

Fe-H...H-C 이수소 결합: *trans*-[FeH(NCSe)(dppe)₂] (dppe=Ph₂PCH₂CH₂PPh₂)의 합성 및 구조

白智榮 · 韓元錫 · 李順遠*
성균관대학교 화학과
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Fe-H...H-C Dihydrogen Bonding: Synthesis and Structure of *trans*-[FeH(NCSe)(dppe)₂](dppe=Ph₂PCH₂CH₂PPh₂)

Jee Young Baeg, Won Seok Han, and Soon W. Lee*
Department of Chemistry (BK21), Sungkyunkwan University, Suwon 440-746, Korea
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요약. *trans*-[FeHCl(dppe)₂] (1)과 KSeCN의 반응으로부터 *trans*-[FeH(NCSe)(dppe)₂] (2)가 합성되었다. 화합물 2·CH₂Cl₂의 구조가 X-ray 회절법으로 규명되었다. 화합물 2 내에서 수소 리간드가 M-H...H-C 유형의 이수소(dihydrogen) 결합에 참여하고 있다.

주제어: *trans*-[FeH(NCSe)(dppe)₂], 이수소 결합, M-H...H-C

ABSTRACT. Reaction of *trans*-[FeHCl(dppe)₂] (1) with KSeCN led to the formation of *trans*-[FeH(NCSe)(dppe)₂] (2). Compound 2·CH₂Cl₂ was structurally characterized by X-ray diffraction, in which the hydride ligand appears to be involved in the dihydrogen bonding of the type M-H...H-C.

Keywords: *trans*-[FeH(NCSe)(dppe)₂], Dihydrogen Bonding, M-H...H-C

INTRODUCTION

Compounds of pseudohalides of a general formula NCX (X=O, S, Se, or Te) are interesting due to their linkage isomerism. Those ligands are potentially ambidentate; that is, they can bond to a metal through either N or X.¹ During the past decade, dihydrogen-bonding compounds have received considerable attentions, because they have their own reactivity and participate in stoichiometric or catalytic reactions.² However, this novel hydrogen bonding remains relatively unexplored.

Recently, we reported Fe(II)-cyanato [*trans*-[FeII(CN)(dppe)₂](dppe=Ph₂PCl₂CH₂PPh₂)]³ and Fe(II)-isothiocyanato [*trans*-[FeII(NCS)(dppe)₂]]⁴ compounds, both of which show the dihydrogen bonding of the

type Fe-H...H-C between the hydride ligand and the C-H bond in the phenyl group of the dppe ligand. As a continuation of our work, we decided to investigate that dihydrogen bond in the Fe(II) isoselenocyanato compound. When *trans*-[FeII(Cl)(dppe)₂] (1) was treated with KSeCN, the product turned out to be a N-coordinated *trans*-[FeH(NCSe)(dppe)₂] (2), which exhibits the Fe-H...H-C dihydrogen bond. Herein we report the synthesis and structure of compound 2.

EXPERIMENTAL SECTION

Unless otherwise stated, all reactions have been performed with standard Schlenk line and cannula techniques under argon. Air-sensitive solids were

manipulated in a glove box filled with argon. 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. Diethyl ether was distilled over sodium metal under argon. Dichloromethane was stirred over CaH_2 and distilled by vacuum transfer. *trans*- $\text{FeH}(\text{Cl})(\text{dppe})_2$ (**1**) was prepared by the literature method.⁵

^1H -, ^{13}C (^1H), and ^{31}P -NMR spectra were recorded with a Varian Unity Inova 500 MHz spectrometer. IR spectra were recorded with a Nicolet Avatar 320 FTIR spectrophotometer. Elemental analyses were performed by the Korea Basic Science Institute.

Preparation of *trans*-[$\text{FeH}(\text{NCSe})(\text{dppe})_2$] (2**).** Compound **1** (0.1 g, 0.11 mmol) and KSeCN (0.023 g, 0.16 mmol) in a mixed solvent (20 mL) of CH_2Cl_2 and MeOH (1:1) were stirred for 1 h at 0 °C. The solvent was removed under vacuum, and the remaining solids were extracted with CH_2Cl_2 (30 mL) and washed with diethyl ether (2×10 mL) and pentane (2×10 mL) to give an orange powder of **2** (0.074 g, 0.078 mmol, 68%). Compound **2** was recrystallized from CH_2Cl_2 -hexane. ^1H -NMR (CDCl_3): δ 7.3–17.03 (40H, m, phenyl, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$), 2.50 (4H, broad m, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$), 2.04 (4H, broad m, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$), -23.73 (1H, quintet, $^2J_{\text{HFe}}=48$ Hz, *trans*-H). ^{13}C (^1H)-NMR (CDCl_3): δ 134.3–127.2 (phenyl), 34.4 ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$). ^{31}P -NMR (CDCl_3): δ 85.8 (d, $^2J_{\text{HFe}}=48$ Hz). Anal. Calcd for $\text{C}_{33}\text{H}_{31}\text{NP}_4\text{SeCl}_2\text{Fe}$: C, 65.72; H, 5.10; N, 1.45. Found: C, 66.50; H, 5.25; N, 1.29. mp: 152–154 °C (dec.). IR (KBr): 2091 (NCSe), 1840 (Fe-H) cm^{-1} .

X-ray Structure Determination. All X-ray data were collected with the use of a Siemens P4 diffractometer equipped with a Mo X-ray tube and a graphite monochromator. The orientation matrix and unit-cell parameters were determined by the least-squares analyses of the setting angles of 68 reflections in the range of $15.0^\circ < 2\theta < 25.0^\circ$. Three check-reflections were measured every 100 reflections throughout data collection and showed no noticeable variations in intensity. Intensity data were empirically corrected for absorption with Ψ -scan data. Decay corrections were also made. All

calculations were carried out with the use of SHELXTL programs.⁶

An orange crystal of **2** of approximate dimensions of $0.26 \times 0.24 \times 0.22$ mm³, shaped as a cube, was used for crystal- and intensity-data collection. The unit-cell parameters and systematic absences, $h0l$ ($h+l=2n+1$) and $0k0$ ($k=2n+1$), unambiguously indicated $P2_1/n$ as a space group. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. The hydride ligand (Hfe) was located in the difference Fourier map and refined isotropically. All remaining hydrogen atoms were generated in idealized positions and refined in a riding model. Details on crystal data and refinement details are given in Table 1. Selected bond lengths and bond angles for **2** are shown in Table 2.

Table 1. X-ray data collection and structure refinement for in **2** · CH_2Cl_2

| | |
|---|---|
| formula | $\text{C}_{33}\text{H}_{31}\text{NP}_4\text{SeCl}_2\text{Fe}$ |
| fw | 1043.55 |
| temperature, K | 293(2) |
| crystal system | monoclinic |
| space group | $P2_1/n$ |
| <i>a</i> , Å | 12.114(2) |
| <i>b</i> , Å | 23.234(5) |
| <i>c</i> , Å | 18.386(4) |
| β , deg | 106.822(8) |
| <i>V</i> , Å ³ | 4954(1) |
| <i>Z</i> | 4 |
| d_{calc} , g cm ⁻³ | 1.399 |
| μ , mm ⁻¹ | 1.314 |
| T_{min} | 0.4211 |
| T_{max} | 0.5435 |
| $F(000)$ | 2144 |
| No. of reflections measured | 8960 |
| No. of reflections unique | 8544 |
| No. of reflections with $I > 2\sigma(I)$ | 4607 |
| No. of parameters refined | 573 |
| 2θ range (°) | 3.550.0 |
| scan type | ω |
| scan speed | variable |
| GOF (goodness-of-fit on F^2) | 1.011 |
| Max., min. in $\Delta\rho$ ($\text{e} \text{Å}^{-3}$) | 0.512, -0.967 |
| <i>R</i> | 0.0747 |
| wR_2^a | 0.1598 |

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

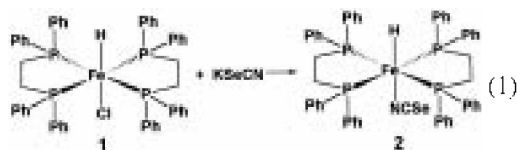
Table 2. Selected bond lengths (Å) and bond angles (°) in $2 \cdot \text{CH}_2\text{Cl}_2$

| | | | | | |
|------------|----------|------------|-----------|------------|-----------|
| Fe1-N1 | 1.966(7) | Fe1-P1 | 2.230(2) | Fe1-P2 | 2.250(2) |
| Fe1-P4 | 2.258(2) | Fe1-P3 | 2.267(2) | Fe1-Hfe | 1.58(7) |
| Se1-C53 | 1.807(8) | N1-C53 | 1.143(9) | | |
| N1-Fe1-P1 | 95.8(2) | N1-Fe1-P2 | 99.3(2) | P1-Fe1-P2 | 84.55(8) |
| N1-Fe1-P4 | 91.3(2) | P1-Fe1-P4 | 172.82(9) | P2-Fe1-P4 | 95.44(8) |
| N1-Fe1-P3 | 86.2(2) | P1-Fe1-P3 | 95.66(8) | P2-Fe1-P3 | 174.50(9) |
| P4-Fe1-P3 | 83.66(8) | N1-Fe1-Hfe | 172(2) | P1-Fe1-Hfe | 76(2) |
| P2-Fe1-Hfe | 82(2) | P4-Fe1-Hfe | 96(2) | P3-Fe1-Hfe | 93(2) |
| C53-N1-Fe1 | 172.9(6) | N1-C53-Se1 | 175.2(7) | | |

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center. CCDC No. 189185 for $2 \cdot \text{CH}_2\text{Cl}_2$. Copies of this information may be obtained free of charge from: The director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk/conts/retrieving.html).

RESULTS AND DISCUSSION

Preparation. At 0 °C, stirring *trans*- $\text{FeH}(\text{Cl})(\text{dppe})_2$ (**1**) and KSeCN in a mixed solvent of MeOH and CH_2Cl_2 ($v:v=1:1$) leads to the formation of a 6-coordinated isoselenocyanato compound *trans*- $[\text{FeH}(\text{NCSe})(\text{dppe})_2]$ (**2**), as shown in eq 1. During the reaction, there is a color change from red to orange. Compound **2** has been characterized by NMR (^1H -, ^{13}C { $^1\text{H}}$ }-, and ^{31}P -NMR), IR, elemental analysis, and X-ray diffraction. Compound **2** appears to be somewhat moisture-sensitive, and therefore it has been stored under argon.



The molecular geometry of **2** can be readily deduced from NMR data and elemental analysis data. Complex **2** exhibits a quintet (δ -23.73) for the hydride ligand in the ^1H -NMR spectra and a doublet (δ 85.8) for the four phosphine ligands in the ^{31}P -NMR spectra. These NMR data indicate that

the hydride ligand couples with the four equivalent phosphorus nuclei in the phosphines (dppe) occupying the equatorial plane and that the orientation between the hydride and the isoselenocyanato ligands is mutually *trans*. The IR spectra display the Fe-H band at 1840 cm^{-1} and the NCSe band at 2091 cm^{-1} .

Structure. The molecular structure of **2** 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 isoselenocyanato ligands at the axial sites. The equatorial plane, defined by the four dppe phosphorus atoms (P1-P4) is relatively planar with the average atomic displacement of 0.0163 Å. The Fe metal lies 0.1241 Å below the equatorial plane.

The hydride ligand (Hfe) could be located and reasonably refined with an isotropic thermal parameter, and the bond length of Fe-H (1.58(7) Å) appears to be somewhat reliable. The mean values of transition metallhydride (M-H) bond lengths determined by neutron diffraction have been summarized by Bau and Drabnis, and the average length of a terminal Fe-H bond is 1.575(17) Å and that of a bridging Fe-H-Fe bond is 1.664(11) Å.⁷

The Fe-N1 bond length of 1.966(7) Å indicates an Fe-N single bond. The N1-C53 bond length of 1.143(9) Å indicates an $\text{N}\equiv\text{C}$ triple bond, and the Se1-C53 bond length is 1.807(8) Å. In addition, the Fe1-N1-C53 and N1-C53-Se1 fragments are essentially linear with the bond angles of 172.9(6)° and 175.2(7)°, respectively. These bonding parameters suggest that canonical form I is a major contribution in which the nitrogen atom is *sp*-hybridized.

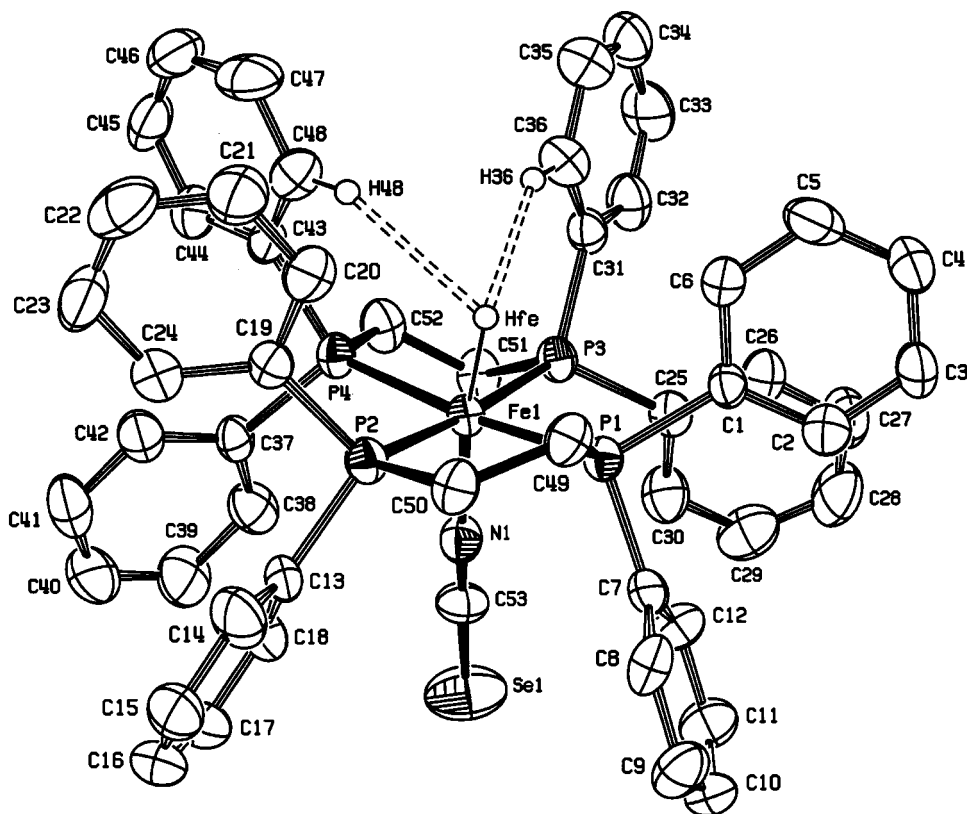
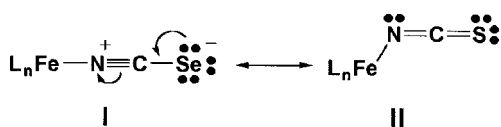


Fig. 1. ORTEP drawing of **2**, showing the atom-labeling scheme and 50% probability thermal ellipsoids.



Compound **2** appears to have a pseudo- C_2 axis that passes through the Fe1, N1, and Hfe atoms and is perpendicular to the equatorial plane. This symmetry might explain the equivalency of the four phosphorus nuclei in the NMR spectra. In other words, the crystal structure explains the NMR spectra of compound **2** that show a quintet for the H ligand in the ^1H -NMR and a doublet for the four P atoms the ^{31}P -NMR spectra. The results of the X-ray structure and NMR spectral data indicate that this compound has the same structure both in solution and in the solid state.

Recently, the hydrogen bond in organometallic compounds has been the focus of research. It is now accepted that most kinds of C-H groups can act as

hydrogen-bond donors.⁸⁻¹⁵ Moreover, it has been recognized for many years that the C-H bonds can act as weak hydrogen-bond proton donors in the order of $\text{C}(\text{sp})\text{-H} > \text{C}(\text{sp}^2)\text{-H} > \text{C}(\text{sp}^3)\text{-H}$.^{16,17} Crabtree and co-workers recently proposed a new type of the dihydrogen bonding ($\text{M-H}\cdots\text{H-C}$) in aryl phosphine (PAr_2) hydride complexes.¹⁸ According to their own work and CSD survey, the H \cdots H distances range from 1.50 to 2.20 Å (mean, 1.96 Å), M-H \cdots H angles from 109 to 170° (mean, 130°) with a strong preference for the range 122-142°, and H \cdots H-C angles from 118 to 164° (mean, 142°) with a strong preference for the range 138-148°. For comparison, the der Waals radius of H is 1.2 Å.

As previously mentioned on the M-H \cdots H-C dihydrogen bonding, Crabtree and co-workers limited their CSD search to compounds with H \cdots H contacts less than 2.20 Å. This value is slightly shorter than the H \cdots H contact identified in the structure of

Table 3. Distances (Å) and angles (°) in the Fe-H...H-C fragment

| | |
|----------|--------------------|
| H...H | Hfe...H36: 2.21 |
| | Hfe...H48: 2.41 |
| Fe-H...H | Fe1-Hfe...H30: 120 |
| | Fe1-Hfe...H48: 115 |
| H...H-C | Hfe...H36-C36: 141 |
| | Hfe...H48-C48: 140 |

compound **2** (Table 3). Compound **2** has the aryl phosphine (dppc) ligand, and the distances and angles of the Fe-H...H-C fragment are highly consistent with the preferred values suggested by the Crabtree's study. On the basis of the bonding parameters described above, the hydride ligand (Hfe) appears to be involved in the dihydrogen bond of the type M-H...H-C. Moreover, the hydride ligand seems to be dihydrogen-bonded simultaneously to two C-H bonds, which might make it possible to locate this ligand in the X-ray diffraction study. This type of the dihydrogen bonding was also observed in *trans*-[FeH(CN)(dppc)₂] and *trans*-[FeH(NCS)(dppc)₂].³¹

In summary, the reaction of *trans*-[FeH(Cl)(dppc)₂] with KSCN gave *trans*-[FeH(NCS)(dppc)₂], which shows the double-dihydrogen bonding of the type M-H...H-C between the hydride ligand and the two C-H bonds in the phenyl groups of the dppc ligands.

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