

[FeH(CN)(dppe)₂] 착물의 합성 및 구조

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Synthesis and Structure of *trans*-Bis[bis(diphenylphosphino)ethane]cyano-hydridoiron(II), *trans*-[FeH(CN)(dppe)₂] (dppe=Ph₂PCH₂CH₂PPh₂)

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요 약

Ar 기류 하에서 *trans*-[FeH(NCCH₂CH₂CH₂Cl)(dppe)₂][BF₄], **1**과 KCN이 반응하여 *trans*-[FeH(CN)(dppe)₂], **2**가 생성되었다. 이 화합물의 구조가 NMR, IR, 원소분석, 그리고 X-ray 회절 법으로 규명되었다. 착물 **2**의 결정학 자료: 단사정계 공간군 *P2₁/c*, *a*=13.580(1) Å *b*=20.178(2) Å, *c*=17.592(3) Å, β=92.22(1)°, *Z*=4, *R*(*wR*₂)=0.0659(0.1692).

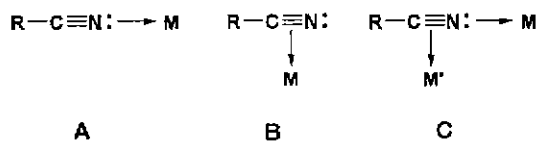
Abstract

Reaction of *trans*-[FeH(NCCH₂CH₂CH₂Cl)(dppe)₂][BF₄], **1**, with KCN under argon led to the formation of *trans*-[FeH(CN)(dppe)₂], **2**. Compound **2** was characterized by NMR, IR, elemental analysis, and X-ray diffraction. Crystallographic data for **2**: monoclinic space group *P2₁/c*, *a*=13.580(1) Å *b*=20.178(2) Å, *c*=17.592(3) Å, β=92.22(1)°, *Z*=4, *R*(*wR*₂)=0.0659(0.1692).

1. Introduction

Transition-metal nitrile (M-N≡C-R) complexes have got continuous attraction because they can serve as convenient precursors for a wide variety of interesting transition-metal complexes. Nitriles have two potential coordination sites, the lone pair of electrons on nitrogen (an end-on fashion, **A**) and the carbon-nitrogen triple bond (a side-on fashion or a π-bond complex, **B**).^{1,2)} In addition, a combined mode (**C**) of these two fundamental modes has often been observed in several polynuclear complexes as well as in some related complexes possessing X-C≡N ligands in which X is other than an alkyl or aryl substituent.³⁾

Recently we reported the synthesis and structure of *trans*-[FeH(NCCH₂CH₂CH₂Cl)(dppe)₂][BF₄]⁻ (dppe=Ph₂PCH₂CH₂PPh₂), **1**, which was prepared from the



reaction of *trans*-[FeH(Cl)(dppe)₂] with NaBF₄ in NCCH₂CH₂CH₂Cl under argon.⁴⁾ The nitrile ligand (NCCH₂CH₂CH₂Cl) in **1** is bonded to the Fe metal in an end-on fashion. Nitrile complexes provide an example of activation because the electrophilicity of the nitrile α-carbon is enhanced on coordination.³⁾ With this in mind, compound **1** was treated with an inorganic nucleophile CN⁻ (KCN). The product, however, turned out to be *trans*-[FeH(CN)(dppe)₂], which is a substitution product, not a nucleophilic addition product (*trans*-[FeH(NC(CN)CH₂CH₂CH₂Cl)(dppe)₂]). Herein we report synthesis and structure of *trans*-[FeH(CN)(dppe)₂], **2**.

2. Experimental Section

Unless otherwise stated, all the reactions have been performed with standard Schlenk line and canula techniques under an argon atmosphere. Air-sensitive solids were manipulated in a glove box filled with argon. Glassware was soaked in KOH-saturated 2-propanol for ca. 24 h and washed with distilled water and acetone before use. Glassware was either flame-dried or oven-dried. Hydrocarbon solvents were stirred over concentrated H_2SO_4 for ca. 48 h, neutralized with K_2CO_3 , stirred over sodium metal, and distilled by vacuum transfer. Dichloromethane was stirred over CaH_2 and distilled by vacuum transfer. The NMR solvent $CDCl_3$ was degassed by several freeze-pump-thaw cycles before use and stored over molecular sieves under argon. $[FeH(CICH_2CH_2CH_2CN)(dppe)_2][BF_4]$, **1**, was prepared by the literature method.⁴¹

1H - and $^{13}C\{^1H\}$ -NMR spectra were recorded with a Bruker AMX 500 MHz spectrometer with reference to internal solvent resonances and reported relative to tetramethylsilane. ^{31}P -NMR spectra were also recorded with a Bruker AMX 500 MHz spectrometer with reference to external 85% H_3PO_4 . IR spectra were recorded with a Nicolet 205 FTIR spectrophotometer. Melting points were measured with a Thomas Hoover capillary melting point apparatus without calibration. The elemental analyses were

performed by the Korea Basic Science Center.

Preparation of $[FeH(CN)(dppe)_2]$, **2.** To a mixed solvent (10 ml) CH_2Cl_2 -MeOH (1:1) were added **1** (0.052 g, 0.05 mmol) and KCN (0.005 g, 0.08 mmol), and the resulting solution was stirred for 12 h. The solvent was removed under vacuum, and the remaining solids were extracted with 30 ml of dichloromethane and washed with hexanes (2×20 ml) to give yellow powder of **2** (0.020 g, 0.023 mmol, 46%). 1H -NMR ($CDCl_3$): 7.516-6.990 (40H, m, phenyl, $Ph_2PCH_2CH_2PPh_2$), 2.467 (4H, broad m, $Ph_2PCH_2CH_2PPh_2$), 1.983 (4H, broad m, $Ph_2PCH_2CH_2PPh_2$), -14.748 (1H, quintet, $^2J_{P-H}=46$ Hz, $H-Fe$). $^{13}C\{^1H\}$ -NMR ($CDCl_3$): 164.421 (CN), 139.591, 138.536, 134.685, 134.206, 129.259, 129.098, 127.671 (phenyl), 34.143 (t, $J_{P-C}=13.1$ Hz, $Ph_2PCH_2CH_2PPh_2$). ^{31}P -NMR ($CDCl_3$): 90.175 (d, $^2J_{P-H}=46$ Hz). Anal. Calcd for $C_{53}H_{49}NP_4Fe$: C, 72.36; H, 5.61; N, 1.61. Found: C, 72.54; H, 5.25; N, 1.72. mp (decom.): 188–190°C. IR (KBr): 2050 (CN) cm^{-1} .

X-ray Structure Determination of **2.** X-ray quality crystals were grown from CH_2Cl_2 -hexanes. All X-ray data were collected with use of a Siemens P4 diffractometer equipped with a Mo X-ray tube and a graphite crystal monochromator. Details on crystal data and intensity data are given in Table 1. The orientation matrix and unit cell parameters were determined by least-squares analyses of the setting angles of 39 reflections in the range $15.0^\circ <$

Table 1. X-ray data collection and structure refinement for $2 \cdot CH_2Cl_2 \cdot H_2O$

formula	$C_{53}H_{49}NOP_4Cl_2Fe$	2θ range ($^\circ$)	3.5-50
formula weight	990.67	scan type	ω
temperature, K	293	scan speed	variable
crystal system	monoclinic	h	0→16
space group	$P2_1/c$	k	0→24
a , Å	13.580(1)	l	-20→20
b , Å	20.178(2)	No. of reflns unique	8,401
c , Å	17.592(3)	No. of reflns with $I > 2\sigma(I)$	6,215
β , deg	92.22(1)	No. of params refined	601
V , Å ³	4.817(1)	Max., in $\Delta\rho$ ($e\text{Å}^{-3}$)	1.091
Z	4	Min., in $\Delta\rho$ ($e\text{Å}^{-3}$)	-0.629
d_{calc} , $g\text{ cm}^{-3}$	1.366	$R(int)$	0.0191
μ , mm^{-1}	0.598	GOF on F^2	1.025
$F(000)$	2,080	R	0.0659
T_{min}	0.5608	wR_2^a	0.1692
T_{max}	0.6118		

^a $wR_2 = \{[w(F_o^2 - F_c^2)^2] / [w(F_o^2)]\}^{1/2}$.

$2\theta < 25.0^\circ$. Three check reflections were measured every 100 reflections throughout data collection and showed no significant variations in intensity. Intensity data were corrected for Lorentz and polarization effects. Decay corrections were also made. The intensity data were empirically corrected with ψ -scan data. All calculations were carried out with use of the SHELXTL programs.⁵⁾

A yellow crystal of **2**, shaped as a block, of approximate dimensions $0.21 \times 0.42 \times 0.78 \text{ mm}^3$, was used for crystal and intensity data collection. The unit cell parameters and systematic absences, $h0l$ ($l=2n+1$) and $0k0$ ($k=2n+1$), unambiguously indicated $P2_1/c$ as a space group. The structure was solved by the direct method and refined by full-matrix least-squares calculations of F^2 initially with isotropic and finally anisotropic temperature factors for all non-hydrogen atoms. The cocrystallized solvent (CH_2Cl_2) exhibited a structural disorder. The best fit for the disordered C and Cl atoms was obtained by considering these atoms to be distributed over two positions with the site occupation factors of 0.41:0.59 [(C54, Cl1, Cl2):(C54A, Cl1A, Cl2A)]. The hydride ligand (Hfe) was located in the difference Fourier map and refined isotropically.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $2 \cdot \text{CH}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
Fe	3487(1)	1694(1)	7086(1)	24(1)
P(1)	4606(1)	1669(1)	8038(1)	27(1)
P(2)	2410(1)	1527(1)	7997(1)	28(1)
P(3)	2360(1)	1647(1)	6137(1)	29(1)
P(4)	4577(1)	1599(1)	6167(1)	29(1)
N(1)	3420(3)	3221(2)	7081(2)	61(1)
C(1)	5713(3)	2197(2)	8064(2)	34(1)
C(2)	6637(3)	1938(2)	7977(2)	42(1)
C(3)	7458(3)	2343(2)	7956(3)	55(1)
C(4)	7352(3)	3019(2)	8027(3)	59(1)
C(5)	6434(3)	3284(2)	8120(3)	58(1)
C(6)	5614(3)	2885(2)	8136(2)	43(1)
C(7)	5112(2)	873(2)	8397(2)	31(1)
C(8)	5601(3)	842(2)	9098(2)	47(1)
C(9)	5941(3)	247(2)	9398(3)	57(1)
C(10)	5807(3)	-327(2)	8973(3)	60(1)
C(11)	5342(3)	-310(2)	8277(3)	53(1)
C(12)	4972(3)	292(2)	7986(2)	38(1)

Table 2. Continued

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
C(13)	1758(3)	731(2)	7954(2)	36(1)
C(14)	2277(3)	147(2)	8104(2)	45(1)
C(15)	1831(4)	-470(2)	8017(2)	57(1)
C(16)	875(4)	-513(2)	7769(3)	62(1)
C(17)	334(4)	58(2)	7614(2)	63(1)
C(18)	773(3)	677(2)	7708(2)	46(1)
C(19)	1428(3)	2110(2)	8265(2)	38(1)
C(20)	774(3)	1939(2)	8816(3)	57(1)
C(21)	80(3)	2394(3)	9062(3)	69(1)
C(22)	58(3)	3023(3)	8773(3)	65(1)
C(23)	731(4)	3196(2)	8246(3)	63(1)
C(24)	1404(3)	2747(2)	7987(2)	48(1)
C(25)	1201(3)	2117(2)	6127(2)	39(1)
C(26)	1221(3)	2802(2)	6060(2)	52(1)
C(27)	348(4)	3160(3)	6085(3)	72(2)
C(28)	-527(4)	2847(3)	6174(3)	76(2)
C(29)	-560(3)	2174(3)	6238(3)	69(1)
C(30)	302(3)	1806(2)	6210(2)	51(1)
C(31)	1944(2)	842(2)	5736(2)	32(1)
C(32)	1409(3)	828(2)	5043(2)	47(1)
C(33)	1164(3)	225(2)	4713(3)	59(1)
C(34)	1431(3)	-362(2)	5058(3)	60(1)
C(35)	1928(3)	-351(2)	5743(3)	56(1)
C(36)	2189(3)	246(2)	6091(2)	40(1)
C(37)	5522(3)	2218(2)	5915(2)	38(1)
C(38)	5544(3)	2843(2)	6229(2)	44(1)
C(39)	6233(3)	3303(2)	5997(3)	56(1)
C(40)	6887(3)	3145(2)	5460(3)	57(1)
C(41)	6862(3)	2531(3)	5133(3)	62(1)
C(42)	6175(3)	2064(2)	5352(2)	51(1)
C(43)	5304(3)	834(2)	6176(2)	37(1)
C(44)	6288(3)	827(2)	6434(2)	52(1)
C(45)	6796(4)	234(3)	6517(3)	70(1)
C(46)	6327(4)	-360(3)	6343(3)	76(2)
C(47)	5355(4)	-362(2)	6076(2)	63(1)
C(48)	4847(3)	231(2)	5991(2)	46(1)
C(49)	3973(3)	1940(2)	8891(2)	34(1)
C(50)	3082(3)	1487(2)	8939(2)	35(1)
C(51)	2961(3)	1981(2)	5298(2)	37(1)
C(52)	3901(3)	1573(2)	5234(2)	36(1)
C(53)	3449(2)	2646(2)	7083(2)	37(1)
O(1)	2093(4)	690(2)	2108(3)	121(2)
Cl(1)	8704(18)	896(8)	9170(2)	271(11)
Cl(2)	8666(10)	129(8)	10160(5)	140(5)
C(54)	8918(18)	170(11)	9216(9)	63(5)
Cl(1A)	8420(5)	871(4)	8854(4)	123(2)
Cl(2A)	8476(9)	-227(10)	10027(8)	224(6)
C(54A)	8650(3)	79(17)	9199(18)	244(18)

^aEquivalent isotropic U (eq) defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected bond distances (Å) and bond angles (°) in $2 \cdot \text{CH}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$

Fe-C(53)	1.921(4)	Fe-P(1)	2.218(1)	Fe-P(3)	2.223(1)
Fe-P(2)	2.238(1)	Fe-P(4)	2.241(1)	Fe-Hfe	1.46(4)
P(1)-C(49)	1.841(3)	P(1)-C(1)	1.841(3)	P(1)-C(7)	1.850(3)
P(2)-C(13)	1.833(4)	P(2)-C(19)	1.853(3)	P(2)-C(50)	1.863(3)
P(3)-C(25)	1.837(4)	P(3)-C(51)	1.841(3)	P(3)-C(31)	1.852(3)
P(4)-C(43)	1.833(3)	P(4)-C(52)	1.851(4)	P(4)-C(37)	1.856(4)
N(1)-C(53)	1.160(5)	C(49)-C(50)	1.520(5)	C(51)-C(52)	1.526(5)
C53-Fe-P1	92.4(1)	C53-Fe-P3	91.3(1)	P1-Fe-P3	176.24(4)
C53-Fe-P2	97.7(1)	P1-Fe-P2	84.45(4)	P3-Fe-P2	94.66(4)
C53-Fe-P4	95.9(1)	P1-Fe-P4	95.19(4)	P3-Fe-P4	84.81(4)
P2-Fe-P4	166.38(4)	C53-Fe-Hfe	176(1)	C49-P1-C1	102.4(2)
C49-P1-C7	99.1(2)	C1-P1-C7	101.6(2)	C49-P1-Fe	106.3(1)
C1-P1-Fe	122.7(1)	C7-P1-Fe	120.8(1)	C13-P2-C19	102.5(2)
C13-P2-C50	102.7(2)	C19-P2-C50	97.7(2)	C13-P2-Fe	115.5(1)
C19-P2-Fe	125.6(1)	C50-P2-Fe	109.4(1)	C25-P3-C51	102.2(2)
C25-P3-C31	101.6(2)	C51-P3-C31	98.8(2)	C25-P3-Fe	123.4(2)
C51-P3-Fe	105.8(1)	C31-P3-Fe	121.0(1)	C43-P4-C52	103.4(2)
C43-P4-C37	101.1(2)	C52-P4-C37	97.6(2)	C43-P4-Fe	115.9(1)
C52-P4-Fe	108.9(1)	C37-P4-Fe	126.6(1)	C50-C49-P1	105.4(2)
C49-C50-P2	106.8(2)	C52-C51-P3	105.1(2)	C51-C52-P4	107.8(2)
N1-C53-Fe	179.7(4)				

The hydrogen atoms in the cocrystallized water (H_2O) were not located. All the other hydrogen atoms were generated in idealized positions and refined in a riding model.

Final atomic positional parameters for non-hydrogen atoms are shown in Table 2. The selected bond distances and bond angles are shown in Table 3.

3. Results and Discussion

Preparation. As mentioned in the Introduction section, nitrile complexes are known to provide an example of activation because the electrophilicity of the nitrile α -carbon is enhanced upon coordination. On the contrary to this expectation, compound **1** reacts with KCN to give $[\text{FeH}(\text{CN})(\text{dppe})_2]$, **2**, which is a substitution product, not a nucleophilic addition product (Eq. 1). In other words, the nucleophile CN^- has attacked directly at the Fe metal, not at the nitrile α -carbon. This pattern of substitution for metal-nitrile complexes has often been observed. For example, a cationic rhenocenitrile adduct $[\text{Cp}_2\text{Re}(\text{NCCH}_3)][\text{BF}_4]$ ($\text{Cp}=\text{C}_5\text{H}_5$) has a labile acetonitrile ligand that can be readily replaced by other

ligands L (L= PPh_3 , CN^tBu , or $\text{HC}\equiv\text{CPh}$).⁶⁾ Compound **2** is air-stable in the solid state, but unstable in solution.

The geometry of **2** can be readily deduced from NMR data (a quintet for hydride in ^1H -NMR and a doublet for phosphorus in ^{31}P -NMR) and elemental analysis data. The NMR data indicate that the hydride ligand couples with the four equivalent phosphorus nuclei in the phosphines occupying the equatorial plane and that the orientation between the hydride and the nitrile is mutually *trans*. The IR spectra of **2** show the CN band at 2050 cm^{-1} .

Structure. The molecular structure of compound **2** with the atomic numbering scheme is shown in Fig. 1. The coordination sphere of the Fe metal can be described as an octahedron, with two bidentate dppe ligands at the equatorial sites and the hydride and nitrile ligands at the axial sites. The equatorial plane, defined by the four dppe phosphorus atoms (P1-P4), is roughly planar with the average atomic displacement of 0.0966 \AA . The Fe metal lies 0.1690 \AA above the equatorial plane.

The hydride ligand (Hfe) could be located and reasonably refined with an isotropic thermal para-

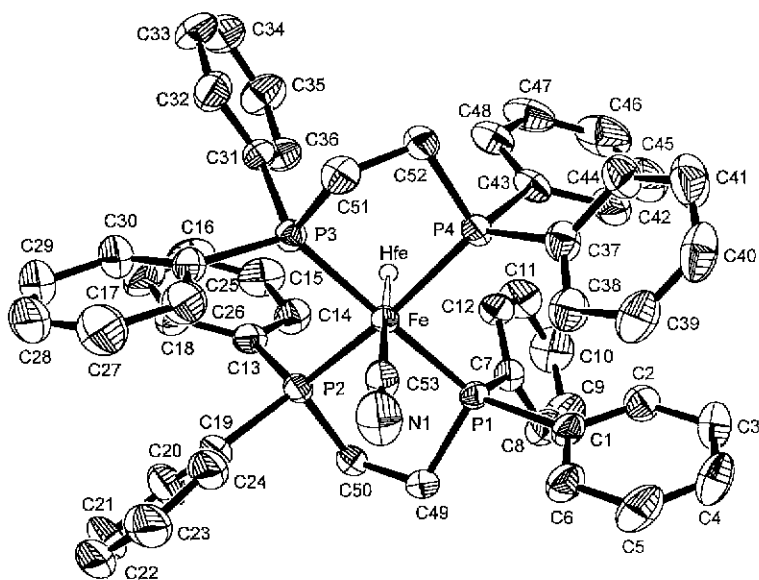
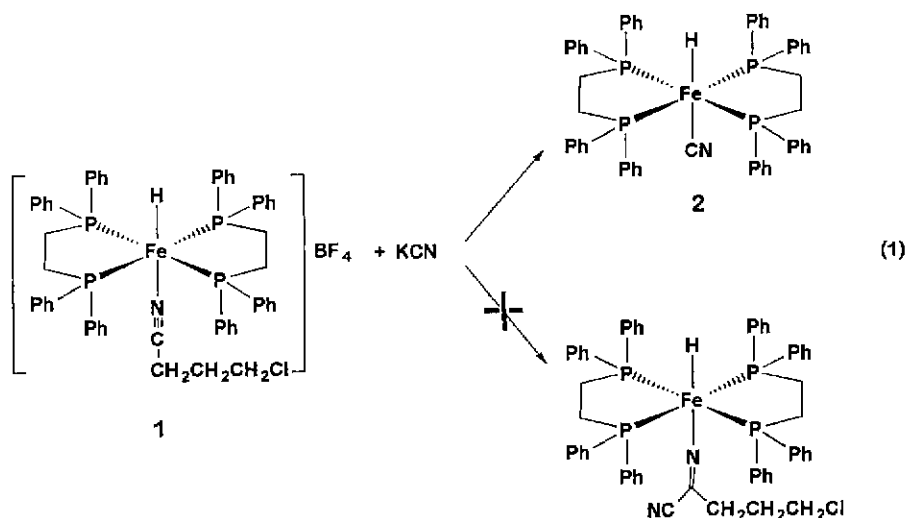


Fig. 1. ORTEP drawing⁽¹¹⁾ of 2, showing the atom-labeling scheme and 50% probability thermal ellipsoids.

meter, and the distances of Fe-H (1.46(4) Å) appears to be somewhat reliable. In the closely related complex, *trans*-[FeH(η^2 -H₂)(dppe)₂][BF₄], which has been prepared by protonation of [FeH₂(dppe)₂] with HBF₄·Et₂O and structurally characterized by X-ray diffraction, the bond distance of Fe-H (terminal) is 1.28(8) Å.⁷ In another related complex, *trans*-[FeH(η^2 -H₂)(dppe)₂][BPh₄], which has been prepared by counterion exchange of *trans*-[FeH(η^2 -H₂)(dppe)₂] [BF₄] with NaBPh₄ and structurally characterized both by X-ray diffraction and by neu-

tron diffraction, the bond distances of Fe-H (terminal) are 1.30(3) Å (X-ray diffraction) and 1.535(12) Å (neutron diffraction), respectively.⁸⁾ The mean values of transition-metal hydride (M-H) bond distances determined by neutron diffraction have been summarized by Bau and Drabnis, and the average distance of a terminal Fe-H bond is 1.575(17) Å and that of a bridging Fe-H bond is 1.664(11) Å.⁹⁾

In 2, the Fe-C53 bond distance of 1.921(4) Å belongs to the higher limit of the range (1.923-1.850 Å) of the Fe-C bond distance found for Fe-

