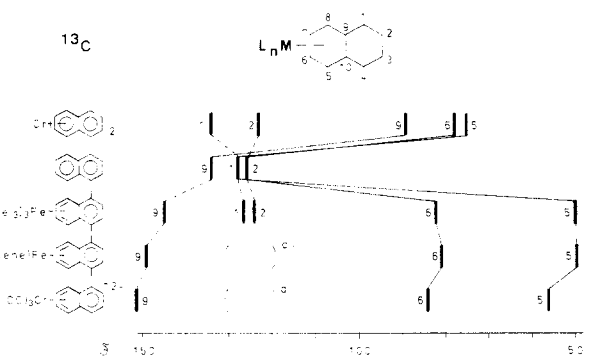


Figure 3. Schematic representations of naphthalene ^{13}C NMR shifts in π-complexes (δ vs TMS; for data see Table II): —, coordinated ring; - - -, free ring; a) obstructed by the solvent.

Table V. UV-Visible Data of 2, 4a, 4b, 7a, and Related Compounds

	absorptns[a] (nm)	ref
2	**283**, **388**, 500	*b*
4a	**287**, **395**, 495	*b*
4b	**287**, **394**, 495	*b*
7a	**276**, **388**	*b*
(η^6-naphthalene)$_2$Fe	**296**, 340, **400**, 520	3d
(η^4-1-methylnaphthalene)$_2$Fe	**336**, 372, 392	3d
(η^6-toluene)(η^4-toluene)Fe	**298**, 350, 365, 390, **427**, 470	3d

[a] Strong absorptions boldfaced. [b] This work. Solvent: pentane or petroleum ether. $T = -20$ °C (**2**, **4a**, **4b**); +20 °C (**7a**).

distances, which is a result of the reduction of π-bond delocalization for these two bonds.

NMR Spectroscopy. Both ^1H and ^{13}C NMR clearly demonstrate the η^4-bonding mode of the naphthalene derivatives in all six compounds described in this paper. The unambiguous assignments of all NMR signals of **7a** and **7b**, which have been proven by selective ^1H–^{13}C double-resonance experiments in the case of **7a**, yielded a set of parameters, which allowed us to assign the NMR signals of **4a** and **4b**. These assignments again helped to define characteristic line positions for the very complex spectra of **2a** and **2b** (two independent ABCDEFGX$_3$ spin systems). All conclusions based on NMR spectroscopy fit together without contradiction.

Schematic representations of characteristic NMR signals are given together with the line positions of related compounds (Figures 2 and 3). The ^1H signals of **4a**, **4b**, **7a**, and **7b** as well as the signals of (η^4-naphthalene)(DMPE)$_2$TaH (**9**)[6] show a strong splitting for the coordinated positions H5,8 and H6,7. H5,8 is shifted approximately 5 ppm to higher field while H6,7 is shifted only by 1–2 ppm. In consequence, these signals are found in the same regions as the corresponding diene protons of (η^6-benzene)(η^4-cyclohexa-1,3-diene)iron.[4d] η^6-Coordinated naphthalenes show significantly different behavior. Their coordination shifts for these two sets of protons are nearly the same.[19,21] ^{13}C NMR, in principle, yields the same result. Again the positions C5,8 are shifted much more to a higher field than C6,7. The bridgehead carbons C9,10 show a *low*-field shift, thus giving clear evidence of not being complexed to the metal. This is in contrast to the findings for (η^6-naphthalene)$_2$Cr (**10b**) and related compounds.[18,19] Corresponding signals of η^4-anthracene complexes[20] are found close to the η^4-naphthalene positions and are close to the signals of (η^6-benzene)(η^4-cyclohexa-1,3-diene)iron,[4d] too.

UV–Visible Spectroscopy. The only evidence for naphthalene or 1-methylnaphthalene to be coordinated to iron in complexes of the type (arene)$_2$Fe is given by UV–vis spectra of matrix-isolated species.[3d] In order to correlate our results with those reported there, we examined the optical spectra of the complexes **2**, **4a**, **4b**, and **7a**. The results are summarized in Table V. In agreement with the NMR results the absorptions of **2**, **4a**, and **4b** are nearly

---

(18) Desobry, V.; Kündig, E. P. *Helv. Chim. Acta* **1981**, *64*, 1288.

(19) Elschenbroich, Ch.; Möckel, R.; Massa, W.; Birkhahn, M.; Zenneck, U. *Chem. Ber.* **1982**, *115*, 334.

(20) Jonas, K.; Deffense, E.; Habermann, D. *Angew. Chem.* **1983**, *95*, 729; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 716; *Angew. Chem. Suppl.* **1983**, 1005.

(21) Kündig, E. P.; Timms, P. L. *J. Chem. Soc., Dalton Trans.* **1980**, 991.

identical, while the three phosphites of **7a**, which replace the η^6-ligands of **2** and **4**, cause significant shifts of the absorption maxima. Our data for **2** and **4** differ from those reported for bis(η^4-1-methylnaphthalene)iron; the difference is smaller for (η^6-toluene)(η^4-toluene)iron, but the best correlation is found for bis(η^6-naphthalene)iron.[3d] A blue shift of only 12–20 nm is observed. The relative intensity of the two strong bands are nearly the same in all four compounds, and the corresponding band to the weak shoulder at 340 nm of bis(naphthalene)iron is unresolved in our cases. A blue shift of that magnitude and a reduction of the number of bands have been observed with isostructural sandwich complexes, where a monocyclic arene replaces a naphthalene derivative.[22] Assuming that a band at 276 nm would be obscured by excess ligand in matrix studies, the absorptions of **7a** might be closely related to the UV–vis data of bis(η^4-methylnaphthalene)iron.[3d]

Discussion

The synthesis of **2** has not been optimized with respect to the yield but with respect to the amount of material produced per time unit. In this way we obtain solutions containing 15–20 g of **2** per run from elemental iron, which takes less than 1 day. As these solutions are storable at low temperatures, they may be used as excellent educts in organometallic syntheses as we have demonstrated already.[14-16] In all substitution reactions, the η^4-bound 1-methylnaphthalene ligand is replaced in the first step. Only successive reactions may replaced the toluene, too. The same behavior is found with complexes **4a** and **4b**. Again the naphthalene derivative is substituted first.

Compounds **2** as well as **4** form two coordination isomers. In both examples the metal prefers the 5–8-η-bonding mode, and in the case of phosphite complexes **7**, only these isomers are obtained. Similar observations have been made with (η^6-alkylnaphthalene)$_2$Cr complexes[21] and with (η^6-1,4-dimethylnaphthalene)Cr(CO)$_3$.[23] At −20 °C solutions containing an excess of either **4a** or **4b** show no sign of changing their relative concentrations within days. Thus, an intramolecular slippage of the metal across the 1,4-dimethylnaphthalene can be ruled out. As a consequence, the experimental ratio for these isomers is not necessarily the thermodynamic equilibrium value.

An attempt to realize a haptotropic rearrangement, $\eta^4 \rightarrow \eta^6$, for the methylnaphthalene ligands of **2** or **4** by electrochemical oxidation failed. The oxidized species do not form the proposed stable dications [(η^6-methylnaphthalene)(η^6-arene)Fe]$^{2+}$ but decompose quickly. Such a process would have afforded a slip–fold mechanism as it was observed with the 2e reduction of (η^6-naphthalene)Cr(CO)$_3$ to form [(η^4-naphthalene)Cr(CO)$_3$]$^{2-}$.[24] As a result it seems likely to assume that temperatures below 0 °C do not allow the defolding of the η^4-bound alkylnaphthalenes of **2** and **4**. This would be the precondition for slippage of the metal as well as for the haptotropic rearrangement. On the other hand, the η^4–η^2 slippage must be possible at 0 °C for these species, as reactions with ligands proceed quite readily at this temperature under the exchange of the naphthalene derivative. In this respect **2** and **4** are closely related to η^6-naphthalene complexes like (η^6-naphthalene)$_2$Cr[19,21,25,26] and (η^6-naphthalene)Cr(CO)$_3$.[27]

Acknowledgment. This work was supported by a generous grant by the Stiftung Volkswagenwerk.

Registry No. **2a**, 116018-76-9; **2b**, 117310-53-9; **3a**, 71465-08-2; **3b**, 82798-49-0; **3c**, 117526-22-4; **4a**, 117526-23-5; **4b**, 117558-98-2; **6a**, 82798-52-5; **6b**, 117526-24-6; **7a**, 117558-99-3; **7b**, 117559-00-9; 1-methylnaphthalene, 90-12-0; iron, 7439-89-6; toluene, 108-88-3; *p*-xylene, 106-42-3; 1,4-dimethylnaphthalene, 571-58-4.

Supplementary Material Available: Tables of anisotropic temperature factors, bond distances and angles, and the best planes (5 pages); a listing of structure factors (10 pages). Ordering information is given on any current masthead page.

---

[22] Morand, P. D.; Francis, C. G. *Inorg. Chem.* **1985**, *24*, 56.

[23] Deubzer, B.; Fritz, H. P.; Kreiter, C. G.; Öfele, K. *J. Organomet. Chem.* **1967**, *7*, 289.

[24] Rieke, R. D.; Henry, W. P.; Arney, J. S. *Inorg. Chem.* **1987**, *26*, 420.

[25] Kündig, E. P.; Timms, P. L. *J. Chem. Soc., Chem. Commun.* **1977**, 912.

[26] Kündig, E. P.; Perret, C.; Spichiger, S.; Bernardinelli, G. *J. Organomet. Chem.* **1985**, *286*, 183.

[27] Cais, M.; Fraenkel, D.; Weidenbaum, K. *Coord. Chem. Rev.* **1975**, *16*, 27. Yagupsky, G.; Cais, M. *Inorg. Chim. Acta* **1970**, *4*, 441.