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Journal of Organometallic Chemistry 556 (1998) 89–95

Journal of Organo metallic Chemistry

# Synthesis, structure and reactivity of an ($\eta^6$-naphthalene)iron(0) complex having a 1,2-bis(dicyclohexylphosphino)ethane ligand

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Received 1 September 1997; received in revised form 26 November 1997

**Abstract**

A zerovalent iron complex having an $\eta^6$-naphthalene ligand, Fe($\eta^6$-$C_{10}H_8$)(dcype) (**3**) [dcype = 1,2-bis(dicyclohexylphosphino)ethane] has been prepared by the reduction of high spin 14 electron dichloroiron(II) complex, $FeCl_2$(dcype) (**1**) with sodium-naphthalene. In refluxing benzene solution of **3**, the coordinated naphthalene can be replaced by benzene giving Fe($\eta^6$-$C_6H_6$)(dcype) (**4**). Exposure of **3** to CO results in the formation of $Fe(CO)_3$(dcype) (**5**). Protonation of **3** with $HBF_4$ yields cationic complex, [FeH($\eta^6$-$C_{10}H_8$)(dcype)][$BF_4$] (**6**), which can be deprotonated by lithium diisopropylamide. 

*Keywords:* Iron(0) complex; Naphthalene complex; Sodium-naphthalene; Reduction of 14e complex; Crystal structure

## 1. Introduction

Synthesis and reactivity of iron(0) complexes have been the subject of intense study relevant to the activation of C–H bonds and small molecules during the past decades. The preparation methods for iron(0) complexes are generally divided into the synthesis using atomic metal [1] or the chemical reduction of iron(II) [2]. In addition, ligand exchange reaction of zerovalent iron complexes such as $Fe(CO)_5$ is also a convenient method for preparation. Among them, much effort has been made to prepare iron(0) complexes by the chemical reduction since Chatt et al. demonstrated the reduction of $MCl_2(diphosphine)_2$ by sodium-naphthalene [2]. A number of reductions of $FeCl_2(diphosphine)_2$ have been carried out by this system, where most of these attempts gave divalent hydridoiron complexes such as $FeH(C_{10}H_7)(diphosphine)_2$ ([2]f–i). We have recently reported isolation of a zerovalent iron complex $Fe(N_2)(depe)_2$ [depe = 1,2-bis(diethylphosphino)ethane] by the reduction of $FeCl_2(depe)_2$ with sodium-naphthalene under a nitrogen atmosphere [3], while the reduction under argon led to the facile intramolecular C–H bond activation giving $FeH(MeCH$-$PEtC_2H_4PEt_2)$(depe) ([3]c). Such chemical reductions of these coordinatively saturated dichloroiron(II) complexes leading to the formation of iron(0) are still limited so far and those of coordinatively unsaturated iron(II) are rare. Followings are the examples; Muetterties et al. reported reductions of 16e $FeCl_2[P(OMe)_3]_3$ and 14e $FeCl_2(PMe_3)_2$ with sodium amalgam giving $Fe[P(OMe)_3]_5$ and $FeH[P(CH_2)Me_2](PMe_3)_3$, respectively [4]. Hoberg et al. reported the first example of a coordinatively unsaturated iron(0) complex, $Fe(C_2H_4)_2(PEt_3)_2$ by the reduction of $FeCl_2$ with magnesium in the presence of ethylene and $PEt_3$ and they determined its crystal structure [5]. Quite recently, Jolly et al. showed a series of reductions of 14e $FeCl_2$(diphosphine) and $FeCl_2(PEt_3)_2$ with activated magnesium in the presence of dienes giving (diene)iron(0) or hydrido(dienyl)iron(II) complexes [6].

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*PII* S0022-328X(97)00770-5

Girolami et al. produced zerovalent Fe($\eta^6$-$C_6H_4Me_2$-1,4)(dippe) [dippe = 1,2-bis(diisopropyl-phosphino)-ethane] by the hydrogenation of Fe($CH_2C_6H_4Me$-4)$_2$(dippe) [7]. However, in most of these reductions, intramolecular C–H bond activation of ancillary phosphine or added diene, or formation of a coordinatively saturated homoleptic complex are observed. In this paper, we wish to report the reduction of 14e dichloroiron(II) complex having a bulky diphosphine $FeCl_2$(dcype) (**1**) [dcype = 1,2-bis(dicyclohexylphosphino)ethane] with sodium-naphthalene giving zerovalent Fe($\eta^6$-$C_{10}H_8$)(dcype) (**3**), the structure and the chemical reactivities of **3** are also described.

## 2. Results and discussion

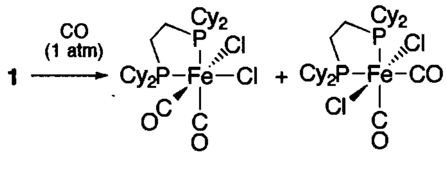
### 2.1. Preparation of $FeCl_2$(dcype) (*1*)

Although Jolly et al. has reported in situ reaction of $FeCl_2 \cdot 1.5THF$, dcype, and a diene in THF in the presence of active Mg [6]b, no isolation and characterization of $FeCl_2$(dcype) (**1**) have been performed. Since the coordinatively unsaturated iron complexes formulated as $FeCl_2L_2$ tend to be stabilized in benzene [8], we thus employed benzene as solvent for the preparation of **1**. Reaction of anhydrous $FeCl_2$ with dcype in benzene at 70°C quantitatively yielded light purple powder of **1**. Recrystallization of **1** from benzene gave light purple needles [Eq. (1)].

$$\mathrm{FeCl_2 + dcype \xrightarrow[\text{benzene}]{70\,^\circ C} \underset{\mathbf{1}}{FeCl_2(dcype)}} \quad (1)$$

However, complete spectroscopic characterization of **1** was unsuccessful due to its paramagnetism. Magnetic susceptibility ($\mu_{eff}$) of **1** measured by Gouy method is 4.99 B.M. which corresponds to four unpaired electrons (4.90 B.M.), suggesting a high spin state of **1**. No strong evidence for the monomeric structure of **1** was given. However, from the known molecular structure of the analogous $FeCl_2$(dippe), **1** is considered to have tetrahedral structure [9]. Similar 14e complex $FeCl_2(PPh_3)_2$ is also reported as a tetrahedral structure [10]. They all have mononuclear high spin configurations ($FeCl_2$(dippe): 4.9–5.0 B.M. [9], $FeCl_2(PPh_3)_2$: 4.88 B.M. [11], 5.07 B.M. [12]).

Because **1** is expected to be a coordinatively unsaturated 14e complex having a sterically congested and electron donating dcype ligand, **1** would be susceptible to addition of the compact and electron withdrawing ligand. Exposure of **1** to a CO atmosphere (1 atm) in a minimum amount of THF at room temperature (r.t.) immediately gave an orange solution, from which orange diamagnetic dicarbonyl complex, *cis,cis,cis*-$FeCl_2(CO)_2$(dcype) (**2a**) precipitated on cooling at $-20$°C for 2 days under CO in 79% yield [Eq. (2)].



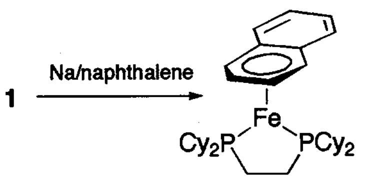
(2)

**2a** **2b**

Complex **2a** contained a small amount of its stereo isomer, *trans,cis,cis*-$FeCl_2(CO)_2$(dcype) (**2b**) ($<4\%$) which could not be separated by the recrystallization. $^{31}P\{^1H\}$-NMR spectrum of **2a** in $C_6D_6$ shows two doublets at 60.59 and 90.20 ppm, indicating that two phosphorus nuclei of dcype are inequivalent, whereas **2b** shows only one singlet at 70.02 ppm. In the IR spectrum of **2a**, two absorption bands due to terminal CO are observed at 2034 and 1975 cm$^{-1}$ with equal intensity, suggesting that two CO ligands are locating in the mutually *cis* configuration. These spectroscopic data support *cis,cis,cis*-$FeCl_2(CO)_2$(dcype) structure of **2a**. Complex **2** easily and completely released the CO ligands with discoloration to give the starting compound **1** at r.t. under reduced pressure. Thus, coordination of CO to **1** is weak and is a reversible process.

### 2.2. Reduction of $FeCl_2$(dcype) (*1*) with sodium-naphthalene

Reduction of **1** with a few times excess of sodium-naphthalene in THF under argon resulted in the formation of a dark brown suspension in a day at r.t. From the reaction mixture, dark green prisms of the zerovalent iron complex having an $\eta^6$-naphthalene ligand, Fe($\eta^6$-$C_{10}H_8$)(dcype) (**3**) were isolated in 30% yield [Eq. (3)].



(3)

**3**

The molecular structure of **3** was unambiguously determined by X-ray crystallography. Two independent molecules in the unit cell were found and have essentially the same structure. Thus, the following discussion will refer to the molecule A. The ORTEP drawing of the molecule A is depicted in Fig. 1 and the crystallographic data and selected bond distances and angles are shown in Tables 1 and 2, respectively.

The bond distances between Fe(1) and aromatic carbons are good criteria for characterization of the hapticity of the naphthalene ligand. The six bond distances of Fe(1)–C(1) [2.105(4) Å], Fe(1)–C(2) [2.099(4) Å], Fe(1)–C(3) [2.097(4) Å], Fe(1)–C(4) [2.105(4) Å], Fe(1)–C(5) [2.202(4) Å], and Fe(1)–C(10) [2.193(4) Å]

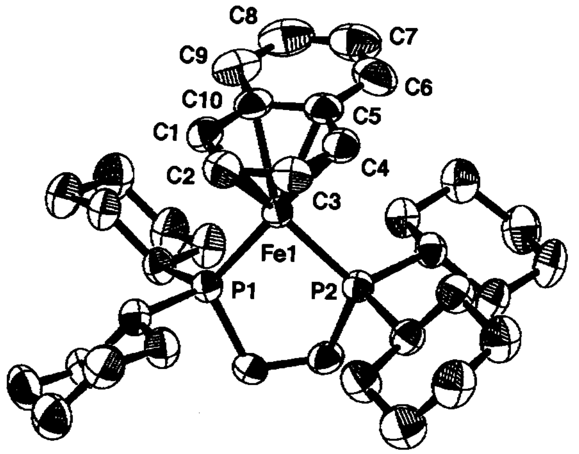



Fig. 1. ORTEP drawing of one of two independent Fe($\eta^6$-$C_{10}H_8$)(dcype) (**3**) molecules (molecule A) with selected atomic numbers. Hydrogen atoms are omitted for clarity.

are basically within the Fe–C bond distances and resembles the values reported in zerovalent ($\eta^6$-arene)iron complexes, Fe($\eta^6$-toluene)(bpy) [2.087–2.112 Å] [1]d, Fe($\eta^6$-toluene)($C_2H_4$)$_2$ [2.08–2.16 Å] [1]f or Fe($\eta^6$-benzene)($\eta^5$-thiadiborolene) [2.058–2.090 Å] [13]. The bond distances of Fe(1)–C(5) [2.202(4) Å] and Fe(1)–C(10) [2.193(4) Å] are slightly longer than those of other Fe–C bonds. The C–C bond distances among C(1), C(2), C(3), C(4), C(5) and C(10) appear in the range 1.403–1.434 Å, while clear bond alternation is found in the uncoordinated aromatic ring C(5)–C(10) [1.364–1.441 Å]. The bond distances of C(5)–C(6) [1.441(6) Å], C(7)–C(8) [1.398(8) Å], and C(9)–C(10) [1.435(6) Å] are slightly longer than those of C(6)–C(7) [1.375(7) Å] and C(8)–C(9) [1.364(7) Å]. This indicates that the resonance structure of naphthalene is not extended to the uncoordinated benzo-ring. Thus, hapticity of the naphthalene ligand is $\eta^6$ in the solid state, although it slightly tilts against the benzo-ring. $^1$H-NMR spectrum of **3** shows two broad singlets at 4.20 and 5.69 ppm assignable to the coordinated naphthalene ring, and multiplets at 7.09 and 7.41 ppm assignable to the uncoordinated moiety. The $^{13}$C{$^1$H}-NMR spectrum shows three singlets at 59.99, 79.46 and 97.62 ppm assignable to the coordinated naphthalene ring and two singlets at 121.07 and 126.89 ppm due to the uncoordinated naphthalene ring. $^{31}$P{$^1$H}-NMR spectrum of **3** shows a singlet at 94.60 ppm, suggesting that two phosphorus nuclei of dcype are magnetically equivalent. These NMR data are consistent with the symmetrical $\eta^6$ coordination of naphthalene to the iron.

Table 1
Crystallographic data of Fe($\eta^6$-$C_{10}H_8$)(dcype) · 0.5$C_6H_{14}$ (**3** · 0.5$C_6H_{14}$)

| | |
|---|---|
| Empirical formula | $C_{39}H_{63}FeP_2$ |
| Formula weight | 649.81 |
| Crystal dimensions (mm$^3$) | 0.67 × 0.43 × 0.17 |
| Crystal system | Monoclinic |
| Space group | $P2_1/a$( # 14) |
| $a$ (Å) | 16.821(2) |
| $b$ (Å) | 22.143(8) |
| $c$ (Å) | 19.537(4) |
| $\beta$ (°) | 97.34(2) |
| $V$ (Å$^3$) | 7217(2) |
| $Z$ | 8 |
| $\mu$ (cm$^{-1}$) | 5.61 |
| $F_{000}$ | 3 984.00 |
| $D_{calc.}$ (g cm$^{-3}$) | 1.196 |
| Radiation | Mo–K$_\alpha$ |
| Temp (K) | 293 |
| Unique reflections | 16 341 |
| Used reflections for refinement | 10 343 ($\|F_o\| > 3\sigma\|F_o\|$) |
| $R^a$ | 0.054 |
| $R_w^b$ | 0.071 |
| $S$ | 1.51 |
| Method of phase determination | Direct methods [22] |

[a] $R = \Sigma(\|F_o\| - \|F_c\|)/\Sigma\|F_o\|$.
[b] $R_w = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{0.5}$.

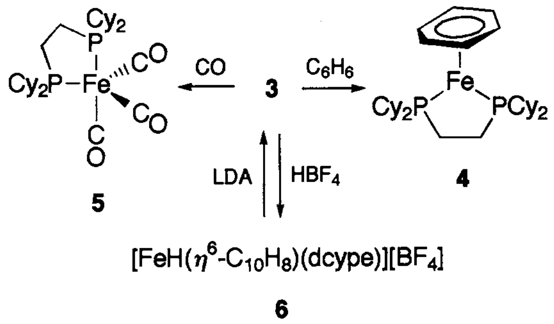
Table 2
Selected bond distances (Å) and angles (°) for **3**

| | | | |
|---|---|---|---|
| **Molecule A** | | | |
| Distances | | | |
| Fe(1)–P(1) | 2.173(1) | Fe(1)–P(2) | 2.182(1) |
| Fe(1)–C(1) | 2.105(4) | Fe(1)–C(2) | 2.099(4) |
| Fe(1)–C(3) | 2.097(4) | Fe(1)–C(4) | 2.105(4) |
| Fe(1)–C(5) | 2.202(4) | Fe(1)–C(10) | 2.193(4) |
| C(1)–C(2) | 1.403(6) | C(2)–C(3) | 1.402(6) |
| C(3)–C(4) | 1.405(6) | C(4)–C(5) | 1.429(6) |
| C(5)–C(6) | 1.441(6) | C(5)–C(10) | 1.434(6) |
| C(6)–C(7) | 1.375(7) | C(7)–C(8) | 1.398(8) |
| C(8)–C(9) | 1.364(7) | C(9)–C(10) | 1.435(6) |
| Angles | | | |
| P(1)–Fe(1)–P(2) | 86.06(4) | C(2)–C(1)–C(10) | 123.7(4) |
| C(1)–C(2)–C(3) | 119.1(4) | C(2)–C(3)–C(4) | 118.7(4) |
| C(3)–C(4)–C(5) | 123.1(4) | C(4)–C(5)–C(6) | 122.7(4) |
| C(4)–C(5)–C(10) | 118.3(4) | C(6)–C(5)–C(10) | 119.0(4) |
| C(5)–C(6)–C(7) | 120.2(5) | C(6)–C(7)–C(8) | 120.8(5) |
| C(7)–C(8)–C(9) | 120.7(5) | C(7)–C(9)–C(10) | 121.6(5) |
| **Molecule B** | | | |
| Distances | | | |
| Fe(2)–P(3) | 2.175(1) | Fe(2)–P(4) | 2.184(1) |
| Fe(2)–C(37) | 2.112(4) | Fe(2)–C(38) | 2.088(4) |
| Fe(2)–C(39) | 2.078(4) | Fe(2)–C(40) | 2.107(4) |
| Fe(2)–C(41) | 2.206(3) | Fe(2)–C(46) | 2.211(4) |
| C(37)–C(38) | 1.419(7) | C(38)–C(39) | 1.383(7) |
| C(39)–C(40) | 1.403(6) | C(40)–C(41) | 1.410(6) |
| C(41)–C(42) | 1.421(6) | C(41)–C(46) | 1.413(6) |
| C(42)–C(43) | 1.348(8) | C(43)–C(44) | 1.401(9) |
| C(44)–C(45) | 1.367(8) | C(45)–C(46) | 1.420(6) |
| Angles | | | |
| P(3)–Fe(2)–P(4) | 85.94(4) | C(38)–C(37)–C(46) | 121.2(4) |
| C(37)–C(38)–C(39) | 119.7(4) | C(38)–C(39)–C(40) | 119.5(4) |
| C(39)–C(40)–C(41) | 121.7(4) | C(40)–C(41)–C(42) | 122.1(4) |
| C(40)–C(41)–C(46) | 119.2(4) | C(42)–C(41)–C(46) | 118.7(4) |
| C(42)–C(43)–C(44) | 121.6(5) | C(43)–C(44)–C(45) | 120.0(5) |
| C(44)–C(45)–C(46) | 120.2(5) | C(37)–C(46)–C(45) | 122.1(5) |

Table 3
Atomic coordinates of $Fe(\eta^6\text{-}C_{10}H_8)(dcype)\cdot 0.5C_6H_{14}$

| | $x$ | $y$ | $z$ | $U_{ij}$ |
|---|---|---|---|---|
| Fe1 | 0.47821(3) | 0.19163(3) | 0.32867(3) | 0.0375(1) |
| Fe2 | 0.20624(3) | 0.16246(3) | 0.80758(3) | 0.0387(1) |
| P1 | 0.56495(5) | 0.12044(5) | 0.31875(5) | 0.0409(3) |
| P2 | 0.57524(5) | 0.25439(5) | 0.31591(5) | 0.0377(3) |
| P3 | 0.12880(6) | 0.08777(5) | 0.82823(5) | 0.0399(3) |
| P4 | 0.10206(5) | 0.22004(5) | 0.81403(5) | 0.0368(2) |
| C1 | 0.3784(2) | 0.1351(2) | 0.3334(3) | 0.053(1) |
| C2 | 0.4057(2) | 0.1574(2) | 0.3995(2) | 0.055(1) |
| C3 | 0.4153(2) | 0.2198(2) | 0.4090(2) | 0.053(1) |
| C4 | 0.3964(2) | 0.2581(2) | 0.3519(2) | 0.052(1) |
| C5 | 0.3664(2) | 0.2365(2) | 0.2846(2) | 0.051(1) |
| C6 | 0.3454(3) | 0.2763(2) | 0.2267(3) | 0.070(2) |
| C7 | 0.3181(3) | 0.2529(3) | 0.1628(3) | 0.077(2) |
| C8 | 0.3099(3) | 0.1906(4) | 0.1529(3) | 0.083(2) |
| C9 | 0.3300(2) | 0.1515(3) | 0.2063(2) | 0.070(2) |
| C10 | 0.3585(2) | 0.1726(2) | 0.2745(2) | 0.051(1) |
| C11 | 0.6676(2) | 0.1503(2) | 0.3166(2) | 0.049(1) |
| C12 | 0.6651(2) | 0.2156(2) | 0.2917(2) | 0.048(1) |
| C13 | 0.5806(2) | 0.0643(2) | 0.3916(2) | 0.048(1) |
| C14 | 0.6024(3) | 0.0952(2) | 0.4609(2) | 0.057(1) |
| C15 | 0.6075(3) | 0.0504(2) | 0.5203(2) | 0.070(2) |
| C16 | 0.6661(3) | −0.0007(3) | 0.5115(2) | 0.078(2) |
| C17 | 0.6459(3) | −0.0314(2) | 0.4435(2) | 0.070(2) |
| C18 | 0.6410(3) | 0.0132(2) | 0.3838(2) | 0.062(1) |
| C19 | 0.5561(2) | 0.0690(2) | 0.2409(2) | 0.047(1) |
| C20 | 0.4855(2) | 0.0251(2) | 0.2383(2) | 0.053(1) |
| C21 | 0.4812(3) | −0.0173(2) | 0.1762(2) | 0.063(1) |
| C22 | 0.4777(3) | 0.0182(2) | 0.1101(2) | 0.071(2) |
| C23 | 0.5472(3) | 0.0627(2) | 0.1117(2) | 0.065(1) |
| C24 | 0.5510(3) | 0.1044(2) | 0.1740(2) | 0.057(1) |
| C25 | 0.5535(2) | 0.3114(2) | 0.2450(2) | 0.0413(10) |
| C26 | 0.6185(3) | 0.3588(2) | 0.2375(2) | 0.056(1) |
| C27 | 0.5923(3) | 0.4033(2) | 0.1804(2) | 0.064(1) |
| C28 | 0.5667(3) | 0.3722(2) | 0.1124(2) | 0.066(2) |
| C29 | 0.5026(3) | 0.3252(2) | 0.1193(2) | 0.059(1) |
| C30 | 0.5296(2) | 0.2797(2) | 0.1754(2) | 0.046(1) |
| C31 | 0.6225(2) | 0.3033(2) | 0.3883(2) | 0.046(1) |
| C32 | 0.6579(3) | 0.2675(2) | 0.4507(2) | 0.061(1) |
| C33 | 0.7017(3) | 0.3084(3) | 0.5067(2) | 0.076(2) |
| C34 | 0.6486(3) | 0.3592(2) | 0.5266(2) | 0.073(2) |
| C35 | 0.6125(3) | 0.3944(2) | 0.4642(2) | 0.066(2) |
| C36 | 0.5676(3) | 0.3526(2) | 0.4105(2) | 0.055(1) |
| C37 | 0.2854(2) | 0.2329(2) | 0.7889(2) | 0.059(1) |
| C38 | 0.2640(2) | 0.1982(3) | 0.7282(2) | 0.064(2) |
| C39 | 0.2735(3) | 0.1361(3) | 0.7305(3) | 0.066(2) |
| C40 | 0.3057(2) | 0.1084(2) | 0.7925(2) | 0.060(1) |
| C41 | 0.3304(2) | 0.1424(2) | 0.8525(2) | 0.050(1) |
| C42 | 0.3643(3) | 0.1149(3) | 0.9153(3) | 0.072(2) |
| C43 | 0.3865(3) | 0.1489(4) | 0.9717(3) | 0.093(2) |
| C44 | 0.3780(3) | 0.2118(4) | 0.9703(3) | 0.093(2) |
| C45 | 0.3455(3) | 0.2400(3) | 0.9111(3) | 0.074(2) |
| C46 | 0.3201(2) | 0.2057(2) | 0.8508(2) | 0.051(1) |
| C47 | 0.0297(2) | 0.1133(2) | 0.8498(2) | 0.046(1) |
| C48 | 0.0092(2) | 0.1756(2) | 0.8191(2) | 0.044(1) |
| C49 | 0.0972(2) | 0.0319(2) | 0.7582(2) | 0.047(1) |
| C50 | 0.0598(2) | 0.0642(2) | 0.6920(2) | 0.055(1) |
| C51 | 0.0296(3) | 0.0205(2) | 0.6342(2) | 0.066(1) |
| C52 | 0.0949(3) | −0.0225(2) | 0.6189(2) | 0.068(2) |
| C53 | 0.1307(3) | −0.0551(2) | 0.6830(3) | 0.060(1) |
| C54 | 0.1628(2) | −0.0113(2) | 0.7413(2) | 0.059(1) |
| C55 | 0.1628(2) | 0.0361(2) | 0.9022(2) | 0.047(1) |
| C56 | 0.1051(3) | −0.0158(2) | 0.9140(2) | 0.060(1) |
| C57 | 0.1404(3) | −0.0558(2) | 0.9746(3) | 0.072(2) |
| C58 | 0.1622(3) | −0.0198(2) | 1.0410(3) | 0.075(2) |
| C59 | 0.2186(3) | 0.0316(2) | 1.0295(2) | 0.067(1) |
| C60 | 0.1837(3) | 0.0717(2) | 0.9697(2) | 0.054(1) |
| C61 | 0.0709(2) | 0.2714(2) | 0.7396(2) | 0.0411(10) |
| C62 | 0.0565(2) | 0.2371(2) | 0.6708(2) | 0.054(1) |
| C63 | 0.0419(3) | 0.2801(2) | 0.6086(2) | 0.068(2) |
| C64 | −0.0282(3) | 0.3219(2) | 0.6157(2) | 0.067(2) |
| C65 | −0.0164(3) | 0.3557(2) | 0.6838(3) | 0.058(1) |
| C66 | −0.0015(2) | 0.3128(2) | 0.7454(2) | 0.049(1) |
| C67 | 0.0993(2) | 0.2731(2) | 0.8881(2) | 0.041(1) |
| C68 | 0.1523(2) | 0.3289(2) | 0.8842(2) | 0.049(1) |
| C69 | 0.1502(3) | 0.3698(2) | 0.9468(2) | 0.059(1) |
| C70 | 0.1777(3) | 0.3357(2) | 1.0139(2) | 0.062(1) |
| C71 | 0.1253(3) | 0.2810(2) | 1.0199(2) | 0.057(1) |
| C72 | 0.1230(2) | 0.2399(2) | 0.9565(2) | 0.051(1) |
| C73 | 0.739(1) | 0.0275(8) | 0.7446(8) | 0.265(8) |
| C74 | 0.789(1) | 0.068(1) | 0.741(1) | 0.38(1) |
| C75 | 0.7894(9) | 0.1035(7) | 0.6879(9) | 0.275(6) |
| C76 | 0.8211(8) | 0.1191(7) | 0.6352(8) | 0.215(5) |
| C77 | 0.8228(8) | 0.1579(7) | 0.5772(8) | 0.237(6) |
| C78 | 0.8568(7) | 0.1489(6) | 0.5246(6) | 0.187(4) |

The present result is in sharp contrast to the previous report on similar reduction of $FeCl_2(dmpe)_2$ [dmpe = 1,2-bis(dimethylphosphino)ethane], where hydrido(n-aphthyl)-iron(II) and homoleptic dimer $Fe_2(dmpe)_5$ have been yielded ([2]g). The formation of zerovalent 18e complex **3** would arise from the reduction of 14e complex **1** with sodium-naphthalene followed by the coordination of naphthalene. Such formation of $\eta^6$-naphthalene complex having a tertiary phosphine ligand is rare, although those complexes having benzene or functionalized benzene are prepared by the metal vapor synthesis [1], hydrogenation of $Fe(CH_2C_6H_4Me\text{-}4)_2$(dippe) [7], or reaction of $Fe(N_2)(depe)_2$ with styrene [14]. Only $Ru(\eta^6\text{-}C_{10}H_8)$(cod) (cod = cycloocta-1,5-diene) was obtained by the reduction of $Ru(acac)_2$(cod) (acac = acetylacetonate) with sodium-naphthalene [15] or by hydrogenation of Ru(cod)(cot) (cot = cycloocta-1,3,5-triene) in the presence of naphthalene [16].




Scheme 1. Ligand exchange reaction of naphthalene in **3** with benzene under reflux giving $Fe(\eta^6\text{-}C_6H_6)$(dcype) (**4**).

### 2.3. Chemical reactions of $Fe(\eta^6$-$C_{10}H_8)(dcype)$ (**3**)

Since an $\eta^6$-naphthalene ligand is one of the most labile arene ligand [16], the chemical reactivities of **3** are topic of interest. Ligand exchange reaction of naphthalene in **3** with benzene smoothly took place under reflux conditions giving $Fe(\eta^6$-$C_6H_6)(dcype)$ (**4**) (Scheme 1). It is interesting to note that neither of arene ligand in analogous iron(0), $Fe(\eta^6$-toluene)(bpy) (bpy = 2,2′-bipyridine) ([1]d) nor $Fe(\eta^6$-$C_6H_4Me_2$-1,4)(dippe) [7] can be replaced by the external arenes even at elevated temperature. $^1$H-NMR spectrum of **4** shows a broad singlet at 4.91 ppm assignable to the coordinated benzene ring and the $^{31}P\{^1H\}$-NMR spectrum showed a singlet peak at 102.15 ppm. It is worth noting that the chemical shift of the $\eta^6$-benzene in the $^1$H-NMR spectrum is 0.23 ppm upfield from that of isomorphous ruthenium analogue, $Ru(\eta^6$-$C_6H_6)(dcype)$ (5.14 ppm) [17].

Complex **3** could be quantitatively transformed to known $Fe(CO)_3(dcype)$ (**5**) [18] by exposure to excess CO (1 atm). IR spectrum of **5** shows stretching bands of terminal CO absorption at 1968, 1890, 1873 $cm^{-1}$ in $CH_2Cl_2$, which are identical with those reported by Angelici et al. [18].

Protonation of **3** was easily carried out by $HBF_4$ in $Et_2O$ to give an orange powder of a cationic hydride complex, $[FeH(\eta^6$-$C_{10}H_8)(dcype)]BF_4$ (**6**). $^1$H-NMR spectrum of **6** in $CD_2Cl_2$ shows a triplet signal at −19.00 ppm due to the hydride. Coordinated and uncoordinated ring protons appear at 5.94 and 6.32 ppm as broad singlets, and at 7.65 and 7.74 ppm as multiplets, respectively. These values are slightly downfield from those of **3**, probably due to decrease in electron density at iron. The $^{31}P\{^1H\}$-NMR spectrum shows a singlet at 103.51 ppm, suggesting symmetrical environment of the dcype ligand. These spectroscopic data support the structure of **6**. It is worthwhile to note that the protonation of zerovalent M(arene)(diene) (M = Fe, Ru) does not give a hydridometal(II) but an allylmetal(II) complex $[M(arene)(allyl)]^+$ [18].

Deprotonation of **6** was achieved by treatment with lithium diisopropylamide (LDA) in THF at 0°C to give **3**. However, neither of other bases such as $Na_2CO_3$ nor $Et_3N$ remained unreacted with **6**. This fact implies that **6** is far less acidic than other protonated Group 8 arene complexes [15,19]. The weak acidity of **6** would be arisen from the ancillary dcype ligand as a strong electron donor.

## 3. Experimental section

### 3.1. General

All manipulations were performed under dry nitrogen or argon using standard Schlenk and vacuum-line techniques. Benzene, hexane, tetrahydrofuran and diethyl ether were dried and distilled under $N_2$ from sodium benzophenone ketyl and dichloromethane was dried and distilled over anhydrous $CaSO_4$. Dcype [1,2-bis(dicyclohexylphosphino)ethane] and its precursor 1,2-bis(dichlorophosphino)ethane were prepared according to the literature method [20]. Anhydrous $FeCl_2$ was purchased from Koso and dried at 120°C for 12 h under vacuum before use. Naphthalene was purchased from Kanto and used as received. $HBF_4 \cdot OEt_2$ (85%) was purchased from Aldrich and used as received. $^1$H- and $^{13}C\{^1H\}$-NMR spectra were recorded on a JEOL LA-300 spectrometer (300 MHz for $^1$H, 75.4 MHz for $^{13}$C) and chemical shifts were reported in ppm from TMS. $^{31}P\{^1H\}$-NMR spectra were recorded on a JEOL LA-300 (122 MHz) and chemical shifts were reported in ppm downfield from external 85% $H_3PO_4$ in $D_2O$. IR spectra were recorded on a JASCO FT/IR-5M spectrometer. Melting points were measured under nitrogen with Yazawa MP-21 capillary melting apparatus and the values are uncorrected. Elemental analyses were performed with Perkin Elmer 2400 series II CHN analyzer. Magnetic Susceptibility was measured by Sherwood Scientific MSB-MKI magnetic susceptibility balance.

### 3.2. Synthesis of $FeCl_2(dcype)$ (**1**)

A benzene (49 ml) solution of anhydrous $FeCl_2$ (0.680 g, 5.37 mmol), dcype (2.44 g, 5.78 mmol) was heated at 70°C and stirred for 24 h. Then, this mixture was filtered through a filter paper and set aside at r.t. Light purple needles of $FeCl_2(dcype)$ (**1**) containing one molecule of benzene per **1** was obtained from the reaction mixture in a day (3.23 g, 5.15 mmol, 96%). Anal. Found: C, 61.25; H, 8.65. Calc. for $C_{32}H_{54}Cl_2FeP_2$: C, 61.25; H, 8.67%. $\mu_{eff} = 4.99$ B.M.

### 3.3. Reaction of $FeCl_2(dcype)$ with CO

A solution of $FeCl_2(dcype)$ (0.1598 g, 0.255 mmol) in a minimum amount of THF (1 ml) was exposed to CO atmosphere at r.t. for 8 h during which the mixture immediately turned to an orange solution. The reddish orange precipitate was obtained in 2 days at −20°C. The resulting precipitate was separated from the solution by using cannula, washed with $Et_2O$ (6 ml) and then dried under flush of CO stream (0.140 g, 0.23 mmol, 91%). **2a**: $^{31}P\{^1H\}$-NMR ($C_6D_6$): $\delta$ 60.59 (d, $J = 35.2$ Hz, 1P), 90.20 (d, $J = 35.2$ Hz, 1P). IR (KBr): 2034(s), 1975(s) $cm^{-1}$ ($\nu_{CO}$). **2b**: $^{31}P\{^1H\}$-NMR: $\delta$ 70.02(s).

### 3.4. Synthesis of Fe($\eta^6$-naphthalene)(dcype) (**3**)

To a THF solution (22 ml) of $FeCl_2$(dcype) (**1**) (2.03 g, 3.24 mmol) was added dropwise in THF solution of sodium naphthalene (55 ml, 15.0 mmol) at r.t. under Ar. After the reaction at r.t. for 23 h, the solvent was evaporated to dryness. The resulting dark green tar was extracted with hexane (140 ml). Volatile matters were removed in vacuo and finally by using oil diffusion pump. Recrystallization of the resulting solid from cold hexane (70 ml) gave dark green crystals of Fe($\eta^6$-naphthalene)(dcype) · $0.5C_6H_{14}$ (**3** · $0.5C_6H_{14}$) (0.593 g, 0.977 mmol, 30%). m.p. 166–167°C (decomp.). Anal. Found: C, 71.67; H, 9.33. Calc. for $C_{78}H_{126}Fe_2P_4$: C, 72.10; H, 9.77%. $^1$H-NMR ($C_6D_6$): $\delta$ 4.20, 5.69 (br, 4H, coord. ring, $C_{10}H_8$), 7.09, 7.41 (m, 4H, uncoord. ring, $C_{10}H_8$). $^{13}C\{^1H\}$-NMR ($C_6D_6$): $\delta$ 59.99, 79.46 (s, coord. ring, $C_{10}H_8$), 97.62 (s, ring junction, $C_{10}H_8$), 121.07, 126.89 (s, uncoord. ring, $C_{10}H_8$). $^{31}P\{^1H\}$-NMR ($C_6D_6$): $\delta$ 94.60 (s).

### 3.5. Preparation of Fe($\eta^6$-benzene)(dcype) (**4**)

A benzene solution (5 ml) of Fe($\eta^6$-naphthalene)(dcype) (0.0139 g, 0.0229 mmol) was refluxed and stirred for 4 h. The dark green reaction mixture turned to dark brown during course of the reaction. The solvent was removed to dryness, and the resultant brown solid was extracted with hexane (8 ml). The filtrate was evaporated to dryness under reduced pressure to give Fe($\eta^6$-benzene)(dcype) (**4**) as dark brown solid (0.0100 g, 0.0180 mmol, 79%). Recrystallization of the resulting solid from hexane (0.5 mL) gave brown hexagonal crystals of **4**. m.p. 127°C (decomp.). Anal. Found: C, 69.03; H, 9.80. Calc. for $C_{32}H_{54}FeP_2$: C, 69.06; H, 9.78%. $^1$H-NMR ($C_6D_6$): $\delta$ 4.91 (br, 6H, $C_6H_6$). $^{31}P\{^1H\}$-NMR ($C_6D_6$): $\delta$ 102.15 (s).

### 3.6. Reaction of Fe($\eta^6$-naphthalene)(dcype) with CO

A THF solution (6 ml) of Fe($\eta^6$-naphthalene)(dcype) (0.0492 g, 0.0811 mmol) was exposed to CO atmosphere (1 atm). The mixture was stirred at r.t. for 42 h, during which the dark green solution turned to dark brown. The solvent was removed to dryness, and the resulting solid was extracted with hexane (14 ml). The filtrate was evaporated to dryness under reduced pressure to give a known orange powder of $Fe(CO)_3$(dcype) (**5**) (0.0425 g, 0.0756 mmol, 93%) [18]. IR ($CH_2Cl_2$): 1968(s), 1890(sh), 1873(s) cm$^{-1}$ ($\nu_{CO}$).

### 3.7. Protonation of Fe($\eta^6$-naphthalene)(dcype) with excess amount of $HBF_4$

A $Et_2O$ solution (10 ml) of Fe($\eta^6$-naphthalene)(dcype) (0.124 g, 0.205 mmol) was added to an excess amount of $HBF_4$ (85% in $Et_2O$, 50 drops) at 0°C. The mixture allowed to warm at r.t. and stirred for 24 h. The supernatant solution was removed by using cannula, and the resulting insoluble materials were washed with $Et_2O$ (20 ml) and dried under reduced pressure to give [FeH($\eta^6$-naphthalene)(dcype)][$BF_4$] (**6**) as an orange powder (0.103 g, 0.148 mmol, 72%). $^1$H-NMR ($CD_2Cl_2$): $\delta$ −19.00 (t, 1H, $J = 84$ Hz, Fe-*H*), 5.96, 6.32 (br, 4H, coord. ring, $C_{10}H_8$), 7.65, 7.74 (m, 4H, uncoord. ring, $C_{10}H_8$). $^{31}P\{^1H\}$-NMR ($CD_2Cl_2$): $\delta$ 103.51 (s).

### 3.8. Deprotonation of [FeH($\eta^6$-naphthalene)-(dcype)][$BF_4$] with an excess amount of LDA

To a THF solution (7 ml) of [FeH($\eta^6$-naphthalene)(dcype)][$BF_4$] (**6**) (0.0248 g, 0.0357 mmol) was added an excess amount of lithium diisopropylamide solution (ca. 0.8 mmol in THF) at 0°C. The mixture allowed to warm to r.t. and stirred for 24 h. The solvent was removed under reduced pressure and the resulting solid was extracted with hexane (10 ml). All volatile matters were removed in vacuo and the resulting dark green powder was finally dried using oil diffusion pump to give Fe($\eta^6$-naphthalene)(dcype) (**3**) as a dark green powder (0.0186 g, 0.0306 mmol, 86%). All $^1$H-, $^{31}P\{^1H\}$-NMR and IR spectra were identical to those of **3**.

### 3.9. Crystallographic analyses for **3**

Dark green crystals were grown from saturated solution of **3** in hexane. A crystal of suitable size was selected and mounted in a glass capillary tube (GLAS, 0.7 mm$\phi$). The data were collected at 20°C using TEXSAN automatic data collection series [21] on a Rigaku R-AXIS II imaging plate system using Mo–$K_\alpha$ radiation ($\lambda = 0.71070$ Å). Using the criteria $|F_o| > 3.0\sigma|F_o|$, 10343 out of 16341 reflections were used and the structure was solved by the direct methods. Absorption and decay corrections were not applied for **3**. The crystal system was monoclinic and the space group was $P2_1/a$ (#14). Two independent molecules of **3** were observed in a unit cell and the ORTEP drawing of one of them is illustrated in Fig. 1. Both independent molecules have comparable bond distances and angles as shown in Table 2. From the difference Fourier map, incorporation of a hexane molecule was found and refined isotropically. All non-hydrogen atoms of **3** were refined anisotropically. The hydrogens were located on the ideal positions and were not refined. The refinements were carried out by using full-matrix least squares techniques on $F$, minimizing the function $w(|F_o| - |F_c|)^2$, where the weight $w$ is defined as $4F_o^2/[\sigma^2(F_o^2)]$. $[\sigma^2(F_o^2) = (S^2(C + R^2B) + (pF_o^2)^2/L_p^2$, where $F_o$ = observed structure factor amplitude, $S$ = scan rate,

$C$ = total integrated peak count, $R$ = ratio of scan time to background counting time, $B$ = total background count, $L_p$ = Lorentz-polarization factor, $p$ = $p$-factor]. We used a $p$ factor (0.050) to downweight the intense reflections and then a goodness of fit of 1.51 was obtained. The final $R$ ($R_w$) value was 0.054 (0.071). Plots of $\Sigma w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $(\sin\theta)/\lambda$ and various classes of indices showed no unusual trends. Crystallographic data are summarized in Table 1. The atomic coordinates are listed in Table 3.

## Acknowledgements

We thank Dr M. Oshima and Prof. H. Suzuki of Tokyo Institute of Technology for collection of X-ray diffraction data of **3**. This work was financially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan.

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