

Synthesis and Structure of Novel Thiolato-, Selenolato- or Telluroolato-Bridged 1,1'-Ferrocenediylplatinum Complexes

Kiyotaka Onitsuka, Toshiya Yoshida, Akio Ichimura,[†] Tomohiro Adachi,^{††} Toshikatsu Yoshida,^{††} and Kenkichi Sonogashira*
 Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sumiyoshi-ku, Osaka 558

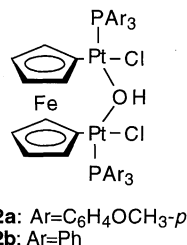
[†]Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558

^{††}Department of Chemistry, Faculty of Integrated Arts and Sciences, University of Osaka Prefecture, Sakai, Osaka 591

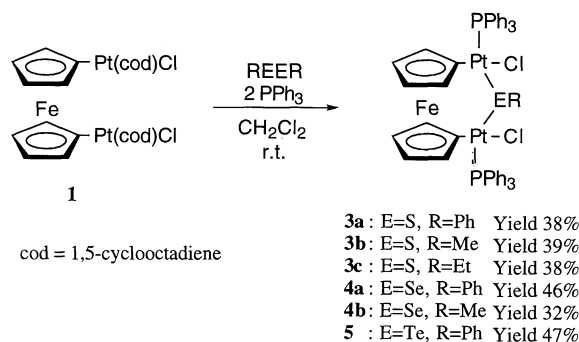
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Reaction of 1,1'-ferrocenediylplatinum complex with disulfide, diselenide or ditelluride results in the formation of thiolato-, selenolato- or telluroolato-bridged 1,1'-ferrocenediylplatinum complexes. The structure of a μ -thiolato complex was determined by an X-ray crystallography. The μ -thiolato complex was also prepared by the treatment of the μ -hydroxo 1,1'-ferrocenediylplatinum complex with thiophenol.

Synthesis and characterization of transition metal thiolato complexes have received much attention for a long time since thiolato ligands have a great affinity for transition metals to give stable complexes.¹ Thus, those have been believed to reduce the reactivity of the metal species, however, some interesting reactions of μ -thiolato complexes were reported.² Recently we have found that 1,1'-ferrocenediylplatinum complex $\{C_5H_4Pt(cod)Cl\}_2Fe$ (**1**) reacts with molecular oxygen in the presence of triarylphosphine to give a μ -hydroxo complex (μ -OH) $\{C_5H_4Pt(PAr_3)Cl\}_2Fe$ (**2**).³ Now we examined the reaction of **1** with disulfide, diselenide, or ditelluride, and observed the formation of 1,1'-ferrocenediyl-di-platinum complexes (**3-5**) possessing thiolato-, selenolato- or telluroolato-bridge.



The treatment of **1** with a half molar amount of disulfide and two equivalents of triarylphosphine at room temperature afforded (μ -SR) $\{C_5H_4Pt(PAr_3)X\}_2Fe$ (**3**), as air-stable green crystals, in 38-39% yields.⁵ In order to determine the molecular structure of **3**, a single-crystal X-ray diffraction analysis of **3a** was performed.⁶ As shown in Figure 1, two platinum atoms, which are in a square planar environment, are bridged by a thiolato ligand as well as the 1,1'-ferrocenediyl group. The thiolato ligand is linked to two Pt atoms approximately at a *trans* position with respect to triphenylphosphine. The Pt-S bond distances are 2.33(2) Å and 2.43(2) Å, which are analogous to those at *trans* position with relative to phosphine in mononuclear Pt thiolato complexes (2.355(8)-2.379(4) Å)⁷ and dinuclear Pt μ -thiolato complexes (2.351(6)-2.380(4) Å).⁸ The Pt(1)-S(1)-Pt(2) bond angle of 116.8(2)° is smaller than the Pt-O-Pt bond angle of 138.9(5)° in **2a**,³ but significantly larger than those of other μ -thiolato Pt complexes (85.1(2)-93.5(2)°).⁸ The Pt-C bond lengths of 2.11(4) and 1.94(3) Å are comparable to those of other



σ -ferrocenylplatinum complexes.^{3,9,10} No direct interaction among the metal atoms is observed since the distances are 3.767(7)-4.057(1) Å. The two cyclopentadienyl groups are essentially parallel and the ferrocenediyl group has a staggered conformation.

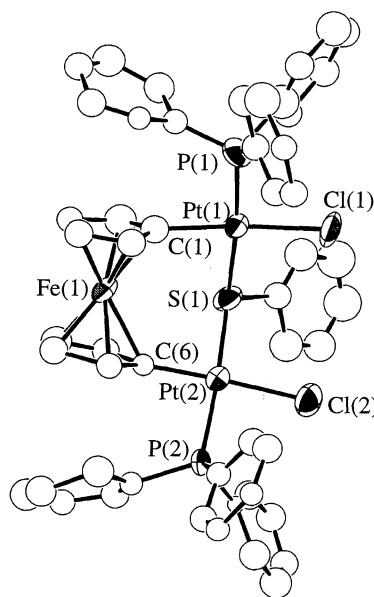
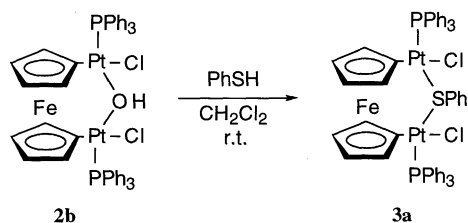


Figure 1. Molecular structure of complex **3a**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Pt(1)-Cl(1) 2.39(1), Pt(1)-S(1) 2.43(2), Pt(1)-P(1) 2.21(2), Pt(1)-C(1) 2.11(4), Pt(2)-Cl(2) 2.38(1), Pt(2)-S(1) 2.33(2), Pt(2)-P(2) 2.29(1), Pt(2)-C(6) 1.94(3), Cl(1)-Pt(1)-S(1) 96.0(4), Cl(1)-Pt(1)-P(1) 89.8(5), S(1)-Pt(1)-C(1) 85(1), P(1)-Pt(1)-C(1) 91(1), Cl(2)-Pt(2)-S(1) 95.7(4), Cl(2)-Pt(2)-P(2) 88.2(4), S(1)-Pt(2)-C(6) 88(1), P(2)-Pt(2)-C(6) 89(1), Pt(1)-S(1)-Pt(2) 116.8(2).

The ^1H NMR spectrum of **3a** showed broad signals attributed to the protons of the 1,1'-ferrocenediyl group at δ 40.16 and 23.12, analogous phenomenon was observed in those of **2³** and 1,1'-ferrocenediyl Pt_2Cu_3 acetylide complex,¹⁰ which depends on the paramagnetic character of ferrocenediyl group caused by the oxidation from Fe^{II} to Fe^{III} . While the iron atom of the ferrocenyl group was oxidized by molecular oxygen in the formation of **2**, complex **3** was generated in the thoroughly degassed conditions, suggesting that disulfide acts as an oxidant. Although we have no definite information on the mechanism of the reaction described here, we believe that complex **3** was produced by the reaction of disulfide with the two Pt atoms along with the electron transfer from the iron atom of the ferrocenyl group.

Similar treatment of **1a** with diselenide or ditelluride in the presence of triarylphosphine also afforded a μ -selenolato (**4**) or μ -telluroolato complex (**5**), respectively.¹¹ The cyclic voltammogram of **3a** exhibited a reversible wave of Fe at $E_{1/2} = -0.71$ V relative to Ag/AgCl similar to that of $E_{1/2} = -0.63$ V in **2a**.³ Similar reversible reduction peaks ($E_{1/2} = -0.73$ V) were also observed in both **4a** and **5**. These data suggest that the atom of the bridging the platinum atoms does not have a large effect on the reduction potential of Fe in complexes **2** and **3**.



Finally, when **2b** was treated with equimolar amounts of thiophenol in dichloromethane at room temperature, the μ -hydroxo ligand was substituted with μ -thiolato ligand to form **3a** quantitatively. In contrast, it is quite of interest that in the reaction of **2b** with methanol or phenol the generation of μ -methoxido or μ -phenoxido complex was not observed.

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References and Notes

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- Spectroscopic data for **3a**: ^1H NMR(CDCl_3): δ 40.16(br, 4H, C_5H_4), 23.12(br, 4H, C_5H_4), 11.56(br, 12H, Ph), 9.87(br, 12H, Ph), 9.41(br, 6H, Ph), 5.18(br, 2H, SPh), 2.94(br, 1H, SPh), 0.81(br, 2H, SPh); ^{31}P NMR(CD_2Cl_2 , PPh_3): δ 35.6(s). For **3b**: ^1H NMR(CD_2Cl_2): δ 41.29(br, 4H, C_5H_4), 22.62(br, 4H, C_5H_4), 11.67(br, 12H, Ph), 9.91(br, 12H, Ph), 9.45(br, 6H, Ph), 2.82(br, 3H, CH_3); ^{31}P NMR(CD_2Cl_2 , PPh_3): δ 79.7(s). For **3c**: ^1H NMR(CD_2Cl_2): δ 41.40(br, 4H, C_5H_4), 22.59(br, 4H, C_5H_4), 11.64(br, 12H, Ph), 9.89 (br, 12H, Ph), 9.43(br, 6H, Ph), 2.51(br, 2H, CH_2), -2.59 (br, 3H, CH_3); ^{31}P NMR(CD_2Cl_2 , PPh_3): δ 89.3(s).
- Crystal data for **3a** $\cdot 2\text{C}_2\text{H}_4\text{Cl}_2$: $0.30 \times 0.20 \times 0.15$ mm, orthorhombic, space group $Pna2_1$ (#33), $a = 17.719(1)$, $b = 15.888(2)$, $c = 18.880(3)$ Å, $V = 5324(2)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.842$ gcm⁻³, $\mu(\text{MoK}\alpha) = 60.65$ cm⁻¹, ω -2 θ scan, $6.0^\circ < 2\theta < 55.1^\circ$, an empirical absorption correction was made using program DIFABS. The structure was solved by Patterson method and refined full-matrix least square method to $R = 0.044$ and $R_w = 0.049$ for 312 parameters against 3137 reflections with $I > 3.0\sigma(I)$ out of 6784 reflections, GOF = 1.64. The refinement of the solvent molecules was not successful.
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- S. Tanaka, T. Yoshida, T. Adachi, T. Yoshida, K. Onitsuka, K. Sonogashira, *Chem. Lett.*, **1994**, 877.
- Spectroscopic data for **4a**: ^1H NMR(CDCl_3): δ 11.77(br, 12H, Ph), 9.85(br, 12H, Ph), 9.36(br, 6H, Ph), 5.32(br, 2H, SePh), 2.79(br, 1H, SePh), 0.83(br, 2H, SePh); ^{31}P NMR(CD_2Cl_2 , PPh_3): δ 74.5(s). For **4b**: ^1H NMR(CD_2Cl_2): δ 42.10(br, 4H, C_5H_4), 20.55(br, 4H, C_5H_4), 11.57(br, 12H, Ph), 9.71(br, 12H, Ph), 9.28(br, 6H, Ph), 5.80(br, 3H, CH_3); ^{31}P NMR(CD_2Cl_2 , PPh_3): δ 123.4(s). For **5**: ^1H NMR(CDCl_3): δ 11.69(br, 12H, Ph), 9.67(br, 12H, Ph), 9.16(br, 6H, Ph), 5.52(br, 2H, TePh), 2.73(br, 1H, TePh), 0.88(br, 2H, TePh); ^{31}P NMR(CD_2Cl_2 , PPh_3): δ 240.1(br). In the ^1H NMR of **4a** and **5** the resonances assigned to the ferrocenyl protons were not observed due to low solubility.