# Sulfide-Bearing Phosphine Ligands: Their Pd Complexes and Application to Copolymerizations of Olefins and CO

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Various types of sulfide–phosphine ligands and their Pd complexes were synthesized and applied to copolymerization of olefins with carbon monooxide.

Sulfur ligands have been used much less than phosphorus ligands, although the number of studies on catalytic systems using sulfur ligands has increased notably in recent decades.[1–3] Compared to phosphorus ligands, sulfur ligands have both lower donor and lower acceptor characteristics. Moreover, the sulfur atom has only two substituents to create a less hindered environment than trivalent phosphorus. Thus, the use of sulfur ligands in reactions catalyzed by transition metals is still relatively unexplored.

Efficient carbonylation of MeOH by using mixed P–S ligands has been reported.[4,5] By comparing $Ph_2PCH_2P(=S)Ph_2$ (dppms) with $Ph_2PCH_2CH_2PPh_2$ (dppe), Haynes reported the acceleration of CO insertion to a methyl–rhodium bond, which was explained to result from (1) the higher steric demand for migration, and (2) the higher $\sigma$-bonding character of the sulfur–rhodium bond to stabilize the transition state when the sulfur is located trans to the carbonyl.[6]

Thioether ligands have higher stability, allowing easier storage and handling than phosphorus ligands. In addition, it is easier to synthesize thioether–phosphine ligands and change both their electronic states and steric states,[2] compared with dppms derivates.[7] From these viewpoints, it would be valuable to attempt to synthesize sulfide-bearing phosphine ligands by assuming that thioether ligands possess the trans effect of sulfur for CO insertion as well as dppms. Dilworth reported phosphine–thioether ligands represented as [*ortho*-(alkylthio)-phenylmethyl]diphenylphosphines which showed low activity for ethylene/CO copolymerization.[8] Here we report synthesis of a new classes of mixed P–thioether ligands and their application to alkene/CO copolymerization.[9–12]

First, it was noted that *o*-(diphenylphosphino)benzyl chloride was a good precursor for mixed P–S ligands.[13] The new ligands **1**–**4** (Figure 1a) were prepared by the reaction of *o*-(diphenylphosphino)benzyl chloride together with the lithiated thioalkoxide, lithiated dithianes, and lithiated sulfide (See Supporting Information). In particular, ligands **3** and **4** are expected to accelerate CO insertion because of steric strain due to bulky TMS groups, which is based on Haynes' insight.[6] The metal complexes (S–P)PdMeCl **5**–**8** were synthesized from S–P ligands **1**–**4** and PdClMe(cod) (Figure 1b). The metal complexes (S–P)PdMeCl **5**–**8** were precursors of catalysts (vide infra).

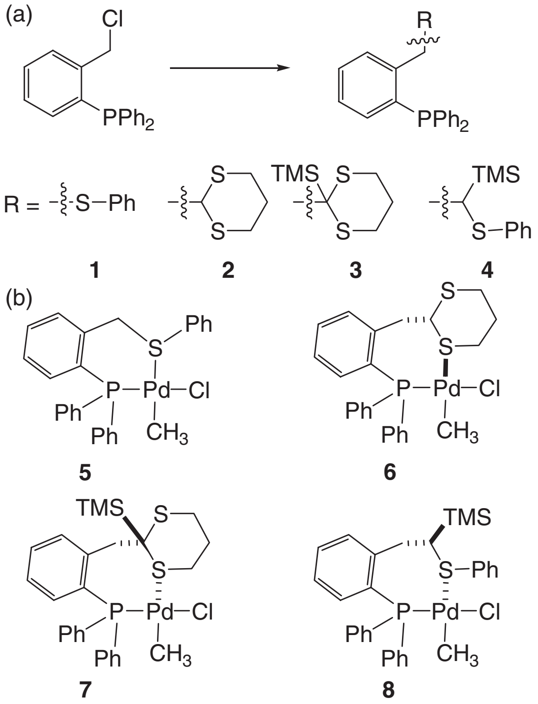

**Figure 1.** Phosphine–sulfide ligands **1**–**4** and Pd complexes **5**–**8**. The stereochemistry represents relative configuration but not absolute.

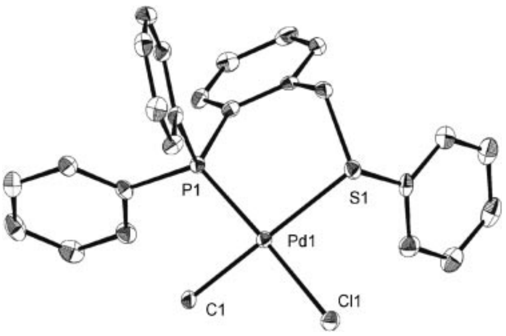

**Figure 2.** ORTEP drawing of **5** (all H atoms are omitted for clarity).

Single-crystal X-ray analyses of **5**–**8** revealed their structures and their ORTEP views are shown in Figures 2–5. Judging from their bond angles and bond lengths, all the local geometries at the palladium atoms of **5**–**8** are square planar with Pd, P, S, C, and Cl. The methyl groups and phosphorus atoms of **5**–**8** are coordinated cis on the palladium centers. In the case of **6**, it should be noted that the pallada-cycle created by coordination and the dithiane ring are trans to each other.[14] On the other hand, due to the steric effect of the TMS group, the pallada-cycle of **7** created by coordination and the dithiane ring are cis to each other.

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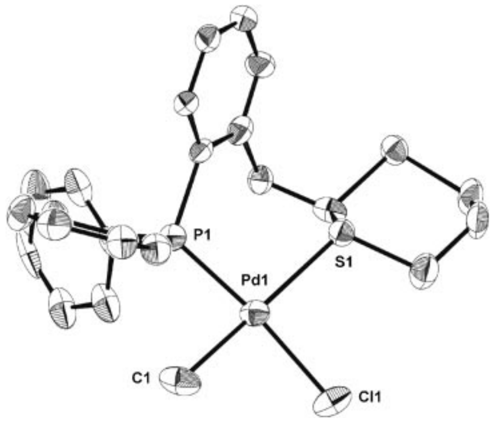


**Figure 3.** ORTEP drawing of **6** (all H atoms are omitted for clarity).

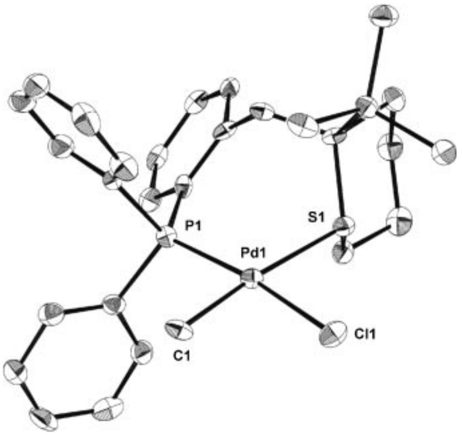


**Figure 4.** ORTEP drawing of **7** (all H atoms are omitted for clarity).

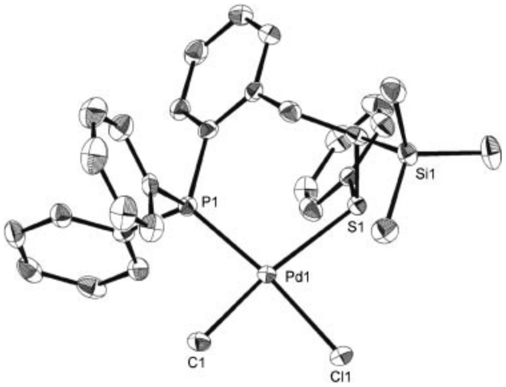
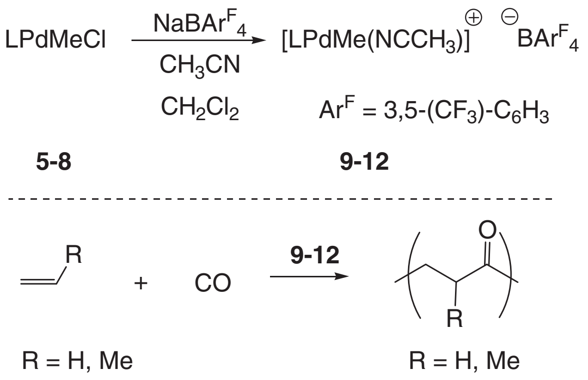


**Figure 5.** ORTEP drawing of **8** (all H atoms are omitted for clarity).



**Scheme 1.** Pd catalysts **9**–**12** and their copolymerization.

**Table 1.** Activity of Polymerization[a)]

| Run | Pd cat. (Precursor) | Activity /g mol Pd$^{-1}$ | $M_n$ | $M_w/M_n$ |
|---|---|---|---|---|
| 1[b)] | **9** (**5**) | 20000 | — | — |
| 2[b)] | **10** (**6**) | 18500 | — | — |
| 3[b)] | **11** (**7**) | 2000 | — | — |
| 4[b)] | **12** (**8**) | 5400 | — | — |
| 5[c)] | **9** (**5**) | 570 | 11000 | 1.05 |
| 6[c)] | **10** (**6**) | 2030 | 15000 | 1.07 |
| 7[c)] | **11** (**7**) | Trace | — | — |
| 8[c)] | **12** (**8**) | Trace | — | — |

a) Conditions are described in experimental section. b) Ethylene was used as an olefin. c) Propylene was used as an olefin.

The application of the palladium complexes **5**–**8** to copolymerization of CO was investigated with ethylene and propylene.[9–12] Displacement of the chloro ligands using NaBAr$^F{}_4$ in the presence of acetonitrile is expected to yield cationic derivatives **9**–**12** in situ in Scheme 1. In the case of copolymerization of CO with ethylene by **9**–**12**, the resultant insoluble white materials were obtained in the following yield at 80 °C for 3 h (Table 1, Runs 1–4): **9** (Activity 20000 g mol Pd$^{-1}$), **10** (Activity 18500 g mol Pd$^{-1}$), **11** (Activity 2000 g mol Pd$^{-1}$), and **12** (Activity 5400 g mol Pd$^{-1}$). In spite of different distortion of the ligand backbone between **5** and **6**, similar activities of **9** and **10** were shown. On the other hand, a large difference of ligand distortion between **7** and **8** had great influence on the activities between **11** and **12**. It would due to the rigidity of the ligand backbone that different activity was observed.[9] In particular, catalyst **9** derived from **5** showed much higher activity per hour than previous examples of phosphine–thioether ligands,[8] although the activity was lower than diphosphine ligands.[9] The products were perfectly alternating CO and $C_2H_4$ copolymer, which was confirmed by their $^{13}$C NMR spectra ($C_6D_6$:$(CF_3)_2CHOH$ = 1:9, v/v). Catalysts **11** and **12** (derived from **7** and **8**) showed much lower activity than catalysts **9** and **10** (derived from **5** and **6**). This large difference of catalyst activity seems to be due to the structural difference derived from steric effect of the TMS group.[9]

Next, propylene was chosen as a substrate. The resultant viscous materials were obtained in the following yield at 25 °C for 4 days (Table 1, Runs 5–8): **9** ($M_n = 11000$, $M_w/M_n = 1.05$, and activity 570 g mol Pd$^{-1}$), **10** ($M_n = 15000$, $M_w/M_n = 1.07$, and activity 2030 g mol Pd$^{-1}$), **11** (Trace amount of oligomer), and **12** (Trace amount of oligomer). Catalysts **9** and **10** provided the completely alternating CO and propylene units. Judging from $^1$H NMR and $^{13}$C NMR spectra (See Supporting Information), their structures were assigned as regioregular and atactic polymers. Although catalyst **9** gave slightly higher yield than catalyst **10** in copolymerization of ethylene and CO, catalyst **9** demonstrated much lower activity of copolymerization of propylene and CO than catalyst **10**. It would due to the different rigidity of the ligand backbone to influence on the stability of the propagation step.[9] It should be pointed out that catalytic activity of catalyst **9** and **10** were much lower than catalysts bearing diphosphine ligands.[9] Both of **11** and **12** demonstrated little activity. This may be due to the steric effect of TMS influencing the propagation step.[9]

In conclusion, new mixed phosphine–sulfide ligands **1–4** and their palladium complexes **5–8** were synthesized. Catalysts **9–12** were prepared in situ from precursors **5–8** to be applied to copolymerization of CO and olefins ethylene and propylene. In spite of lower activity than palladium catalysts bearing diphophine ligands, catalysts **9** and **10** demonstrated higher activity for ethylene/CO alternating copolymerization than previous palladium catalysts with phosphine–sulfide ligands. Furthermore, catalysts **9** and **10** provided propylene/CO alternating copolymer to yield regioregular and atactic polyketone, despite lower activity than palladium catalysts bearing diphosphine ligands. Although catalyst **9** gave slightly higher yield than catalyst **10** in the case of copolymerization of ethylene and CO, catalyst **9** demonstrated much lower activity toward copolymerization of propylene and CO than catalyst **10**.

## Experimental

**Copolymerization of CO and Ethylene.** A solution of Pd complex **5–8** (20.0 µmol) in $CH_2Cl_2$ (1.00 mL) was added a solution $NaBAr^F_4$ (20.0 µmol) in $CH_3CN$ (0.800 mL). The solution was stirred at room temperature for 2 h, filtered to remove NaCl and concentrated in vacuo. The product **9–12** was dissolved in $CH_2Cl_2$ (23.0 mL) and degassed by three freeze thaw cycles. Resultant solutions were transferred into a 50-mL autoclave. All reactor valves were closed and the solution was then heated to 80 °C for 10 min. The reactor was pressurized to 4.0 MPa ($CO{:}C_2H_4 = 1{:}1$ by moles) and stirred at 80 °C for 3 h. It was then cooled to room temperature, vented and opened. Under air, the suspension was filtrated and the residue was washed with $CH_2Cl_2$ ($3 \times$ ca. 20 mL) and dried under reduced pressure at 60 °C to obtain white powder.

**Copolymerization of CO and Propylene.** The catalyst **9–12** prepared as above (20.0 µmol) was dissolved in $CH_2Cl_2$ (4.00 mL) and degassed by three freeze thaw cycles. The resultant solution was transferred into a 50-mL autoclave. After treating with CO (1 atm), the solution was charged with propylene (0.3 MPa). The mixture was stirred under CO (2.0 MPa) for 4 days at 25 °C. After the pressure was released, 0.2 mL of MeOH was added to cleave Pd–C bonds by carbomethoxylation. After 1 h, the reaction mixture was poured into MeOH (100 mL) under air to precipitate gray poly(propylene-*alt*-CO).

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC-711978, -711979, -722616, and -722617 for compounds **5**, **6**, **7**, and **8**, respectively. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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## Supporting Information

Experimental procedures and identification data of newly synthesized compounds. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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14 Small amount of unidentified isomer was detected (Isomer ratio ca. 9:1).