Synthesis and Structure of a Novel 1,1'-Ferrocenediyldiplatinum Complex Having μ_3(2S,N)-NCS Ligands

Kiyotaka Onitsuka,*# Toshiya Yoshida, Fumiyuki Ozawa, and Kenkichi Sonogashira*†
Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sumiyoshi-ku, Osaka 558
†*Department of Applied Science and Chemistry, Faculty of Engineering, Fukui University of Technology, 3-6-1 Gakuen, Fukui 910*

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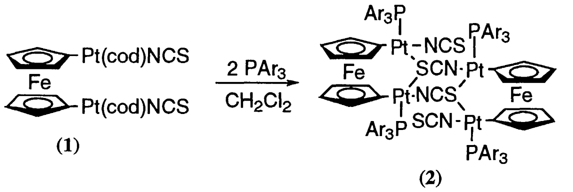
The treatment of 1,1'-ferrocenediyldiplatinum complex $\{C_5H_4Pt(cod)NCS\}_2Fe$ (**1**) with 2 equivalents of PAr_3 results in the formation of a novel dimeric μ_3(2S, N)-NCS complex (**2**), of which structure has been determined by an X-ray diffraction analysis. Reaction of **1** with MeSSMe in the presence of triphenylphosphine gave a μ-thiolato complex (**3**).

Recently much attention was given to the molecular design of multinuclear complexes taking advantage of the structural and electronic feature of the bridging ligands.[1] We have been interested in the chemistry of ferrocenyl transition metal complexes because of their unique structure and potential applications in material science.[2] Recently we have shown the syntheses of μ-hydroxo complex $(\mu\text{-OH})\{C_5H_4Pt(PAr_3)X\}_2Fe$ (X = Cl, Br) and μ-chalcogenolato complex $(\mu\text{-ER})\text{-}\{C_5H_4Pt(PAr_3)Cl\}_2Fe$ (E = S, Se, Te), in which Fe atoms of ferrocenediyl group adopt oxidation state of +III, by the reaction of 1,1'-ferrocenediyldiplatinum complex $\{C_5H_4Pt(cod)X\}_2Fe$ with molecular oxygen or dichalcogenide in the presence of triarylphosphine.[3] In the course of our study, we found that $\{C_5H_4Pt(cod)NCS\}_2Fe$ (**1**) has a slightly different reactivity from those of halide complexes. Herein we wish to report the synthesis and structure of a novel dimeric 1,1'-ferrocenediyldiplatinum complex having μ_3(2S, N)-NCS ligands.



(**1**)

(**2**)

a: Ar = Ph
b: Ar = $C_6H_4OCH_3$-*p*

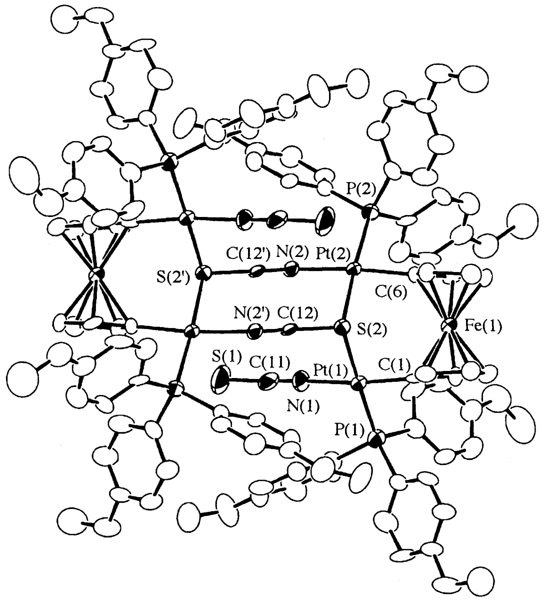
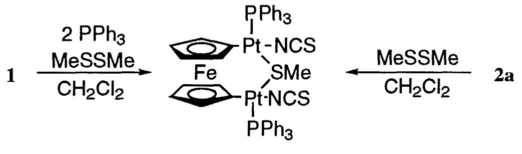


Figure 1. Molecular structure of **2b**. Hydrogen atoms are omitted for clarity.

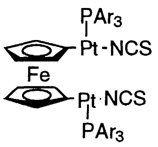
Treatment of complex **1** with 2 equivalents of PPh_3 in dichloromethane at room temperature gave red crystals (**2a**) in 51% yield. Similar reaction of **1** with $P(C_6H_4OCH_3\text{-}p)_3$ also produced red crystals (**2b**) in 75% yield. The color of the products indicates that the Fe atom of ferrocenediyl group may be Fe^{II}, since all of paramagnetic 1,1'-ferrocenediyldiplatinum complexes having Fe^{III} are green.[3,4] The oxidation state of Fe atom in **2** was confirmed by the cyclic voltammogram. Reversible redox peaks (Fe^{II}/Fe^{III}) were observed at $E_{1/2} = -0.54$ V for **2a** and $E_{1/2} = -0.50$ V for **2b** relative to Ag/AgCl.[3] The IR spectrum of **2b** showed two absorptions attributed to $\nu(C\equiv N)$ at 2150 cm^{-1} and 2100 cm^{-1} whereas an absorption due to $\nu(C\equiv N)$ was observed at 2100 cm^{-1} in the IR spectrum of the starting material **1**. The ^{31}P NMR of **2b** exhibited two singlet signals accompanied by satellite signals at δ 15.38 ($J_{Pt-P} = 4592$ Hz) and 14.24 ($J_{Pt-P} = 4675$ Hz). These data suggest that two platinum atoms bound to ferrocenediyl bridge are unequivalent. The structure of **2b** was unambiguously identified by X-ray crystallography.[5] As shown in Figure 1, complex **2b** has a dimeric structure, in which two NCS ligands bridge three Pt atoms in μ_3(2S, N) fashion. To our best knowledge, only one example of μ_3(2S, N)-NCS complex has been reported,[6,7] though such coordination mode has been found in the crystal structure of inorganic NCS salts.[8]

The molecule of **2b** lies on the crystallographic center of symmetry. The bond distances of Pt(1)–S(2) and Pt(2)–S(2) are 2.393(5) Å and 2.398(6) Å, respectively. These values are smaller than that of $[PtMe_3\{\mu_3(2S, N)\text{-}NCS\}]_4$ [2.52(2)–2.57(2) Å][7], but consistent with that in $[\{\mu_2(S, N)\text{-}NCS\}Pt(PPh_3)Cl]_2$ [2.408(4) Å].[9] The bond angles of Pt(1)–S(2)–C(12) and Pt(2)–S(2)–C(12) are 102.4(6)° and 102.5(8)°, respectively, which are comparable with those in $[PtMe_3\{\mu_3(2S, N)\text{-}NCS\}]_4$ [99(2)–100(2)°][7], $[\{\mu_2(S, N)\text{-}NCS\}Pt(PPh_3)Cl]$ [102.9(5)°][9] and $[\{\mu_2(S)\text{-}NCS\}Cu]_2(C_{18}H_{20}N_4O_2)$ [106.8° and 109.2°].[10] The bond length of Pt(1)–N(1) [2.04(2)Å] is slightly shorter than that of Pt(2)–N(2) [2.08(2)Å]. The bond angle of Pt(2)–N(2)–C(12') is 162(2)° while that of Pt(1)–N(1)–C(11) is 178(2)°. Although both NCS ligands have a linear structure, it is of interest that the S–C bond length of bridging NCS [1.70(2) Å] is longer than that of terminal NCS [1.64(2) Å] while the C–N bond length of bridging NCS [1.10(2) Å] is shorter than that of terminal NCS ligand [1.15(3) Å]. These phenomena may be due to the difference of π-bond order between bridging and terminal NCS ligands, which are supported by the IR spectrum of **2b** (vide infra).

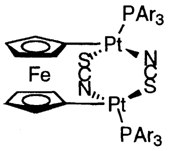


(**3**)

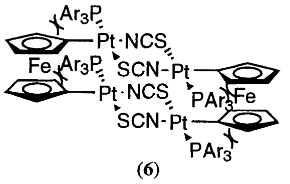
Although complex **2** was selectively produced in the reaction of **1** with PPh_3 even in the presence of O_2, treatment of **1** with PPh_3 and MeSSMe gave a green μ-thiolato complex (**3**) in 35% yield. Reaction of **2a** with MeSSMe also led to the formation of **3** in 34% yield.



(**4**)



(**5**)



(**6**)

In the first step of the reaction, a coordinatively unsaturated species (**4**), of which halide analogue is proposed to be a reactive intermediate in the activation of O_2 and dichalcogenide, is given by the ligand exchange reaction between cyclooctadiene and triarylphosphine. Ferrocenediyl bridge inhibits the formation of intramolecular μ_2(S, N)-NCS bridged complex (**5**) so far as platinum moieties keep a square planer structure. Bulky triarylphosphine ligands have to be situated on the planes of cyclopentadienyl rings to form a dimeric complex (**6**) having double μ_2(S, N)-NCS bridge. These steric factors may give rise to the formation of μ_3(2S, N)-NCS bridged complex **2**. Furthermore, complex **2** undergoes the selective activation of dichalcogenide in contrast to halide analogue.[3] Thus, molecular oxygen is not able to coordinate the platinum atoms of **2** since sulfur atom has a great affinity with platinum.[11] The activation of molecular oxygen giving μ-hydroxo complex consequently did not take place. However, the great coordination ability of MeSSMe to platinum may cause the generation of μ-thiolato complex **3**.

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References and Notes

\# Present address: The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567.

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5 Crystal data for **2b**: $C_{136}H_{132}Fe_2N_4O_{12}P_4Pt_4S_4$, FW = 3158.74, triclinic, space group $P\bar{1}$, a = 15.575(8) Å, b = 16.081(9) Å, c = 15.287(7) Å, α = 108.56(4)°, β = 107.20(4)°, γ = 68.44(4)°, V = 3305(7) Å^3, Z = 1, D_{calcd} = 1.587 gcm^{-3}, μ(Mo–Kα) = 46.29 cm^{-1}. Data were measured on a Rigaku AFC5R diffractmeter in the range of $6° < 2\theta < 55.1°$ with ω-2θ scan technique. The reflections were corrected for Lorentz-polarization effect and absorption using DIFABS. The structure was solved by Patterson method and refined by full-matrix least-squares method using anisotropic thermal parameters for all non-H atoms. The hydrogen atoms were located at calculated positions. The final agreement factors are R = 0.058 and R_w = 0.066 for 648 parameters against 6327 reflections with $I > 3.0\sigma(I)$ out of 15833 total reflections.

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