

trans-[FeH(NCS(Me)-S)(dppe)₂]I 화합물의 *trans*- [Fe(NCS)₂(Ph₂P(O)CH₂CH₂P(O)Ph₂)₂][I₃]로 산화

李志馬華 · 李順遠*

성균관대학교 자연과학부 화학과

(2000. 7. 7 접수)

Oxidation of *trans*-[FeH(NCS(Me)-S)(dppe)₂]I to *trans*- [Fe(NCS)₂(Ph₂P(O)CH₂CH₂P(O)Ph₂)₂][I₃] (dppe = PPh₂CH₂CH₂PPh₂)

Ji Hwa Lee and Soon W. Lee*

Department of Chemistry, Sungkyunkwan University, Natural Science Campus, Suwon 440-746, Korea

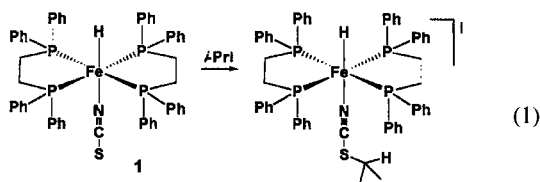
(Received July 7, 2000)

ABSTRACT. The Fe(II)-isothiocyanato complex *trans*-[FeH(NCS)(dppe)₂] (1) reacted with iodomethane (MeI) to give methyl isothiocyanide-Fe(II) complex, *trans*-[FeH(NCS(Me)-S)(dppe)₂]I (2). Compound 2 was oxidized to *trans*-[Fe(NCS)₂(Ph₂P(O)CH₂CH₂P(O)Ph₂)₂][I₃] (3), which was structurally characterized by X-ray diffraction. The molecular structure of 3 showed a bent Fe-NCS group. Crystallographic data for 3: triclinic space group *P* $\bar{1}$, *a*=11.071(2) Å, *b*=12.054(2) Å, *c*=12.121(1) Å, α =101.02(1)°, β =95.887(9)°, γ =110.34(1)°, *Z*=1, *R*(*wR*)=0.0567(0.1294).

INTRODUCTION

Transition-metalisothiocyanato (M-NCS) complexes have got continuous attraction.¹⁻¹¹ In particular, these have provided an extensive series of examples of linkage isomerism (*N*- or *S*-bonded NCS). We have become interested in the nucleophilic properties of the NCS sulfur atom and recently reported the preparation and structure of *trans*-[FeH(NCS(*i*-Pr)*S*)(dppe)₂]I (dppe=PPh₂CH₂CH₂PPh₂), which has been prepared by the electrophilic attack of the mild electrophile *i*-PrI at the NCS sulfur atom (eq 1).¹²

Because of our continuous interest in investigating the nucleophilicity of the NCS sulfur atom in the neutral Fe(II)-NCS complexes, we set out the reaction of the *trans*-[FeH(NCS)(dppe)₂] with another electrophile, iodomethane (MeI). Here we report the synthesis and characterization of *trans*-[FeH(NCS(Me)-S)(dppe)₂]I (2). We also report the molecular structure of *trans*-[Fe(NCS)₂(Ph₂P(O)CH₂CH₂P(O)Ph₂)₂][I₃] (3), which was formed by the oxidation of 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. Glassware was soaked in KOH-saturated 2-propanol for about 24 h and washed with distilled water and acetone before use, and it was either flame-dried or oven-dried. Diethyl ether (Et₂O) was distilled over sodium metal under argon. Dichloromethane was stirred over CaH₂ and distilled by vacuum transfer. The NMR solvent (CDCl₃) was degassed by freeze-pump-thaw cycles before use and stored over molecular sieves under argon. Iodomethane (CH₃I)

was purchased from Aldrich company. Compound *trans*-[FeH(NCS)(dppe)] (**1**) was prepared by treating *trans*-[FeHCl(dppe)₂] with KSCN.

¹H- and ¹³C{¹H}-NMR spectra were recorded with a Varian Unity Inova 500 MHz spectrometer with reference to internal solvent resonances and reported relative to tetramethylsilane. ³¹P-NMR spectra were also recorded with a Varian Unity Inova 500 MHz spectrometer with reference to external 85% H₃PO₄. IR spectra were recorded with a Nicolet 205 FTIR spectrophotometer. Melting points were measured with a Thomas Hoover capillary melting point apparatus without calibration.

Preparation of *trans*-[FeH(NCSMe)(dppe)]2**, (**2**).** Compound **1** (0.137 g, 0.015 mmol) was dissolved in 1 mL of iodomethane, and the solution was stirred for 1 h. During stirring, a red slurry turned to a yellow one. The resulting solution was filtered, and the remaining solid was washed with Et₂O (310 mL) and then dried under vacuum to give 0.132 g (0.125 mmol, 84%) of **2**.

¹H-NMR (CDCl₃): δ 7.388–6.760 (4H, m, Ph₂PCH₂-CH₂PPh₂), 2.614 (3H, s, NCSCCH₃), 2.581 (4H, broad, Ph₂PCH₂CH₂PPh₂), 2.079 (4H, broad, Ph₂PCH₂CH₂-PPh₂), 19.904 (1H, quintet, ²J_{P-H}=47 Hz, H-Fe). ¹³C{¹H}-NMR (CDCl₃): δ 135.840, 134.627, 134.153, 133.686, 133.158, 130.658, 129.523, 129.263, 128.479, 1287.819 (phenyl), 118.940 (NCSCCH₃), 33.491 (Ph₂PCH₂CH₂PPh₂), 18.324 (NCSCCH₃). ³¹P-NMR (CDCl₃): δ 84.020 (d, ²J_{P-H}=47 Hz). mp (dec.): 168–170 °C. IR (KBr): 2122 (N≡C), 1871 (Fe-H) cm⁻¹.

Formation of *trans*-[Fe(NCS)₂]Ph₂P(O)CH₂CH₂P(O)-Ph₂][I₃], (3**).** When the recrystallization of compound **2** from CH₂Cl₂/Et₂O was tried, it transformed to *trans*-[Fe(NCS)₂]Ph₂P(O)CH₂CH₂P(O)Ph₂][I₃], (**3**). IR (KBr): 2030 (NC), 1127, 1150 (P=O) cm⁻¹. mp (dec.): 108–110 °C.

X-ray Structure Determination of **3.** 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. The orientation matrix and unit cell parameters were determined by least-squares analyses of the setting angles of 26 reflections in the range 15.0 < 2θ < 25.0°. 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 empir-

Table 1. X-ray data collection and structure refinement for **3**

formula	C ₅₄ H ₄₈ N ₂ O ₄ P ₄ S ₂ I ₃ Fe
fw	1413.49
temperature, K	296(2)
crystal system	triclinic
space group	P1
a, Å	11.071(2)
b, Å	12.054(2)
c, Å	12.121(1)
α, deg	101.02(1)
β, deg	95.887(9)
γ, deg	110.34(1)
V, Å ³	1584.4(7)
Z	1
d _{calc} , g cm ⁻³	1.602
μ, mm ⁻¹	4.032
T _{min}	0.5046
T _{max}	0.6199
F(000)	695
No. of reflections measured	5184
No. of reflections unique	4904
No. of reflections with I > 2σ(I)	4183
No. of parameters refined	320
2θ range (°)	3.5–50.0
scan type	ω
scan speed	variable
GOF (goodness-of-fit on F ²)	1.035
Max., min. in Δρ (e Å ⁻³)	0.823, -1.019
R	0.0567
wR ₂ ^a	0.1294

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

ically corrected with ψ-scan data. All calculations were carried out with use of the SHELXTL programs.¹³

A red crystal of **3**, shaped as a plate of approximate dimensions 0.78 × 0.30 × 0.08 mm³, was used for crystal and intensity data collection. Details on crystal data and intensity data are given in Table 1. The unit cell parameters indicated the triclinic unit cell with the two possible space groups: $P\bar{1}$ and P1. A statistical analysis of reflection intensities suggested a centrosymmetric space group, and the structure analysis converged only in $P\bar{1}$. The structure was solved by the direct method and refined by full-matrix least-squares calculations of F², initially with isotropic and finally anisotropic temperature factors for all non-hydrogen atoms. All the other hydrogen atoms were generated in idealized positions and refined in a

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3**

	x	y	z	<i>U</i> (eq) ^a
Fe(1)	5000	-5000	5000	28(1)
S(1)	1760(2)	-7955(2)	6229(2)	86(1)
P(1)	3554(1)	-6705(1)	2316(1)	32(1)
P(2)	3410(1)	-3175(1)	5960(1)	34(1)
O(1)	3722(3)	-4204(3)	5327(3)	44(1)
O(2)	3814(3)	-5895(3)	3487(2)	43(1)N(1)
N(1)	3959(4)	-6361(4)	5683(4)	55(1)
C(1)	2209(4)	-8114(4)	2168(4)	38(1)
C(2)	1395(5)	-8211(5)	2979(4)	52(1)
C(3)	357(5)	-9312(5)	2864(5)	67(2)
C(4)	125(5)	10276(6)	1983(5)	68(2)
C(5)	915(5)	10202(5)	1188(5)	61(1)
C(6)	1976(5)	9119(4)	1278(4)	49(1)
C(7)	3198(4)	5969(4)	1246(4)	41(1)
C(8)	3793(8)	4754(6)	1422(6)	100(3)
C(9)	3494(10)	4166(7)	582(8)	129(4)
C(10)	2666(7)	4775(7)	356(6)	84(2)
C(11)	2048(9)	6003(7)	559(6)	103(3)
C(12)	2305(8)	6589(6)	249(5)	82(2)
C(13)	1986(4)	3753(4)	6580(4)	40(1)
C(14)	1219(5)	4994(5)	6244(5)	58(1)
C(15)	133(6)	5449(7)	6737(7)	84(2)
C(16)	206(6)	4716(8)	7518(8)	89(2)
C(17)	528(7)	3503(7)	7866(6)	82(2)
C(18)	1649(6)	3000(5)	7412(5)	61(1)
C(19)	3167(4)	2241(4)	5048(4)	45(1)
C(20)	2445(9)	1519(7)	5275(6)	96(3)
C(21)	2297(11)	805(8)	4562(7)	112(3)
C(22)	2846(7)	794(8)	3634(8)	100(3)
C(23)	3468(11)	1562(14)	3347(10)	182(7)
C(24)	3618(10)	2301(11)	4069(8)	140(5)
C(25)	4936(4)	7095(4)	2034(3)	35(1)
C(26)	4718(4)	2201(4)	7119(4)	37(1)
C(27)	3052(5)	7025(4)	5924(4)	47(1)
I(1)	3576(1)	832(1)	8393(1)	87(1)
I(2)	5000	0	10000	88(1)

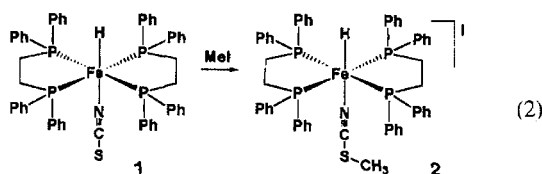
^aEquivalent isotropic *U* defined as one third of the trace of the orthogonalized *U_i* tensor.

riding model.

Final atomic positional parameters are shown in Table 2. Selected bond distances and bond angles for **3** is shown in Table 3.

RESULTS AND DISCUSSION

Preparation. An Fe(II)-organic isothiocyanide complex, *trans*-[FeH(NCS(Me)-S)(dppe)₂][I] (**2**), has been prepared by the electrophilic attack of iodomethane (MeI) at the isothiocyanato sulfur in a neutral Fe(II)-isothiocyanato (Fe-NCS) complex, *trans*-[FeH(NCS)(dppe)₂] (**1**), (eq 2). Stirring the iodomethane solution containing **1** at room temperature for 1 h gives the desired product in high yield (84%). In this reaction, the iodomethane behaves both as a reagent and as a solvent. Compound **2** is stable in the solid state, but unstable in solution.

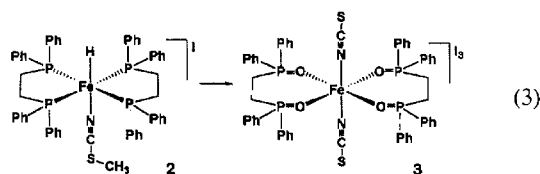


Compound **2** has been characterized by NMR (¹H-, ¹³C{¹H}-, and ³¹P-NMR) and IR spectroscopy. In the ¹H-NMR spectra of **2**, isothiocyanide methyl protons (NCS-CH₃) appear as a singlet at δ 2.614 ppm, and the hydride ligand as a quintet (δ -19.904 ppm) because of its coupling (²*J*_{P-H}=47 Hz) with the four equivalent phosphorus nuclei in the dppe ligands. As expected, the ³¹P-NMR spectra exhibit a doublet (δ 84.020 ppm) for the dppe phosphorus nuclei with a coupling constant of ²*J*_{P-H}=47 Hz. These NMR data confirm the structure of **2**, in which the hydride and the methyl isothiocyanide ligands are *trans* to each other in axial the sites and the two dppe ligands occupy the equatorial sites. In the ¹³C{¹H}-NMR spectra, the isothiocyanide methyl carbon (NCS-CH₃) appears at δ 18.324 ppm and the NCS carbon at δ 118.940 ppm. In addition, the Fe-H and NC bands appear at 1871 and 2122 cm⁻¹, respectively.

The compound **2** in solution seems to be air-sensitive. During the crystal growth of **2**, it transformed to *trans*-[Fe(NCS)₂(Ph₂P(O)CH₂CH₂P(O)Ph₂)₂][I₃] (**3**), probably because of air-oxidation (eq 3). However, we cannot rule out the possibility that the trace amount of water, present in the crystallization solvent mixture (CH₂Cl₂-Et₂O), reacts with **2** to give **3**. In this transformation, the Fe metal formally oxidized from +2 to +3, the counterion I from -1 to -1/3, and the dppe ligands to the corresponding phosphine oxides (Ph₂P(O)CH₂CH₂P(O)PPh₂).

Table 3. Selected bond distances (Å) and bond angles (°) in **3**

Fe1-N1	2.027(4)	Fe1-O1	1.999(3)	Fe1-O2	2.005(3)
P1-O2	1.496(3)	P2-O1	1.496(3)	P1-C25	1.798(4)
P2-C26	1.794(4)	N1-C27	1.151(6)	C27-S1	1.611(5)
I1-I2	2.917(6)				
O1-Fe1-O2	87.0(1)	O1-Fe1-N1	88.6(2)	O2-Fe1-N1	89.0(2)
Fe1-N1-C27	157.6(4)	N1-C27-S1	178.4(4)	P1-O2-Fe1	150.1(2)
P2-O1-Fe1	150.4(2)	O1-P2-C26	115.5(2)	O2-P1-C25	111.8(2)



As expected from the formal oxidation state of Fe^{3+} (d^5), the compound **3** does not show NMR spectra probably because of its paramagnetic nature. In the IR spectra of compound **3**, the Fe-H band has disappeared, and the two new P=O bands appear at 1127 and 1150 cm^{-1} . The NC band has a strong intensity at 2030 cm^{-1} , which has shifted to the lower frequency by 91 cm^{-1} with respect to that in the compound **3**.

Structure. The structure of **3** with the atomic numbering scheme is shown in Fig. 1. The coordination sphere of the Fe metal can be described as an octahedron in which the Fe atom lies on the inversion center. This is

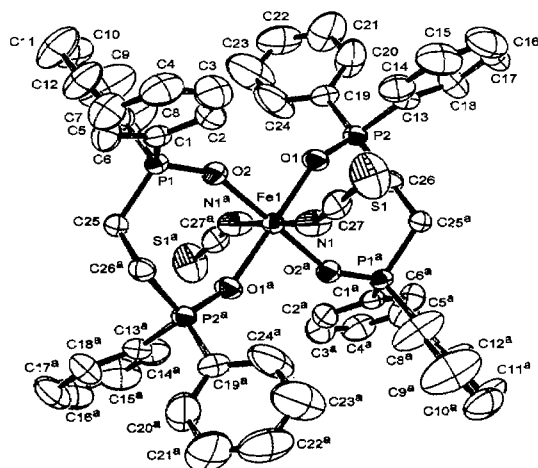
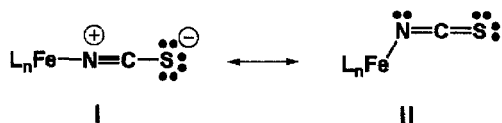


Fig. 1. ORTEP drawing the cationic part of **3**, $\text{trans-}[\text{Fe}(\text{NCS})_2(\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_2]^+$, showing the atom-labeling scheme and 50% probability thermal ellipsoids. Symmetry-equivalent atoms (denoted by the letter a) are generated by the center of symmetry.

why this molecule has the Z value of 1 instead of 2. In other words, the asymmetric unit of a unit cell contains only one half of the molecule. The four oxygen atoms in phosphine oxide ligands occupy the equatorial sites, and the two *trans* NCS ligands occupy the axial sites. The linear anion (I_3) is not bonded to the Fe metal and acts as a counterion, in which the central iodine (I2) lies on the crystallographic inversion center. The equatorial plane, defined by the Fe and four phosphine oxide oxygen atoms, is essentially planar because it is generated by the crystallographic inversion operation.

The Fe1-O1 and Fe1-O2 bond distances are 1.999(3) Å and 2.005(3) Å, respectively. The O1-P2 and O2-P1 bond distances are essentially the same (1.493(3) Å). The Fe1-N1 bond distance of 2.027(4) Å indicates a Fe-N single bond, because a metal-nitrogen single bond is expected to lie within 1.95-2.15 Å.¹⁴ The N1-C27 bond distance of 1.151(6) Å indicates an $\text{N}\equiv\text{C}$ triple bond, and the C27-S1 bond distance of 1.611(5) Å is significantly shorter than a C-S single bond (1.81 Å). In structurally characterized transition-metal-isothiocyanato (M-NCS) complexes, the N-C bond distance lies within 1.129-1.160 Å and the C-S bond distance within 1.632-1.650 Å.¹⁵ The Fe1-N1-C27 and N1-C27-S1 bond angles are 157.6(4)° and 178.4(4)°, respectively. Fe(II)-NCS complexes exhibit the Fe-N-CS bond angles in a wide range of 120-180°, with a preference to the range 150-180°.¹⁶ The bonding parameters of the Fe-NCS group in compound **3** indicate a bent Fe-NCS group and suggest the resonance form II to be a major contribution, in which the nitrogen atom is sp^2 -hybridized. In the crystal structure of KSCN, the following bonding parameters were observed: (1) The S-C-N moiety is linear with a bond angle of 178(1)°. (2) The S-C bond distance is 1.69(1) Å, considerably shorter than the C-S single bond distance of 1.81 Å. (3) The C-N bond distance is 1.51(1) Å (a $\text{C}\equiv\text{N}$

triple bond).¹⁷



In summary, we have prepared *trans*-[FeH(NCS(Me)-S)(dppe)₂]**I** (**2**) by the electrophilic attack of iodomethane at the NCS sulfur atom in *trans*-[FeH(NCS)(dppe)₂]**I** (**1**). Compound **2** underwent oxidation to *trans*-[Fe(NCS)₂(Ph₂P(O)CH₂CH₂P(O)Ph₂)₂][I₃] (**3**). In this oxidation reaction, the Fe metal formally oxidized from +2 to +3, the counterion I from -1 to -1/3 (in the form of I₃), and the dppe ligands to the corresponding phosphine oxides (Ph₂P(O)CH₂CH₂P(O)PPh₂). The molecular structure of **3** shows a bent Fe-NCS group.

The authors wish to acknowledge the financial support of the Korea Research Foundation made in the Program Year 1997.

REFERENCES

1. Flint, C. D.; Goodgame, M. *Inorg. Chem.* **1969**, *8*, 1833.
2. Burbridge, C. D.; Goodgame, D. M. L. *Inorg. Chim. Acta* **1970**, *4*, 231.

3. Nelson, S. M.; Kelly, W. S. J.; Ford, G. H. *J. Chem. Soc., A*, **1971**, 388.
4. Cotton, S. A.; Gibson, J. F. *J. Chem. Soc., A*, **1971**, 859.
5. Dahlhoff, W. V.; Nelson, S. M. *J. Chem. Soc., A*, **1971**, 2184.
6. David, P. G. *J. Inorg. Nucl. Chem.* **1973**, *35*, 1463.
7. Drew, M. G. B.; Othman, A. H. *J. Chem. Soc., Dalton Trans.* **1976**, 1394.
8. Berndt, A. F.; Barnett, K. W. *J. Organomet. Chem.* **1980**, *182*, 211.
9. Rossi, R.; Duatti, A.; Magon, L.; Toniolo, L. *Inorg. Chim. Acta* **1981**, *48*, 243.
10. Long, G. J.; Galcazzi, G.; Russo, U.; Valle, G.; Calogero, S. *Inorg. Chem.* **1983**, *22*, 507.
11. Ballester, L.; Gutierrez, A.; Perpinan, MF; Rico, S.; Azcondo, M. T.; Bellitto, C. *Inorg. Chem.* **1999**, *38*, 4430.
12. Lee, J. H.; Lee, S. W. *Korean J. Cryst.* **2000**, *11*, 10.
13. Bruker, SHELXTL, Structure Determination Software Programs, Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, 1997.
14. Davis, B. R.; Payne, N. C.; Ibers J. A., *Inorg. Chem.*, **1969**, *8*, 2719.
15. Orpen, A. G.; Brammer, L.; Brammer, F. H.; Kennard O.; Watson, D. G., *J. Chem. Soc., Dalton Trans.*, **1989**, S25.
16. Drew, M. G. B.; Othman, A. H. *Acta Cryst.* **1975**, *B31*, 613.
17. Akers, C.; Peterson, S. W.; Willet, R. D. *Acta Cryst.* **1968**, *B24*, 1125.