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Nitrosyl and carbene iron complexes bearing $\kappa^3$-SNS thioamide pincer type ligand

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The previously reported monochelate iron complex with $\kappa^3$ SNS thioamide pincer ligand, 2,6-bis(N-2,6-bis(diphenylmethyl)-4-isopropylphenyliminothiolate)pyridine ($L_{\text{DPM}}$), [Fe(THF)$_2$(κ$^3$-L$_{\text{DPM}}$)], gave novel complexes, [Fe(NHC)(κ$^3$-L$_{\text{DPM}}$)] and [Fe(NO)$_2$(κ$^3$-L$_{\text{DPM}}$)], by the substitution reactions with N-heterocyclic carbene (NHC) and NO molecule, respectively. The X-ray crystal structure of complex [Fe(NHC)(κ$^3$-L$_{\text{DPM}}$)] revealed a unique square planar iron(II) complex, which was determined to be in an intermediate spin state ($S = 1$) in benzene from the Evans method. The complex [Fe(NO)$_2$(κ$^3$-L$_{\text{DPM}}$)] was determined to be a trigonal bipyramidal geometry from the X-ray analysis and was indicated to be diamagnetic from $^1$H NMR spectrum. The $\nu$(NO) stretching vibration of this complex showed two peaks at 1840 cm$^{-1}$ and 1790 cm$^{-1}$, and also the Fe–N–O bond angles were 168.9(2) and 168.03(19)$^\circ$. These findings suggest that the two coordinated NO molecules have neutral radical character, and they antiferromagnetically coupled with the high-spin iron center.

Results and discussion

We have previously reported very interesting iron complex, [Fe(THF)$_2$(κ$^3$-L$_{\text{DPM}}$)], which can carry out substitution reaction very easily, and also studied that the $\sigma$-donor ability of S atom of the ligand can be able to be changed by the protonation/deprotonation on thioamide pincer ligand. Furthermore, we have interested in the reactivity of the monochelate iron complex with thioamide pincer ligand toward biologically important nitrosyl molecule and catalytically interesting carbene compound.

Scheme 1. Synthesis of compound [Fe(NHC)(κ$^3$-L$_{\text{DPM}}$)].

Synthesis of Iron(II)-NHC Complex

N-heterocyclic carbenes (NHC) have been reported in organometallic chemistry, which are well-known as a strong electron-donor and moderate $\pi$ acceptor abilities. There are many reports that second- and third-row transition metal complexes...
with NHC play an important role in catalysis chemistry because of its strong biding ability. Recently, catalytic studies using iron-NHC complex increased in because of its low toxicity and high abundance, although it has been still scarce. We attempted to synthesize an iron-NHC complex with thioamide pincer ligand.

The red precipitate of [Fe(THF)(κL-LDPM)] reacts with NHC carbene in benzene, and the resulting green solution was added in hexane and stored in the refrigerator at ~30 °C. (Scheme 1). The complex [Fe(NHC)(κL-LDPM)] was yielded as green crystalline solids. The complex [Fe(NHC)(κL-LDPM)] has been characterized by 1H NMR and elemental analyses. The complex [Fe(NHC)(κL-LDPM)] is paramagnetic, because 1H–NMR spectra display broadened resonances in the range of ~38 - 47 ppm. Its solution magnetic moment was determined to be 2.81 μB (S = 1) at 296 K by the Evans method, suggesting that the pincer type ligand backbone and the strong NHC play an important role in catalysis chemistry because of its strong biding ability.

The crystal structure of [Fe(NHC)(κL-LDPM)] was determined by X-ray analysis (Figure 1). The complex [Fe(NHC)(κL-LDPM)] forms a square planar structure with the SNS pincer type ligand and one coordinated NHC carbene; the Fe(1)–N(1), Fe(1)–S(1), Fe(1)–N(1′), and Fe(1)–C(41) bond lengths are 1.965(2), 2.2217(6), 2.2217(6), and 1.939(3) Å respectively. The Fe(1)–N(1), Fe(1)–S(1) and Fe(1)–S(1′) bond lengths are similar to those (Fe(1)–N(1), Fe(1)–S(1), Fe(1)–S(2) = 1.980(2), 2.2676(11), 2.2638(11) Å for [Fe(CO)κ3-L-DPM], 1.9844(17), 2.2807(10), 2.2744(10) Å for [Fe(CN-xyllyl)(κL-LDPM)] of low spin iron(II) complexes reported previously, and shorter than those (Fe(1)–N(1), Fe(1)–S(1), Fe(1)–S(2) = 2.1593(19), 2.3600(8), 2.3621(8) Å for [Fe(THF)κ3-L-DPM]) of high spin iron(II) complex reported previously. The Fe(1)–C(41) bond length is similar to those of previously reported square planar intermediate spin state iron(II) complexes with carbene (1.801(9) Å – 2.010(9) Å) and is shorter than those of tetrahedral iron(II) complexes with carbene (2.075(4) – 2.363(15) Å). This means that the pincer type ligand backbone and the strong σ-donation from NHC ligand lead to a strong ligand field for the metal, enabling the antibonding dπ–dπ orbital to efficiently destabilize. The sum (360°) of bond angles around the metal, S(1)–Fe(1)–N(1) 86.838(15), N(1)–Fe(1)–S(1′) 86.838(15), S(1)–Fe(1)–C(41) 93.162(15) and S(1′)–Fe(1)–C(41) 93.162(15), reveal that the complex is a planar geometry. The C(1)–S(1) and C(1)–N(2) bond lengths of [Fe(NHC)(κL-LDPM)] are 1.7577(18) Å and 1.281(3) Å, respectively, indicating that the pincer ligand is an iminothiolate form. We have successfully synthesized a square planar iron–NHC complex [Fe(NHC)(κL-LDPM)] with an intermediate spin iron ion by using the monochelate iron complex [Fe(THF)κ3-L-DPM]). The UV-vis absorption spectrum of [Fe(NHC)(κL-LDPM)] in THF exhibited one medium absorption at 360 nm (ε = 8700) and two weak broadened absorption bands at 581 (ε = 1150) and 627 nm (ε = 1420), both of which are assigned to MLCT bands (Figure S4). The cyclic voltammogram (CV) of [Fe(NHC)(κL-LDPM)] showed reversible redox couples at E1/2 = –0.41 V (vs. Fe/C) in THF under Ar, which was assigned to Fe(II)/Fe(III) and Fe(II)/Fe(III) of the metal center (Figure S3). As compared with those of dichloro NHC iron complex [FeCl2(IMes)] (E1/2 = –0.54 V (vs. Fe/C)) and bis-THF iron complex [Fe(THF)2(κL-LDPM)] (E1/2 = –0.05 V (vs. Fe/C)), the redox potential of [Fe(NHC)(κL-LDPM)] is higher than [FeCl2(IMes)] (~0.54 V vs. Fe/C), probably due to π-back donation of Fe(II) to thioamide ligand, and is lower than [Fe(THF)2(κL-LDPM)] because of strong donation from NHC.

Scheme 2. Synthesis of compound [Fe(NO)2(κL-LDPM)].

Reaction of [Fe(THF)2(κL-LDPM)] with NO

Nitrosyl chemistry has been interested from the viewpoint of biological functions such as a neurotransmission, vasodilation, and blood clotting and chemical property as a non-innocent ligand, and well studied by some bioinorganic and inorganic chemists for several decades. NO molecule is a stable free radical with a single unpaired electron on σ* orbital. Additionally the NO molecule coordinated to metal complex is very interesting, because it can work as a nitrosyl cation (NO+), a neutral radical, and a nitrosyl anion (NO−). These are detected from M–NO bond angles; ~180 ° for cation, ~120 ° for anion state. We attempted to synthesize iron–NO complex with thioamide pincer ligand and to investigate the chemical property of the coordinated NO ligand. The tolune solution of [Fe(THF)2(κL-LDPM)] reacts with NO, and then the reaction mixture shows color change from orange to dark brown solution (Scheme 2). The volatiles were
removed under the vacuum. The reaction mixture was washed by n-pentane. The brown powder of [Fe(NO)₂(κ²-L_DPM)] was collected by filtration. The crystal structure of [Fe(NO)₂(κ²-L_DPM)], as shown in Figure 2, revealed that the coordination geometry of dinitrosyl complex [Fe(NO)₂(κ²-L_DPM)] is a trigonal bipyramidal structure (τ = 0.80); the bond angles around metal are as follows, the angles N(1)–Fe–N(4) 118.14(9), N(1)–Fe–N(5) 121.30(10) and N(4)–Fe–N(5) 120.37(10) for the trigonal plane (sum of angles = 360°) and the angle S(1)–Fe–S(2) 169.49(3)°. The Fe(1)–N(1), Fe(1)–S(1), Fe(1)–S(2), Fe(1)–N(4), and Fe(1)–N(5) bond lengths of [Fe(NO)₂(κ²-L_DPM)] are 2.028(7), 2.2802(7), 2.2844(8), 1.667(3), and 1.664(2) Å, respectively. These bond lengths are significantly shorter than those of the previously reported high spin iron(II) complexes Fe(1)–N(1), Fe(1)–S(1), Fe(1)–S(2) = 2.164(4), 2.459(2), 2.458(2) Å for [FeBr₂(κ²-H₂-L_DPM)], 2.1593(19), 2.3600(8), 2.3621(8) Å for [Fe(THF)₂(κ²-L_DPM)] with thioamide pincer-type ligand. Furthermore, this complex, as is described below, demonstrated to be diamagnetic in solution state. The CV of [Fe(NO)₂(κ²-L_DPM)] in THF exhibited one medium absorption at 361 nm (ε = 14000) assignable to MLCT (dπ → π*NO) of metal to nitrosyl ligand (Figure S4). The CV of [Fe(NO)₂(κ²-L_DPM)] exhibited a reversible redox couple at E_{1/2} = –0.7611 V (vs. Fe⁺/Fe) in THF under Ar, which is assigned to the Fe(II)/Fe(III) one of the metal center (Figure S3).

In general, {Fe(NO)₂}⁶ complex has a suitable decomposition pathway that leads to generation of very stable {Fe(NO)}⁷ complex accompanied by release of NO. However, the complex [Fe(NO)₂(κ²-L_DPM)] is stable for a light at 23 °C under Ar atmosphere, although such an iron nitrosyl complex is generally light-sensitive. The UV-vis absorption spectrum of [Fe(NO)₂(κ²-L_DPM)] in THF exhibited one medium absorption at 361 nm (ε = 14000) assignable to MLCT (dπ → π*NO) of metal to nitrosyl ligand (Figure S4). The CV of [Fe(NO)₂(κ²-L_DPM)] exhibited a reversible redox couple at E_{1/2} = –0.7611 V (vs. Fe⁺/Fe) in THF under Ar, which is assigned to the Fe(II)/Fe(III) one of the metal center (Figure S3).
Preparation of iron complex with ligand H$_3$L$_{DPM}$

For a simpler ligand, 2,6-bis(N-2,6-diisopropylphenylthioamide)pyridine (H$_3$L$_{DIP}$), was prepared according to the literature reported previously, where H$_3$L$_{DIP}$ has two diisopropyl groups at 2 and 6 positions of N-phenyl group, which is smaller substituent than 2,6-bis(diphenylmethyl)phenyl of H$_3$L$_{DPM}$ ligand. The X-ray structure of H$_3$L$_{DIP}$ molecule, which was recrystallized from chloroform, is shown in Figure S5. The C(1)–S(1), C(2)–S(2) bond lengths of the ligand are 1.649(4), 1.642(4) Å, and the C(1)–S(1) bond lengths are 1.681(4), 1.683(4), C(33)–N(5) 1.327(5), C(32)–N(6) 1.324(5), C(1)–S(1) 1.681(4), C(2)–S(2) 1.673(4), C(32)–S(3) 1.678(4), C(1)–S(1) 1.681(4), C(2)–S(2) 1.673(4), C(32)–S(3) 1.678(4).

Fig. 3. ORTEP drawing of [Fe(κ$^3$H$_3$L$_{DIP}$)$_2$(2-Br)] with ellipsoids at 30% probability level. The hydrogen atoms and aromatic substituent on N–thioamide unit have been omitted for clarity except for H(2a), H(3a), H(5), and H(6a) atoms. Selected bond lengths (Å): Fe(1)–N(1) 1.943(3), Fe(1)–N(4) 1.948(3), Fe(1)–S(1) 2.3172(10), Fe(1)–S(2) 2.2572(11), Fe(1)–S(3) 2.2547(11), Fe(1)–S(4) 2.3193(11), C(1)–N(2) 1.325(5), C(2)–N(3) 1.326(5), C(33)–N(5) 1.327(5), C(32)–N(6) 1.324(5), C(1)–S(1) 1.681(4), C(2)–S(2) 1.673(4), C(32)–S(3) 1.678(4), C(33)–S(4) 1.678(4).

Treatment of FeBr$_2$ with H$_3$L$_{DIP}$ in ethanol under an argon atmosphere at room temperature gave a dark green solution after 24 h (Scheme 3). Fortunately, we obtained a single crystal by slow evaporation of ethanol solution. The X-ray structure, which is different from that of [FeBr$_2$(κ$^3$H$_3$L$_{DIP}$)$_2$], revealed a bischelate iron complex [Fe(κ$^3$H$_3$L$_{DIP}$)$_2$(2-Br)], which forms a distorted octahedral structure with two thioamide ligands of H$_3$L$_{DIP}$, pyridine nitrogen and two sulfur atoms of thioamide groups (Figure 3). The Fe(1)–N(1) and Fe(1)–N(2) bond lengths are 1.943(3) and 1.949(3), respectively, and the Fe(1)–S(1), Fe(1)–S(2), Fe(1)–S(3), and Fe(1)–S(4) bond lengths are 2.3145(10), 2.2542(10), 2.3174(10), and 2.2536(11) Å, respectively. These bond lengths are similar to those of low spin iron(II) complexes reported previously ([Fe(CO)$_3$(κ$^2$L$_{DPM}$)])

Fe(1)–N(1), Fe(1)–S(1), Fe(1)–S(2) = 1.980(2), 2.2676(11), 2.2638(11) Å; [Fe(CN-xylyl)(κ$^3$L$_{DPM}$)]; Fe(1)–N(1), Fe(1)–S(1), Fe(1)–S(2) = 1.9844(17), 2.2807(10), 2.2744(10) Å. The solid state magnetic moment by the Evans method showed also to be diamagnetic, indicating that this iron complex is in a low spin state. The complex [Fe(κ$^3$H$_3$L$_{DIP}$)$_2$(2-Br)] is easily decomposed with coordinating solvents such as pyridine. When H$_3$L$_{DIP}$ was used instead of H$_3$L$_{DPM}$, main product was not monochelate but bischelate complex. These results suggest that the bulky substituents of 2,6-bis(diphenylmethyl)phenyl unit on thioamide N-aryl group are very important to form the monochelate complex.

Biological implications

Recently, the center of active site FeMoco in nitrogenase enzyme was determined to be a carbon atom, and then the Fe-C bond has been suggested to contribute to the activation of dinitrogen molecule through the π-back donation from the metal.$^{18,19}$ Here we showed that the Fe(1)–N(1) bond at trans position of Fe(1)–C(1) one in NHIC ligand was shortened in comparison with that in [Fe(TTHF)(κ$^3$L$_{DPM}$)], indicating that the strong σ-donor from NHC carbon made π-back donation from the metal to dinitrogen molecule enhanced. So we can propose that the central carbon atom in FeMoco may promote the electron donation from the metal to dinitrogen.

Dinitrosyl iron complexes (DINCs) have been suggested as storage and transporters of NO in vivo$^{20}$ as well as intermediates of iron-catalyzed degradation and formation of S-nitrosothiols (RSNO). In our system, the iron complex with thioamide pincer type ligand also demonstrated the formation of novel stable [Fe(NO)$_2$(κ$^3$L$_{DPM}$)] complex. However, this complex released NO molecule in the air, although it did not decompose by a light irradiation. In near future, we will attempt to study on the reversibility of capture/elimination of NO molecule using the [Fe(NO)$_2$(κ$^3$L$_{DPM}$)] complex.

Conclusion

We synthesized monochelate iron(II) complexes with thioamide pincer type ligand bearing N-phenyl groups and studied its ligand substitution reactions. Bulkier diphenylmethyl substituents on 2 and 6 positions of the thioamide-N phenyl groups lead to formation of novel monochelate iron complex [Fe(TTHF)(κ$^3$L$_{DPM}$)]. This iron complex gave [Fe(NHC)(κ$^3$L$_{DPM}$)] and [Fe(NO)$_2$(κ$^3$L$_{DPM}$)] by the substitution reactions with carbene (NHC) and nitrosyl, respectively. The complex [Fe(NHC)(κ$^3$L$_{DPM}$)] formed a square planar geometry, which had an intermediate spin state. For the complex [Fe(NO)$_2$(κ$^3$L$_{DPM}$)], the two coordinated NO molecules were characterized as a neutral radical, which antiferromagnetically coupled with a high-spin iron(II) metal center.

Experimental

Materials

All manipulations were performed under an atmosphere of dry and oxygen-free dinitrogen by means of standard Schlenk or
Glovebox techniques. Reagents and solvents employed were commercially available. All anhydrous solvents were purchased from Wako Ltd. and were degassed with argon. $^1$H and $^{13}$C NMR spectra were recorded on a Varian 300 MHz spectrometer. 2,6-

Bis(N-2,6-diisopropylphenylamidopyridine)pyridine, 1,3-bis(2,6-diisopropylphenyl)imidazo[2,1-f]pyridine (NHC) and [Fe(THF)[$\kappa^2$-L$_{DPM}$]] were synthesized according to literature.21,22

X-ray crystallography

Each crystal was mounted on a glass fiber, and diffraction data were collected using a Rigaku/MSC Mercury CCD with graphite monochromated Mo-K$\alpha$ radiation at $-100$ °C or $-120$ °C. Crystal data and experimental details are listed in Table S1. The crystal structures of all Fe(II) complexes were solved by a combination of direct methods (SIR9223 or SIR200424) and Fourier techniques.

All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined by the riding model using the appropriate HFIX command in SHELXL97.25 A Shelldrick weighting scheme was applied. Plots of $\Sigma (|F_{o}| - |F_{c}|)^2$ versus $|F_{o}|$, reflection order in data collection, $\theta$, and various classes of indices showed no unusual trends. Neutral atomic scattering factors were taken from International Tables for X-ray Crystallography edited by G. M. Sheldrick.26 Anomalous dispersion effects were included in $F_{calc}$,27 where the values for $\Delta f^2$ and $\Delta f$ were taken from those of Creagh and McAuley.28 The values for the mass attenuation coefficients are those of Creagh and Hubbell.29 All calculations were performed using the crystallographic software package, CrystalStructure.

Syntheses of compounds

[Fe(NHC)[$\kappa^2$-L$_{DPM}$]]: To a toluene solution of NHC (90 mg, 2.31 x 10$^{-3}$ mmol) was added a stirred slurry of [Fe(THF)[$\kappa^2$-L$_{DPM}$]] (300 mg, 2.31 x 10$^{-3}$ mmol) in toluene (5 mL). The solution was stirred overnight. The slurry of reaction mixture was dissolved as green solution. To the reaction mixture of green solution was added n-pentane (10 mL) dropwise. The reaction mixture was stored in the refrigerator at $-35$ °C overnight, leading to formation of green crystals of [Fe(NHC)[$\kappa^2$-L$_{DPM}$]] (122 mg, 7.91 x 10$^{-2}$ mmol, 34%).

[Fe(NO)$_2$[$\kappa^2$-L$_{DPM}$]]: The slurry of [Fe(THF)[$\kappa^2$-L$_{DPM}$]] (1.00 g, 7.72 x 10$^{-3}$ mmol) in toluene (30 mL) was stirred under NO atmosphere overnight. The slurry of [Fe(NO)$_2$[$\kappa^2$-L$_{DPM}$]] was dissolved as a dark brown solution. The volatiles were removed in vacuo. The compound [Fe(NO)$_2$[$\kappa^2$-L$_{DPM}$]] was given as a dark brown powder (655 mg, 5.40 x 10$^{-3}$ mmol, 70%). The dark brown crystals of [Fe(NO)$_2$[$\kappa^2$-L$_{DPM}$]] were obtained from CH$_2$Cl$_2$.

2,6-bis(N-2,6-diisopropylphenylthioamide)pyridine (H$_2$L$_{DPM}$): Lawesson’s reagent (14.0 g, 0.035 mol) was added to a toluene (120 mL) solution of 2,6-bis(N-2,6-diisopropylpheny)lamido(pyridine (7.59 g, 0.016 mol), and the mixture was heated at 100 °C for 6 h. Once cooled, the precipitate was filtered off and the solvent was removed under vacuum. 2,6-Bis(N-2,6-diisopropylphenylthioamide)pyridine was recrystallized from hot acetonitrile to give yellow plate crystals (yield: 7.45 g, 83%).

1H-NMR ($\delta$ ppm vs TMS in CDCl$_3$, 300 MHz): 10.75 (s, 2H, NH), 9.05 (d, 2H, CH py(3,5)), 7.81 (t, 1H, CH py(4)), 7.39 (t, 2H, CH ph(4)), 7.28 (d, 4H, CH ph(3,5)), 3.01 (m, 4H, CH(CH$_2$)$_2$), 1.27 (d, 12H, CH(CH$_2$)$_2$), 1.15 (d, 12H, CH(CH$_2$)$_2$).

C-NMR ($\delta$ ppm vs TMS in CDCl$_3$, 600 MHz): 191.8 (C=S), 149.0 (Cpy(2, 6)), 145.6 (Cph(2, 6)), 138.8 (Cpy(3)), 133.5 (Cpy(1)), 129.4 (C ph(4)), 128.0 (Cpy(3, 5)), 124.1 (Cph(3, 5)), 29.1 (CH(CH$_2$)$_2$), 24.5 (CH(CH$_2$)$_2$), 23.0(CH(CH$_2$)$_2$).

ESI-TOF Mass: m/z 540.2 [M + Na$^+$]. FTIR(KBr, cm$^{-1}$): ν 3318 (NH), 2963, 2866 (CH), 1101 (C=S), δ 1489 (CNH). Anal. Calcd. for C$_{33}$H$_{40}$N$_2$S$_2$: C, 60.32; H, 6.33; N, 6.59. Found: C, 60.24; H, 6.36; N, 6.57.

[Fe($\kappa^2$-H$_2$L$_{DPM}$)](2·Br)$_2$: To a toluene (2 mL) solution of H$_2$L$_{DPM}$ (100 mg, 1.93 x 10$^{-1}$ mmol) was added FeBr$_2$ (41.6 mg, 1.93 x 10$^{-2}$ mmol), and then stirred at room temperature. After 24 h, the mixture was filtered and redissolved with ethanol. The green crystal of [Fe($\kappa^2$-H$_2$L$_{DPM}$)](2·Br)$_2$ was obtained from slow evaporation to yield dark green needle crystals. (18 mg, 1.44 x 10$^{-2}$ mmol, 7 %)

ESI-TOF Mass: m/z 545.2 [M – 2Br$^-$], 1089.4 [M – 2Br – H$^+$]. FTIR(KBr, cm$^{-1}$): ν 3064 (NH), 2963, 2866 (CH$_3$), δ 1503, 1462 (CNH). Anal. Calcd. for C$_{33}$H$_{42}$Br$_4$N$_4$S$_2$Fe: C, 59.51; H, 6.28; N, 6.72. Found: C 59.64; H 5.95; N 6.69.

Acknowledgements

We gratefully acknowledge for the support of this work by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and by Japan Society for the Promotion of Science “Strategic Young Researcher Overseas Visits Program for Accelerating Brain Circulation”.

Notes and references

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$^\ddagger$ Electronic Supplementary Information (ESI) available: CCDC 1028474
