March, 1983] NOTES *Bull. Chem. Soc. Jpn.*, **56**, *953—954 (1983)*

Catalytic Activity of $PdCl_2$ Complexes Having Sulfur Compounds as Ligands

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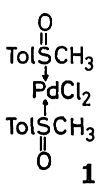
(Received July 8, 1982)

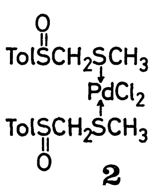
Synopsis. The $PdCl_2$ complexes coordinated with methyl *p*-tolyl sulfoxide (1:2), methylthiomethyl *p*-tolyl sulfoxide (1:2), and 1,3-bis[(*p*-tolylsulfinyl)methylthio]propane (1:1) as ligands were prepared. Among these complexes, bis(methyl *p*-tolyl sulfoxide)palladium dichloride catalyzed effectively cyclotrimerization of diphenylethyne and rearrangement of 3-acetoxy-1-tridecene to 1-acetoxy-2-tridecene.

Sulfur-containing compounds are well known to coordinate strongly to many kinds of metals or metal salts and to poison metallic catalysts, and there are several reports[1] for catalytic reactions using metal complexes with sulfur compounds as ligands. Now we wish to report preparation of three types of $PdCl_2$ complexes (**1**, **2**, and **3**) containing methyl *p*-tolyl sulfoxide (**4**), methylthiomethyl *p*-tolyl sulfoxide (**5**), and 1,3-bis[(*p*-tolylsulfinyl)methylthio]propane (**6**) as ligands, and their catalytic activities for cyclotrimerization of diphenylethyne and rearrangement of 3-acetoxy-1-tridecene.



$$\overset{\overset{O}{\|}}{\mathrm{TolSCH_3}}\downarrow\mathrm{PdCl_2}\uparrow\underset{\underset{O}{\|}}{\mathrm{TolSCH_3}}$$

1



$$\overset{\overset{O}{\|}}{\mathrm{TolSCH_2SCH_3}}\downarrow\mathrm{PdCl_2}\uparrow\underset{\underset{O}{\|}}{\mathrm{TolSCH_2SCH_3}}$$

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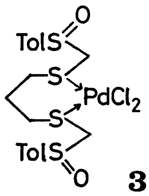

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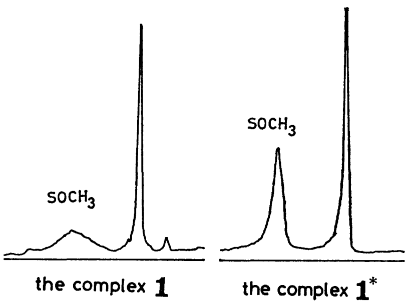
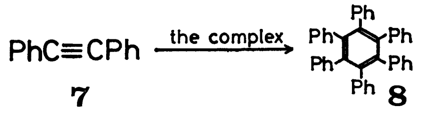
Complexes **1**, **2**, and **3** were easily obtained by simple stirring of $PdCl_2$ and sulfur compounds **4**, **5**, and **6**, respectively, in CH_2Cl_2 at room temperature. Their structures were assigned by their elemental analyses and IR spectra.[2] The absorption of sulfinyl stretching of **1** appears at a higher frequency (1148 cm^{-1})[5] than that (1030 cm^{-1}) of **4** itself, indicating that the lone-pair electrons of the sulfur atom coordinates to $PdCl_2$. Whereas, **2** and **3** showed their sulfinyl absorptions at 1050 cm^{-1} and 1045 cm^{-1}, respectively, in accord with the assigned structures. We also prepared the $PdCl_2$ complex (**1***) with optically active (*R*)-methyl *p*-tolyl sulfoxide (**4***) as a ligand. The protons of the sulfinyl methyl group of **1*** were observed as a relatively sharp singlet in the NMR spectrum, while those of **1** appeared as a very broad signal as shown in Fig. 1, implying that **1** consisted of two diastereomeric isomers (*dl* and *meso* forms) and underwent fast ligand-exchange in solution.

Next, the catalytic activities of the thus prepared complexes were examined for cyclotrimerization of diphenylethyne (**7**) to form hexaphenylbenzene (**8**).[6] To a solution of **7** in CH_2Cl_2, was added the complex (**1**, **2**, or **3**) (0.03 mol equiv.) and the resulting solution was stirred at 30 °C for 24 h. The yield of **8** based on the used complex was 405% for **1**, 40% for **2**, and 13% for **3**. When insoluble $PdCl_2$ was utilized, **8** was obtained in only 25% yield. These facts indicate that, in the complex **3**, ligand (**6**) coordinates to $PdCl_2$ strongly enough to retard the cyclotrimerization.

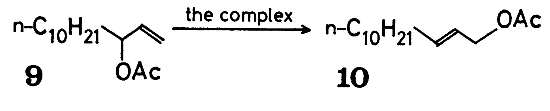


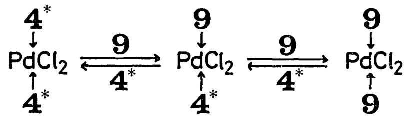
the complex **1** the complex **1***

Fig. 1. ¹H NMR signals of methyl protons of complexes **1** and **1***.



Recently, $(CH_3CN)_2PdCl_2$ was disclosed to promote the rearrangement of 1-alken-3-yl acetates.[7] We also found that **1** catalyzed the conversion of 3-acetoxy-1-tridecene (**9**) to 1-acetoxy-2-tridecene (**10**). When a solution of **9** and **1** (0.03 mol equiv.) in CH_2Cl_2 was stirred at 30 °C for 2 h, a 1:2.1 mixture of **9** and **10** was obtained in a total yield of 92%. Since the ratio remained unchanged even after a prolonged reaction time (16 h), and the similar treatment of **10** afforded a mixture of **9** and **10** in a comparable ratio (1:2.2), it was shown that **9** and **10** were in equilibrium under the present conditions. Although **2** exhibited slight effects on the rearrangement of **9** into **10** (**9**:**10**=10:1 after 149 h), **3** did not promote the rearrangement at all. This tendency seems to be in good relationship with the coordinating strength of the ligand. Furthermore, complex (**1***) with optically active (*R*)-methyl *p*-tolyl sulfoxide was employed in the above rearrangement. Stirring a solution of **9** and **1*** (0.03 mol equiv.) in CH_2Cl_2 gave a mixture of **9** and **10** (1:2.1), but the remained **9** was optically inactive. This phenomenon may be reasonably explained by complete ligand-displacement of **1*** with **9** to produce complex (**12**). For appearance of the optical activity in the remained **9**, complex (**11**) containing both **9** and **4*** must be produced. Hence, we investigated the catalytic rearrangement of **9** in the coexistence of **4***. In the reaction using 0.03 mol equiv. of $PdCl_2$ and





1* **11** **12**

1.0 or 2.0 mol equiv. of **4*** (at room temperature for 8—16 h), no rearrangement took place. When 0.5 mol quiev. of **4*** was used, the rearrangement proceeded slowly and a 10:1 mixture of **9** and **10** was obtained after 16 h. The remained **9** exhibited an optical purity of 2%. This indicates that enantioselectivity in the initial ligand-displacement of **1*** with racemic **9** is approximately 20%.

Thus we have shown that methyl *p*-tolyl sulfoxide (**4**) can coordinate to $PdCl_2$ to make it soluble in CH_2Cl_2, and thus-formed complex (**1**) catalyzes efficiently cyclotrimerization of **7** and rearrangement of **9** to **10** by means of ligand-displacement.

Experimental

The melting points were measured by a Yamagimoto micro melting point apparatus and were uncorrected. The ^{1}H NMR spectra were taken with a Hitachi R-600 spectrometer, and the IR spectra were recorded on a JASCO A-200 spectrometer. Optical rotations were measured on a JASCO DIP-140 polarimeter.

Bis(methyl p-*tolyl sulfoxide)palladium Dichloride (1) and Bis-(methylthiomethyl* p-*tolyl sulfoxide)palladium Dichloride (2).* To a solution of **4** (232 mg: 1.50 mmol) in CH_2Cl_2 (10 ml), was added $PdCl_2$ (116 mg: 0.654 mmol), and the resulting mixture was stirred at room temperature for 1 d. Evaporation and recrystallization from benzene–hexane gave **1** as orange crystals (167 mg: 53%): mp 121—122 °C; ^{1}H NMR ($CDCl_3$): δ 2.42 (6H, s), 3.09 (6H, broad), 7.40 (4H, d, J= 8 Hz), and 7.74 (4H, d, J=8 Hz); IR (KBr): 1148 cm^{-1}. Found: C, 39.60; H, 4.03%. Calcd for $C_{16}H_{20}Cl_2O_2PdS_2$: C, 39.56; H, 4.15%.

In a similar manner, complex **1*** was prepared as orange crystals: mp 75—76 °C (from benzene–hexane).

Complex **2** was analogously obtained in 95% yield: yellow crystals; mp 147—148 °C (from hexane–CH_2Cl_2); ^{1}H NMR ($CDCl_3$): δ 2.43 (6H, s), 2.67 (6H, s), 4.00 (2H, d, J=13.6 Hz), 4.28 (2H, d, J=13.6 Hz), 7.38 (4H, d, J=8 Hz), and 7.58 (4H, d, J=8 Hz); IR (KBr): 1050 cm^{-1}. Found: C, 37.35; H, 4.17. Calcd for $C_{18}H_{24}Cl_2O_2PdS_4$: C, 37.41; H, 4.19.

Complex (3) of $PdCl_2$ *with 1,3-Bis[(*p-*tolylsulfinyl)methylthio]-propane.* To a solution of **6** (300 mg: 0.727 mmol) in CH_2Cl_2 (10 ml), was added $PdCl_2$ (129 mg: 0.728 mmol) and the resulting mixture was stirred at room temperature for 1 d. Evaporation and recrystallization from CH_2Cl_2–hexane afforded **3** as yellow crystals (328 mg: 77%): mp 141—142 °C; ^{1}H NMR ($CDCl_3$): δ 1.59 (2H, broad s), 2.41 (6H, s), 2.79—3.28 (4H, m), 3.99 (1H, d, J=13 Hz), 4.09 (1H, d, J=13 Hz), 4.67 (1H, d, J=13 Hz), 4.74 (1H, d, J=13 Hz), 7.34 (4H, d, J=8 Hz), and 7.54 (4H, d, J=8 Hz); IR (KBr): 1045 cm^{-1}. Found: C, 38.29; H, 4.05%. Calcd for $C_{19}H_{24}Cl_2O_2PdS_4$: C, 38.68; H, 4.10%.

Cyclotrimerization of Diphenylethyne (7). To a solution of **7** (200 mg) in CH_2Cl_2 (5 ml), was added **1**, **2**, **3**, or $PdCl_2$ (0.03 mmol equiv. to **7**), and the resulting mixture was stirred at 30 °C for 1 d. Evaporation and chromatography on silica gel [hexane and benzene–CH_2Cl_2 (1:1)] gave **8** as a colorless solid which was identified by comparison of its IR spectrum with that of the authentic sample.[8] The yields of **8** (the recovered **7**) using **1**, **2**, **3**, and $PdCl_2$ were 73.3 mg (127 mg), 7.3 mg (194 mg), 2.4 mg (193 mg), and 4.6 mg (186 mg), respectively. The value in parentheses means the yield of the recovered **7**.

Rearrangement of 3-Acetoxy-1-tridecene (9). Starting material **9** was prepared by the lit.[9] procedure. Rearrangement product **10** was obtained by the reaction of 1-bromo-2-tridecene (908 mg: 3.48 mmol) with AcOK (425 mg: 4.33 mmol) and KI (8 mg) in AcOH (10 ml) at 80 °C for 11 h, which gave a mixture of **9** and **10** (1:5.05) (617 mg: 74%): a colorless oil; IR (neat): 1742 cm^{-1}. Found: C, 75.07; H, 11.52%. Calcd for $C_{15}H_{28}O_2$: C, 74.95; H, 11.74%. ^{1}H NMR ($CDCl_3$) of **10** ($CDCl_3$): δ 0.90 (3H, diffused t), 1.31 (18H, broad s), 2.01 (3H, s), 4.51 (2H, d, J=5 Hz), and 5.57 (2H, m).

To a solution of **9** (200 mg) in CH_2Cl_2 (10 ml), was added **1** (12 mg: 0.03 mol equiv.), and the resulting mixture was stirred at 30 °C for 2 h under nitrogen atmosphere. Evaporation and chromatography on silica gel [benzene–hexane (1:1)] gave a mixture (184 mg) of **9** and **10**, the ratio of which was determined to be 1:2.1 by a GLC analysis [Silicone DC 550 column (1 m)/nitrogen gas carrier (1 kg/cm^2)/160 °C].

Rearrangement of **9** *in the Coexistence of* **4***. After $PdCl_2$ (8.8 mg) was added to a solution of **4*** (129 mg) in CH_2Cl_2 (5 ml) and the resulting mixture was stirred at room temperature for 3 h, **9** (400 mg) was added together with CH_2Cl_2 (15 ml). The mixture was further stirred for 16 h at room temperature. Evaporation and chromatography gave a mixture (382 mg) of **9** and **10** (10:1) which showed α_D of 0.022 ± 0.002 ($CHCl_3$, c 15.1), *i.e.* $[\alpha]_D$ of 0.16. The optical purity of the remained **9** was calculated to be 2.0%, from the lit.[9] value ($[\alpha]_D$ +7.28 for (R)-**9** of 91.8% e.e.).

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2) At the present time, the data for the geometric isomerism of **1** and **2** are not available, but these complexes are thought to have *trans*-geometry by analogy to the already reported facts that the geometry of $PdCl_2$ complex having a sulfide[3] or a sulfoxide[4] as a ligand is *trans*.

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