Oxidative Addition of Aryl Disulfides to Pd(0) Complexes: Synthesis and Structures of Bis(thiolato) Pd(II) Complexes

Yong-Joo Kim, Keun-Young Choi, Seon Gye Lee, Zhen Nu Zheng, and Soon W. Lee

Department of Chemistry, Kangnung-Wonju National University, Gangneung 210-702, Korea
*E-mail: yykim@kangnung.ac.kr
†Department of Chemistry, Sungkyunkwan University, Natural Science Campus, Suwon 440-746, Korea
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The oxidative addition of dihalo-organic compounds to zerovalent transition-metal complexes is a well-known fundamental reaction, which affords self-assembled transition-metal complexes or π-conjugated polymers in catalytic reactions. In particular, dinuclear group 10 metal complexes with bridging aryl groups act as catalytic intermediates or potential precursors in the preparation of π-conjugated conducting polymers or electronic and optical materials. These potential precursors in the preparation of organic unsaturated molecules or the adduct formation of thiolato complexes are regarded as an intermediate or precursor related to the addition of organic disulfides to the thiolato complexes. Oxidation-metal complexes or metal complexes or π-conjugated polymers in catalytic reactions.

In particular, dinuclear group 10 metal complexes containing an aryl disulfide bridge (–Ar–S–S–Ar–) by the C–X oxidative-addition product. Herein, we report the synthesis of such mononuclear bis(thiolato) Pd(II) complexes. These thiolato complexes are regarded as an intermediate or precursor related to the addition of organic disulfides to the organic unsaturated molecules or the adduct formation of organic disulfides and isocyanides catalyzed by late transition-metal complexes.

Many reactions, except for a few cases, for the preparation of thiolato complexes typically use zerovalent group 10 metal complexes containing low basic PPh₃ ligand as a supporting ligand. In this study, we used Pd(0) complexes containing PMe₃ or PEt₃ ligands, which are more basic than PPh₃. Reactions of [Pd(styrene)(PR₃)₂] (PR₃ = PMe₃, PEt₃), which was generated from trans-[PdEt₂(PR₃)₂] and styrene, with p-chlorophenyl disulfide in a 2:1 or 1:1 molar ratio afforded the bis(arylthiolato) Pd(II) complexes, trans-[Pd(SC₆H₄(Cl,p)-Cl)L₂] (L = PMe₃ (1), PEt₃ (2)) in moderate-to-good yields (Eq. (1) in Scheme 1). A one-step reaction of trans-[PdEt₂(PMe₃)₂] with p-chlorophenyl disulfide in 2:1 molar ratio also produced complex 1 in 69% yield.

The peak-intensity ratios of the aromatic hydrogens to the C–X oxidative addition product instead of an initially expected C–X oxidative-addition product. Herein, we report the synthesis of such mononuclear bis(thiolato) complexes. These thiolato complexes are regarded as an intermediate or precursor related to the addition of organic disulfides to the organic unsaturated molecules or the adduct formation of organic disulfides and isocyanides catalyzed by late transition-metal complexes.

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sulfide-bridged dinuclear complex, \([\text{Pd}(\text{SPh})_2(\text{PPh}_3)_2]\), was formed. However, when ortho- or meta-nitrophenyl disulfide was used, a mononuclear dithiolato Pd(II) complex, \(\text{trans-[Pd}(\text{SC}_6\text{H}_4\text{-X})_2(\text{PPh}_3)_2] (X = \text{o- or m-NO}_2)\), was obtained as a sole product. Although the \(p\)-chlorophenyl disulfide is employed in our reaction system, its reactivity is consistent with that found for the ortho- or meta-nitrophenyl disulfide that had been treated with \([\text{Pd}(\text{PPh}_3)_2]\). Kuniyasu and co-workers\(^9\) reinvestigated the Graziani’s reactions and revealed that a mixture of a dinuclear complex \({[\text{Pd}_2(\text{SPh})_4(\text{PPh}_3)_4]}\) and a mononuclear complex \({[\text{Pd}(\text{SPh})_2(\text{PPh}_3)_2]}\) were formed initially, and the mononuclear species was eventually converted to the dinuclear species. Ananikov \textit{et al.}\(^{10}\) spectroscopically characterized the \(trans/cis\) isomers of both the mononuclear complex, \([\text{Pd}(\text{SPh})_2(\text{PPh}_3)_2]\), and the dinuclear \(trans/cis\) isomers of \([\text{Pd}_2(\text{SPh})_4(\text{PPh}_3)_4]\). Ananikov \textit{et al.}\(^{11}\) recently described the replacement of PAR ligand by PAR, R or PR, ligands shifts the equilibrium to destabilize dinuclear complexes and stabilize mononuclear metal complexes after oxidative addition.

On the other hand, oxidative addition with a disulfide-containing bulky thioether was reported to afford mononuclear or trinuclear Pd sulfide complexes with S–S bond cleavage.\(^{12}\) In addition, several mononuclear thiolo Ni(II) complexes were obtained by reactions of \([\text{Ni}(\text{cod})_2]\), \([\text{NiMe}_2(\text{PMe}_3)_2]\), and \([\text{Ni}(\text{acac})_2]\) with diaryl sulfide, aryl thiol, and aryl disulfide, respectively.

In this work, the tetrakis(phosphine) Pd(0) complex, \([\text{Pd}(\text{PMePh}_3)_4]\), reacted with \((\text{SC}_6\text{H}_4\text{-p-Cl})_2(\text{PMePh}_3)_2\) (3) in 95% yield (Scheme 2). The C–Cl bond cleavage product, arylthiolato-bridged dinuclear complex, was not observed, as confirmed by NMR. The above results (Schemes 1 and 2) indicate that \(\text{PMe}_3\) and \(\text{PMePh}_3\) ligands, which are more basic than the \(\text{PPh}_3\), as well as the activated halo-aryldithiolato compounds used in this work induces the cleavage of the S–S bond (or S–S oxidative addition), which leads to the formation of mononuclear bis(thiolato) Pd(II) complex.

We further investigated the reactivity between \([\text{Pd}(\text{styrene})-(\text{PMe}_3)_2]\) and several non-activated disulfides such as thiophen disulfide, dianiline disulfide, and \(p\)-tolyl disulfide (Scheme 3). In contrary to our expectation, all reactions exclusively afforded the mononuclear dithiolato Pd(II) complexes (4-7) in moderated-to-good yields. Therefore, these results suggest that the basicity of the phosphine ligands, rather than that of the non-activation of the organic group in the aryl disulfide, is important for the selective S–S oxidative addition for mononuclear bis(thiolato) Pd(II) complexes without other products such as the dinuclear complex.

All single crystals for X-ray crystallography were grown from \(\text{CH}_2\text{Cl}_2/\text{hexane}\) at \(-35\,^\circ\text{C}\). Details on crystal data of complexes 1, 3, and 5 are summarized in Supporting Information. The molecular structures of 1, 3, and 5 are given in Figures 1-3, respectively. The asymmetric unit of complex 1 consists of two half molecules, which are crystallographically independent. Both Pd atoms are located on the crystallographic inversion centers. The thiolato group in each the structure is coordinated almost perpendicular to the square-planar face. In complexes 3 and 5, the Pd atom lies at the crystallographic center of symmetry, and the remaining atoms occupy general positions.

In summary, we observed that aryl disulfides (ArS–Ar) underwent S–S oxidative addition to zerovalent Pd complexes, \([\text{Pd}(\text{styrene})(\text{PR}_3)_2]\) and \([\text{Pd}(\text{PMe}_3)_2]\), to exclusively produce bis(arylthiolato) Pd(II) complexes, \([\text{trans-[Pd}(\text{SAr})_2(\text{PR}_3)_2]\). NMR measurements confirmed that neither the C–Cl bond cleavage products nor the arylthiolato-bridged dinuclear complexes were observed. This reaction could also be carried out with several non-activated disulfides such as phenyl disulfide, thiethyl disulfide, dianiline disulfide, and \(p\)-tolyl disulfide.

**Experimental**

**General Procedures.** All manipulations of air-sensitive compounds were performed under \(\text{N}_2\) or \(\text{Ar}\) by standard Schlenk techniques. Solvents were distilled from \(\text{Na–benzophenone}\). The analytical laboratories at Kangnung–Wonju National University carried out elemental analyses with CE instruments EA1110. IR spectra were recorded on a Perkin Elmer BX spectrophotometer. NMR \({^1\text{H}}, {^{13}\text{C}}\{^1\text{H}\}\), and \({^{31}\text{P}}\{^1\text{H}\}\) spectra were obtained on a JEOL Lamda 300 and
fide, thienyl disulfide, dianiline disulfide and PEtPMe3. The reaction mixture for 18 h at room temperature, the solvent was completely removed under vacuum, and then the resulting residue was solidified with hexane. The solids were filtered and washed with hexane (2 mL × 2) to obtain the crude solids. Recrystallization from CH3Cl/n-hexane afforded pale yellow crystals of trans-[Pd(SC6H4-p-Cl)2(PMe3)] (1), 0.067 g, 73%. C13H13Cl2P3S2Pd (545.80): calcd. C 39.61, H 4.80, S 11.75; found C 39.33, H 4.87, S 11.45.

Figure 1. ORTEP drawing of compound 1 with 50% probability thermal ellipsoids. Labeled atoms with “A” are related to unlabeled ones by the crystallographic inversion symmetry. Selected bond lengths (Å) and angles (°): Pd1–P1 2.3153(6), Pd1–S1 2.3391(5), Pd2–P2 2.3145(6), Pd2–S2 2.3422(6), S1–C1 1.739(2), S2–C4 1.701(3), S2–C1 1.720(2); P1–Pd1–P1A 180.00(3), P1–Pd1–S1 87.06(3), P1–Pd1–S1A 92.94(3), P1–Pd1–P1A 180.00(2), P1–Pd1–S1 86.88(2), P1–Pd1–S1A 93.12(2), P1–Pd1–P1A 180.00(3), P2–Pd2–S2 92.95(2), P2–Pd2–S2A 87.05(2), P2A –Pd2–P2, 180.00(3).

ECA 600 MHz spectrometer. Chemical shifts were referenced to internal MeSi or to external 85% H3PO4. X-ray analyses were obtained at Korea Basic Science Institute (Jeonju center) and CCRF (Cooperative Center for Research Facilities in the Sungkyunkwan University). Trans-[PdEt2(PR3)2] (R = PMe3, PEt3) was prepared by the literature method.10 Phenyl disulfide, thienyl disulfide, diaminie disulfide and p-tolyl disulfide were commercially available.

Preparation of trans-[Pd(SC6H4-p-Cl)2(PR3)] (PR3 = PMe3 (1); PEt3 (2)). Styrene (78 μL, 0.68 mmol) and tetrahydrofuran (THF, 3 mL) were added sequentially to a Schlenk flask containing trans-[PdEt2(PMe3)2] (0.107 g, 0.34 mmol) at 0 ºC. The mixture was heated at 55 ºC for 30 min to give a yellow solution. p-Chlorophenyl disulfide (0.049 g, 0.17 mmol) was added to the mixture at room temperature, and then the yellow solution turned into a dark yellow solution. After stirring for 2 h at room temperature, the solvent was completely removed under vacuum, and then the resulting residue was solidified with hexane. The solids were filtered and washed with hexane (2 mL × 2) to obtain the crude solids. Recrystallization from CH3Cl/n-hexane afforded pale yellow crystals of trans-[Pd(SC6H4-p-Cl)2(PMe3)] (1), 0.067 g, 73%. C13H13Cl2P3S2Pd (545.80): calcd. C 39.61, H 4.80, S 11.75; found C 39.33, H 4.87, S 11.45.

Figure 2. ORTEP drawing of compound 3 with 40% probability thermal ellipsoids. Labeled atoms with “A” are related to unlabeled ones by the crystallographic inversion symmetry. Selected bond lengths (Å) and angles (°): Pd1–P1 2.3185(4), Pd1–S1 2.3358(4), C1–S1–Pd1 108.47(5), Pd1–S1–P1 87.05(2), P1–Pd1–P1A 180.00(3), P1–Pd1–S1 86.88(2), P1–Pd1–S1A 93.12(2), P1–Pd1–P1A 180.00(3), P1A –Pd1–P1, 180.00(3).


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Figure 3. ORTEP drawing of compound 5 with 40% probability thermal ellipsoids. Labeled atoms with “A” are related to unlabeled ones by the crystallographic inversion symmetry. Selected bond lengths (Å) and angles (°): Pd1–P1 2.3175(7), Pd1–S1 2.3422(6), S1–C1 1.739(2), S2–C4 1.701(3), S2–C1 1.720(2); P1–Pd1–P1A 180.00(3), P1–Pd1–S1 87.05(2), P1–Pd1–S1A 92.94(3), C1–S1–P1 105.37(8), C4–S2–C1 92.38(14).
removed under vacuum, and then the resulting residue was solidified with diethyl ether. The resulting solids were filtered and washed with hexane (2 mL x 2) to obtain the crude solids. Recrystallization from CH₂Cl₂/n-hexane afforded brown crystals of trans-[Pd(SC₆H₄-p-Cl)(PMe₃)].(3, 0.321 g, 95%). C₈H₈ClP₂S₂Pd (794.08): calcld. C 57.48, H 4.31, S 8.08; found C 57.03, H 4.31, S 7.75. ¹H NMR (300 MHz, CDCl₃) δ 1.91 (t, J = 3.3 Hz, 6H, P(CH₃)₂H), 6.65 (m, 4H, Ar–H), 6.96 (m, 4H, Ar–H), 7.22–7.36 (m, 12H, Ar–H), 7.45–7.52 (m, 8H, Ar–H). ¹³C¹H NMR (75 MHz, CDCl₃) δ 13.0 (t, JCP = 16 Hz, P(CH₃)₂H), 127.1, 127.6, 128.1 (t, JCP = 5.0 Hz, Ar), 130.0, 132.2, 132.5 (t, JCP = 6.2 Hz, Ar), 132.9, 145.1. ³¹P¹H NMR (120 MHz, CDCl₃) δ 9.1(s).

Preparation of trans-[Pd(S-C₆H₄)(PMe₃)] (4), trans-[Pd(S-C₆H₄S₂)(PMe₃)] (5), and trans-[Pd(S-C₆H₄S₂-P-C₆H₄)(PMe₃)] (X = NH₂, (6); X = Me, (7)). Styrene (114 µL, 0.99 mmol) and THF (3 mL) were sequentially added to a Schlenk flask containing trans-[PdEt₂(PMe₃)] (0.157 g, 0.50 mmol) at 0 °C. The mixture was heated at 55 °C for 30 min to give a yellow solution. Phenyl disulfide (0.108 g, 0.99 mmol) was added to the mixture at room temperature, and then the initial orange solution turned into a yellow suspension. After stirring for 2 h, the solvent was completely removed under vacuum, and then the resulting solids were filtered and washed with hexane (2 mL x 3) to obtain the crude solids. Recrystallization from CH₂Cl₂/hexane gave yellow crystals of trans-[Pd(S-C₆H₄)(PMe₃)] (4, 0.159 g, 73%). C₈H₈S₂P₂S₂Pd (476.91): calcld. C 45.29, H 5.98, S 13.22. ¹H NMR (300 MHz, CDCl₃) δ 13.5 (t, J = 3.3 Hz, 18H, P(CH₃)₃), 6.91–6.96 (m, 2H, Ph), 7.04–7.09 (m, 4H, Ph), 7.54–7.57 (m, 4H, Ph). ¹³C¹H NMR (75 MHz, CDCl₃) δ 13.7 (t, JCP = 16 Hz, P(CH₃)₃), 122.0, 127.8, 131.3 (t, JCP = 1.2 Hz, Ph–C), 147.4. ³¹P¹H NMR (75 MHz, CDCl₃) δ 6–13.1(s).

The formation of complex 4 was confirmed by comparing its spectral data with those reported previously. Complexes 5–7 were analogously prepared. Spectroscopic data are summarized in Supporting Information.

X-ray Structure Determination. All X-ray data were collected on a Bruker Smart APEX or APEX2 diffractometer equipped with a Mo X-ray tube. Collected data were corrected for absorption with SADABS based upon the Laue symmetry by using equivalent reflections. All calculations were carried out with SHELXTL programs. All structures were solved by direct methods.

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre, CCDC No. 954099 (for 1) and 954100 (for 3) and 954101 (for 5). 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: http://www.ccdc.cam.ac.uk).

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References