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# Effect of phosphine and phosphine sulfide ligands on the cobalt-catalyzed reductive coupling of 2-iodobutane with *n*-butyl acrylate

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# ABSTRACT

Tris[2-(diphenylphosphino)ethyl]phosphine disulfide (pp<sub>3</sub>S<sub>2</sub>), in which two terminal phosphino groups are selectively sulfidated, was prepared by utilizing the selective sulfidation reaction of [Pdl(pp<sub>3</sub>)]I. Co(II) complexes with bidentate, tridentate and tetradentate phosphines and pp<sub>3</sub>S<sub>2</sub> were prepared from anhydrous Col<sub>2</sub>. X-ray crystal analyses revealed that the reaction of Col<sub>2</sub> with 1 equivalent of 1,2-bis(diphenylphosphino)ethane (p<sub>2</sub>) gave rise to partial oxidation of p<sub>2</sub> to give the dicationic octahedral  $[Co(p_2O_2)_2(CH_3CN)_2]^{2+}$  (p<sub>2</sub>O<sub>2</sub> = p<sub>2</sub> dioxide) and dianionic p<sub>2</sub>O-bridged tetrahedral dinuclear  $[Col_3(p_2-O)Col_3]^{2-}$  (p<sub>2</sub>O = p<sub>2</sub> monoxide) complexes, while the reaction with 2 equivalents of p<sub>2</sub> gave the square-pyramidal  $[Col(p_2)_2]^+$  complex. The catalytic activity for the Co-catalyzed coupling reaction of 2-iodobutane with *n*-butyl acrylate was compared using multidentate phosphines and phosphine sulfides as ligands, and the efficiency of the phosphine sulfides was shown. The tendency for multidentate phosphine to deactivate the Co-catalysis can substantiate an oxidative addition driven mechanism in which the multidentate ligand should interfere with the formation of the alkyl halide Co(III) adduct and subsequent coordination of an alkene.

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# 1. Introduction

Carbon-carbon bond formation reactions by transition metal catalysts are now quite versatile and indispensable in organic syntheses. In particular, direct C-H bond transformation is a highly attractive strategy because of the commonness of C-H bonds [1]. Although some of the second row transition metal catalysts, such as Rh, Pd and Ru complexes, have proven to be highly effective in the direct coupling processes [2], the development of new cost-effective catalysts is significant for industrial use. In line with the above challenge, several Co-catalyzed reactions using a Grignard reagent have been reported, where a radical generation mechanism was proposed [3]. However, these catalytic reactions cannot be used for the coupling of an alkyl halide with an electronwithdrawing alkene because Grignard reagents are quite reactive to the activated alkene. Recently, Cheng et al. reported efficient Co-catalyzed C<sub>sp3</sub>-C<sub>sp3</sub> bond forming reactions of primary, secondary and tertiary alkyl halides with electron-withdrawing alkenes under mild conditions without Grignard reagents [4], and they proposed an oxidative addition driven mechanism in which an alkene is bound to a Co(III) adduct formed by the oxidative addition of Co(I) with an alkyl halide. Although PPh<sub>3</sub> or bidentate phosphines were used for the bound ligand in that work, the steric and electronic properties of the ligand on the Co center should be quite significant factors affecting the catalytic activity in the oxidative addition driven mechanism. Thus, in the present report, the steric and electronic effects of ligands are investigated by using some sterically different multidentate phosphines and more  $\pi$ -accepting and polarizable phosphine sulfides, which are electronically more efficient for the oxidative addition–reductive elimination mechanism in the Pd(0) catalytic cycle [5]. The observed differences in the catalytic activity provide further insight into the reaction mechanism of the catalytic cycle from the view point of coordination chemistry.

# 2. Experimental

# 2.1. Reagents

Tris[2-(diphenylphosphino)ethyl]phosphine (pp<sub>3</sub>, Aldrich), bis[2-(diphenylphosphino)ethyl]phenylphosphine (p<sub>3</sub>, Aldrich), 1,2-bis(diphenylphosphino)ethane (p<sub>2</sub>, Wako), anhydrous cobalt(II) iodide (Kishida Chemical), tetrakis(acetonitrile)palladium(II) tetrafluoroborate ([Pd(CH<sub>3</sub>CN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub>, Aldrich), tetra(*n*-butyl) ammonium iodide (Wako), sulfur (Wako), zinc powder (Wako),





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2-iodobutane (Tokyo Chemical), *n*-butyl acrylate (Kishida Chemical) and dibenzyl ether (Kishida Chemical) were used for the preparation and catalytic reactions without further purification.

# 2.2. Preparation

# 2.2.1. Tris[2-(diphenylphosphino)ethyl]phosphine disulfide (pp<sub>3</sub>S<sub>2</sub>)

The disulfide complex [PdI<sub>2</sub>(pp<sub>3</sub>S<sub>2</sub>)] was prepared by the reaction of [PdI(pp<sub>3</sub>)]I [6] (0.362 g, 0.351 mmol) with sulfur (0.0225 g, 0.702 mmol) in degassed chloroform (ca. 10 cm<sup>3</sup>) under N<sub>2</sub> at 40 °C for 3 days. The reaction solution was concentrated to a small volume, and to this was added diethyl ether. The resultant yellow solid was filtered and air-dried. Yield: 0.28 g (70%). *Anal.* Calc. for C<sub>42</sub>H<sub>42</sub>I<sub>2</sub>P<sub>4</sub>S<sub>2</sub>Pd·0.5CHCI<sub>3</sub>: C, 44.20; H, 3.71; N, 0.00; S, 5.55. Found: C, 44.48; H, 3.75; N, 0.00; S, 5.57%. <sup>31</sup>P{<sup>1</sup>H} NMR (CHCI<sub>3</sub>)  $\delta$ : 44.4 (d, 2P, sulfide), 70.0 (d, 1P, terminal), 78.1 (m, 1P, center); <sup>3</sup>J<sub>P(sulfide)-P(center)</sub> = 55.0 Hz, <sup>3</sup>J<sub>P(terminal)-P(center)</sub> = 17.8 Hz.

The disulfide Pd(II) complex prepared above,  $[PdI_2(pp_3S_2)]$ -0.5CHCl<sub>3</sub> (0.190 g, 0.165 mmol), and pp<sub>3</sub> (0.122 g, 0.182 mmol) were dissolved in degassed chloroform (ca. 5 cm<sup>3</sup>) and reacted under N<sub>2</sub> at 50 °C for 1 day. The formed red pp<sub>3</sub> complex [PdI(pp<sub>3</sub>)]I [6] was removed by silica gel column chromatography with chloroform as the eluent. The <sup>31</sup>P NMR spectrum of the concentrated colorless eluate indicated that the eluate contained unreacted pp<sub>3</sub> and dissociated free pp<sub>3</sub>S<sub>2</sub>. The concentrated chloroform eluate was mixed with an aqueous solution of K<sub>2</sub>[PdCl<sub>4</sub>] to form red  $[PdCl(pp_3)]Cl$  [6,7] in the chloroform layer. Aqueous K<sub>2</sub>[PdCl<sub>4</sub>] was added until the <sup>31</sup>P NMR signals of pp<sub>3</sub> completely disappeared, showing only the signals of pp<sub>3</sub>S<sub>2</sub> and [PdCl(pp<sub>3</sub>)]Cl [6,7]. Then, the red Pd(II) complex was removed by silica gel column chromatography, eluting with chloroform. The colorless eluate was concentrated and to this was added diethyl ether to obtain pure pp<sub>3</sub>S<sub>2</sub>. Yield: 0.049 g (40%). Anal. Calc. for C<sub>42</sub>H<sub>42</sub>P<sub>4</sub>S<sub>2</sub>·0.5H<sub>2</sub>O: C, 67.82; H, 5.82; N, 0.00; S, 8.62. Found: C, 67.81; H, 5.67; N, 0.00; S, 8.36%. <sup>31</sup>P{<sup>1</sup>H} NMR (CHCl<sub>3</sub>) δ: -19.7 (q, 1P, center), -13.1 (d, 1P, terminal), 44.4 (d, 2P, sulfide);  ${}^{3}J_{P(center)-P(terminal)} = 27.5$  Hz,  ${}^{3}J_{P(cen-P(terminal))} = 27.5$  Hz,  ${}^{3}J_{P(terminal)} = 27.5$  Hz, ter)-P(sulfide) = 30.7 Hz.

# 2.2.2. [Col(p<sub>2</sub>)<sub>2</sub>]I (1)

Anhydrous CoI<sub>2</sub> (0.0510 g, 0.163 mmol) and p<sub>2</sub> (0.130 g, 0.326 mmol) were dissolved in degassed THF and reacted under N<sub>2</sub> at room temperature for 2 h. The reaction solution was concentrated under N<sub>2</sub>, and to this was added degassed diethyl ether to obtain the resultant brown solid by filtration. The solid was recrystallized from chloroform, and single crystals suitable for an X-ray analysis were obtained. Yield: 0.13 g (55%). *Anal.* Calc. for C<sub>52</sub>H<sub>48</sub>P<sub>4</sub>. Col<sub>2</sub> (1)·CHCl<sub>3</sub>: C, 50.82; H, 3.94; N, 0.00. Found: C, 50.58; H, 3.87; N, 0.00%.

#### 2.2.3. $[Co(p_2O_2)_2(CH_3CN)_2][CoI_3(p_2O)CoI_3]$ (2)

This complex salt was obtained by a procedure similar to that described for **1**, using 1 equivalent of  $p_2$  instead of 2 equivalents. Single crystals suitable for an X-ray analysis were obtained by recrystallization from acetonitrile. Yield: 0.050 g (40%). *Anal.* Calc. for  $C_{82}H_{78}N_2O_5P_6Co_3I_6$  (**2**): C, 42.91; H, 3.42; N, 1.22. Found: C, 42.67; H, 3.45; N, 1.09%.

### 2.2.4. [Col(p<sub>2</sub>O<sub>2</sub>)<sub>2</sub>]I (3)

This bis(P<sub>2</sub>O<sub>2</sub>) complex was obtained by a procedure similar to that described for **1**, using P<sub>2</sub>O<sub>2</sub> prepared by the oxidation of p<sub>2</sub> with 10% aqueous H<sub>2</sub>O<sub>2</sub> in chloroform instead of P<sub>2</sub>. Yield: 0.16 g (65%). *Anal.* Calc. for  $C_{64}H_{60}O_4P_4CoI_2$  (**3**)·3C<sub>4</sub>H<sub>4</sub>O: C, 55.79; H, 4.39; N, 0.00; S, 0.00. Found: C, 55.90; H, 4.37; N, 0.07; S, 0.00%.

#### 2.2.5. $[CoI_2(L)]$ ( $L = pp_3$ (**4**), $p_3$ (**5**), and $pp_3S_2$ (**6**))

These phosphine and phosphine disulfide complexes were obtained by a procedure similar to that described for **1**, using 1 equivalent of pp<sub>3</sub> for **4**, p<sub>3</sub> for **5** and pp<sub>3</sub>S<sub>2</sub> for **6** instead of 2 equivalents of p<sub>2</sub>. Yields: 0.14 g (74%) for **4**, 0.10 g (63%) for **5** and 0.16 g (72%) for **6**. *Anal.* Calc. for  $C_{42}H_{42}P_4Col_2$  (**4**)·1.5CHCl<sub>3</sub>: C, 44.94; H, 3.77; N, 0.00; S, 0.00. Found: C, 44.82; H, 3.88; N, 0.04; S, 0.00%. *Anal.* Calc. for  $C_{34}H_{33}P_3Col_2$  (**5**)·CHCl<sub>3</sub>: C, 43.49; H, 3.55; N, 0.00; S, 0.00. Found: C, 44.19; H, 3.60; N, 0.00; S, 0.00%. *Anal.* Calc. for  $C_{42}H_{42}P_4$ . S<sub>2</sub>Col<sub>2</sub> (**6**)·2C<sub>4</sub>H<sub>4</sub>O·1.5CHCl<sub>3</sub>: C, 45.39; H, 3.81; N, 0.00; S, 4.71. Found: C, 45.16; H, 3.88; N, 0.08; S, 4.59%.

#### 2.2.6. [Col(pp<sub>3</sub>)] (7)

This Co(I) complex was obtained by a procedure similar to that described in the literature [8]. <sup>31</sup>P{<sup>1</sup>H} NMR (CHCl<sub>3</sub>)  $\delta$ : 59.5 (d, 3P, terminal), 157.9 (q, 1P, center); <sup>3</sup>J<sub>P(center)-P(terminal)</sub> = 37.2 Hz.

# 2.3. Crystal structure determination

The measurements for 1.3CHCl<sub>3</sub> and 2 were made on a Rigaku Mercury CCD X-ray diffractometer using graphite-monochromated Mo K $\alpha$  ( $\lambda$  = 0.71075 Å) radiation at 200 K. Cell parameters were refined using the program CRYSTALCLEAR (Rigaku and MSC, version 1.3, 2001) and the collected data were reduced using the program CRYSTALSTRUCTURE (Rigaku and MSC, version 3.8, 2006). Empirical absorption corrections were applied. The structures were solved by direct methods using SIR 92 [9] and refined by full-matrix least-squares techniques using SHELXL-97 [10]. All non-hydrogen atoms for 1.3CHCl<sub>3</sub> and **2** were refined anisotropically and hydrogen atoms were included in calculated positions. The structure of **2** contains Col<sub>3</sub> moieties disordered over two different orientations for 11 and three different orientations for 12, 13, 14, 15, and 16<sup>1</sup>.

# 2.4. General procedure for the cobalt-catalyzed coupling reaction

Reactions of *n*-butyl acrylate (0.128 g, 1.00 mmol) with 2-iodobutane (0.184 g, 1.00 mmol) were carried out in a sealed tube containing degassed acetonitrile ( $2 \text{ cm}^3$ ), the cobalt catalyst (0.040 mmol), zinc powder (0.164 g, 2.50 mmol), water (0.018 g, 1.0 mmol) and dibenzyl ether (0.015 g, 0.075 mmol) under N<sub>2</sub> at 80 °C. The yields were calculated by the <sup>1</sup>H NMR intensity of the methylene protons of the formed *n*-butyl-4-methylhexanoate on the basis of the intensity of the methylene protons of dibenzyl ether contained as an internal reference and followed as a function of time.

#### 2.5. Measurements

<sup>31</sup>P and <sup>1</sup>H NMR spectra for solutions were recorded on a JEOL JNM-A400 FT-NMR spectrometer operating at 160.70 and 399.65 MHz, respectively. In order to determine the chemical shifts of the <sup>31</sup>P NMR signals, a 3-mm-o.d. NMR tube containing the sample solution was coaxially mounted in a 5-mm-o.d. NMR tube containing deuterated water as a lock solvent and phosphoric acid as a reference.

<sup>&</sup>lt;sup>1</sup> Crystal data for 1·3CHCl<sub>3</sub>: C<sub>55</sub>H<sub>51</sub>Cl<sub>9</sub>Col<sub>2</sub>P<sub>4</sub>,  $M_r$  = 1467.62, triclinic, space group  $P\bar{1}$ , a = 14.4437(15) Å, b = 20.182(2) Å, c = 20.612(2) Å,  $\alpha = 93.404(3)^{\circ}$   $\beta = 91.004(3)^{\circ}$   $\gamma = 93.107(3)^{\circ}$  V = 5987.8(11) Å<sup>3</sup>, Z = 4,  $\rho_{calcd} = 1.628$  Mg m<sup>-3</sup>, crystal size 0.26 × 0.23 × 0.12 mm<sup>3</sup>, F(000) = 2908,  $\mu$ (Mo K $\alpha$ ) = 1.862 mm<sup>-1</sup>, GOF = 1.080, 26866 independent reflections ( $R_{int} = 0.0588$ ). The final *R* indicates were  $R_1 = 0.0635$  ( $I > 2\sigma(I)$ ) and  $wR_2 = 0.1641$  (all data). Crystal data for **2**: C<sub>82</sub>H<sub>78</sub>Co<sub>31</sub>e<sub>N</sub>O<sub>25</sub>P<sub>6</sub>,  $M_r = 2295.47$ , monoclinic, space group  $P_2_1$ , a = 11.583(3) Å, b = 20.038(5) Å, c = 20.039(5) Å,  $\beta = 105.090(8)^{\circ}$  V = 4491(2) Å<sup>3</sup>, Z = 2,  $\rho_{calcd} = 1.698$  Mg m<sup>-3</sup>, crystal size 0.25 × 0.10 × 0.05 mm<sup>3</sup>, F(000) = 2226,  $\mu$ (Mo K $\alpha$ ) = 2.764 mm<sup>-1</sup>, GOF = 1.117, 20075 independent reflections ( $R_{int} = 0.0577$ ). The final *R* indicates were  $R_1 = 0.0819$  ( $I > 2\sigma(I$ )) and  $wR_2 = 0.1411$  (all data).

# 3. Results and discussion

#### 3.1. Synthesis

The selective sulfidation of two terminal phosphino groups of the tetradentate tris[2-(diphenylphosphino)ethyl]phosphine (pp<sub>3</sub>) was reported previously for the five-coordinated trigonal-bipyramidal Pd(II) complex, [PdCl(pp<sub>3</sub>)]Cl [11]. The disulfide complex exists in equilibrium between the five-coordinate pseudo-trigonalbipyramidal complex and the four-coordinate square-planar one with two pendant phosphine sulfide groups in chloroform [11a]. In this work, such reactivity of the pp<sub>3</sub> complex was applied to the preparation of  $pp_3S_2$  ( $pp_3$  disulfide) (Scheme 1). The selective sulfidation of two terminal phosphino groups of pp3 was carried out with [PdI(pp<sub>3</sub>)]I instead of the corresponding chloro complex, [PdCl(pp<sub>3</sub>)]Cl. The obtained disulfide complex exhibited <sup>31</sup>P NMR behavior similar to that of the chloro complex, with broadening of the signals, suggesting an equilibrium between the five and four coordinate structures as observed for the chloro complex [11a]. The pp<sub>3</sub>S<sub>2</sub> ligand was successfully dissociated from the Pd(II) complex by competitive coordination of  $pp_3$  to form the more stable five coordinate [PdI(pp<sub>3</sub>)]I [6]. The reason for use of the iodo complex instead of the chloro one is that the electron-accepting ability of the iodo ligand is greater than that of chloro one, which may promote coordination of phosphine  $\sigma$  donors to form the five coordinate pp<sub>3</sub> complex [6], and accordingly the pp<sub>3</sub>S<sub>2</sub> ligand may dissociate more easily from the pp<sub>3</sub>S<sub>2</sub> complex. Furthermore, taking advantage of the stability of the five-coordinate Pd(II) complex with the tetradentate  $pp_3$  ligand compared to the  $pp_3S_2$  complex equilibrated between the four and five-coordinate structures, unreacted pp<sub>3</sub> was successfully removed from the mixture of free  $pp_3$  and  $pp_3S_2$  by complexation with  $K_2[PdCl_4]$ , followed by separation with a silica gel column (see Section 2).

For a comparison of the catalytic activity of the Co(II) complexes with different bound ligands, the preparation of the 1:1 complexes with a phosphine or phosphine chalcogenide was attempted. However, the reaction of anhydrous Col<sub>2</sub> with 1 equiv of 1,2bis(diphenylphosphino)ethane (p<sub>2</sub>) gave rise to partial oxidation of p<sub>2</sub>, probably during recrystallization, to give **2** which consists of the dicationic octahedral bis(p<sub>2</sub>O<sub>2</sub>) complex,  $[Co(p_2O_2)_2(CH_3-CN)_2]^{2+}$  (p<sub>2</sub>O<sub>2</sub> = p<sub>2</sub> dioxide), and the dianionic p<sub>2</sub>O-bridged dinuclear tetrahedral complex,  $[Col_3(p_2O)Col_3]^{2-}$  (p<sub>2</sub>O = p<sub>2</sub> monoxide), in which p<sub>2</sub>O does not act as a bidentate chelate (see below). This fact indicates that the 1:1 complex,  $[Col_2(p_2)]$ , is not stable because the p<sub>2</sub> chelate bite distance is too small to give the tetrahedral Co(II) complex (see below). Consequently, the 1:2 complexes were prepared using 2 equivalents of p<sub>2</sub> or p<sub>2</sub>O<sub>2</sub> to give **1** and **3**.



Fig. 1. ORTEP diagram of 1.3CHCl<sub>3</sub>.

## 3.2. Crystal structure

The perspective views of 1.3CHCl<sub>3</sub> and 2 are shown in Figs. 1 and 2, respectively. The bis(p<sub>2</sub>) complex **1**, prepared with a 1:2 Col<sub>2</sub>/p<sub>2</sub> ratio, takes a five-coordinate square-pyramidal geometry with one iodide group in the apical position. The other iodide ion is surrounded by three chloroform molecules. The chelate bite angles of the p<sub>2</sub> bidentate ligands are considerably smaller than 90° (P1-Co1-P2 = 82.09(5)° and P3-Co1-P4 = 81.57(5)°). This structure indicates that the five-membered chelate of p<sub>2</sub> is too small to form a regular square plane for the Co(II) centre. It is obvious that formation of a tetrahedral geometry, expected for the mono(p<sub>2</sub>) complex [Col<sub>2</sub>(p<sub>2</sub>)], would give rise to further distortion because the chelate bite angle should be 109° for a regular tetrahedral geometry.

Complex **2**, which was obtained from a 1:1  $\text{Col}_2/\text{p}_2$  ratio, consists of the dicationic octahedral complex  $[\text{Co}(\text{p}_2\text{O}_2)_2(\text{CH}_3\text{CN})_2]^{2+}$  and the dianionic  $\text{p}_2\text{O}$ -bridged dinuclear complex with two tetrahedral  $\text{Co}(\text{II})\text{I}_3$  moieties linked by phosphino and phosphine oxide groups. The complex cation takes a nearly regular octahedral geometry in which the chelate bite angles of the  $\text{p}_2\text{O}_2$  ligands are almost 90° (89.6–90.7°). This is attributed to the flexibility and steric adjustability of the seven-membered  $\text{p}_2\text{O}_2$  chelate. Though large deviations of the bond distances and angles were observed in the two distorted tetrahedral Co(II) moieties, the averaged I–Co–I bond angles for the phosphine complex moiety (114.1°) and the phosphine oxide complex moiety (113.8°) are obviously larger than



#### Scheme 1. Isolation of pp3S2.



Fig. 2. ORTEP diagram of 2 showing  $[Co(p_2O_2)_2(CH_3CN)_2]^{2+}$  (a) and  $[Col_3(p_2-O)Col_3]^{2-}$  (b), individually.

the averaged I-Co-P (103.5°) and I-Co-O (104.7°) bond angles, due to the repulsion between the large iodide anions. It should be noted that the averaged Co-I bond distance for the phosphine complex moiety (2.52 Å) is considerably shorter than that for the phosphine oxide complex moiety (2.61 Å), in spite of the larger steric bulkiness of the diphenylphosphino group in the coordination sphere compared to the phosphine oxide group. Such a difference in bond distances may suggest that the electron donation of the soft diphenylphosphino group to the hard tetrahedral Co(II) ion is relatively weaker than that of the hard phosphine oxide group, resulting in smaller electronic repulsion on the Co(II) center with a phosphino group rather than that with a phosphine oxide group. This is consistent with the fact that the Co-P distance in the tetrahedral Co(II) moiety in **2** (2.463(5)Å) is significantly longer than the averaged Co–P distance of the five-coordinate Co(II) complex **1** (2.283 Å), though the ionic radius of four-coordinate tetrahedral Co(II) should be smaller than those for five- or six-coordinate Co(II). On the other hand, the Co-O distance in the tetrahedral Co(II) moiety in 2 (1.892(8) Å) is reasonably shorter than the averaged Co-O distance in the six-coordinate octahedral Co(II) moiety in 2 (2.036 Å).



**Fig. 3.** Change in the yield of butyl-4-methylhexanoate with time in the cobaltcatalyzed coupling reaction using  $1 (\bigcirc), 3 (\bullet), 4 (\triangle), 5 (\blacktriangle), 6 (\Box)$  and a mixture of Col<sub>2</sub> and pp<sub>3</sub>S<sub>4</sub> ( $\blacksquare$ ).

#### 3.3. Cobalt-catalyzed coupling reaction

The catalytic activities of the  $p_2$ ,  $pp_3$  and bis[2-(diphenylphosphino)ethyl]phenylphosphine  $(p_3)$  phosphine complexes, 1, 4 and **5**, and the  $pp_3S_2$  phosphine sulfide complex **6** for the cobaltcatalyzed coupling reaction of an alkyl halide with an alkene were compared using 2-iodobutane and n-butyl acrylate as the substrates. The changes in the yield of the formed *n*-butyl-4-methylhexanoate are plotted in Fig. 3. If an excess of *n*-butyl acrylate (more than 2 equivalents) and more Co catalyst (0.1 equivalents) were used, as described in the literature [4], a much higher yield was obtained for each ligand. However, in the present experiments, equimolar amounts of substrates and 0.04 equivalents of the Co catalysts were used in order to make the difference in the activity clearer. The catalytic activity of the phosphine sulfide complex **6** is definitely higher than those of the phosphine complexes 1, 4 and 5. The efficiency of phosphine sulfides was also shown by the reaction with a mixture of  $pp_3S_4$  ( $pp_3$  tetrasulfide) [5a] and CoI<sub>2</sub> (Fig. 3). Among the phosphine complexes, complex 4, with the tetradentate phosphine ligand pp<sub>3</sub>, showed the lowest activity, and the bidentate phosphine,  $p_2$ , does not deactivate the catalysis even in the case of the  $bis(p_2)$  complex **1**. On the other hand, the phosphine oxide group gives rise to deactivation, as observed for the reaction using the  $bis(p_2O_2)$  complex **3** as an analogue of **1**.

Phosphines have been reported to be quite versatile ligands so far, especially for Pd catalyzed coupling reactions [12]. However, phosphines are usually susceptible to oxidation to give inactive Pd black and addition of excess phosphines inhibits the catalytic reactions by blocking the substrate coordination. More recently, it has been reported that phosphine sulfides are more effective ligands for some Pd catalyzed C-C coupling reactions because phosphine sulfides can stabilize the active Pd(0) species, even in the air, and do not interfere with the oxidative addition of Pd(0) and subsequent coordination of substrates on Pd(II) [5]. The nature of P=X (X = O, S, Se) bonds has been extensively discussed and reviewed over the years [13]. In line with these discussions, the  $\pi$  accepting ability of the P=S bond of phosphine sulfides can stabilize low-valent metal centers to promote the generation of the catalytically active species. Also the polarizability of the P=S bond can be effective for coordination to higher positively charged metal ions, so as not to interfere with the oxidative addition of the active species. Furthermore, because phosphine sulfides are weak  $\sigma$  donors, forming relatively weak  $\sigma$  bonds, the coordination of another substrate and subsequent migration on the oxidized metal center are not blocked. The polarization of P=S bonds by coordination is observed even in the solid state, that is the P=S distances for coordinated  $p_2S_2$  and  $pOp_2S_3$  ligands (2.009–2.018 Å for  $[PdCl_2(p_2S_2)]$  [14],



 $R_2$  = Electron-withdrawing group

Scheme 2. Oxidative addition driven mechanism.



R<sub>1</sub> = Alkyl group

R<sub>2</sub> = Electron-withdrawing group

Scheme 3. Radical generation mechanism.

1.984–2.005 Å for  $[Pd(p_2S_2)_2](BF_4)_2$  [5b] and 2.005–2.011 Å for  $[Pd_3Cl_6(pp_3S_3)_2]$  [15]) are definitely elongated compared with those in the free phosphine sulfide, e.g.  $pp_3S_4$  (1.957–1.958 Å) [16], while such a difference in bond distances is not clearly observed for phosphine oxides (1.449–1.518 Å for the bound P=O in **6** and 1.473–1.487 Å for the pendant P=O in  $[Pd(4-ClC_6H_4S)(pp_3-O)]^+$  and  $[Pd(4-ClC_6H_4S)_2(pp_3O_2)]$  [17]). The present comparison of the catalytic activities also indicates the efficiency of phosphine sulfides in the case of the Co(I)/Co(III) catalytic cycle. On the other hand, the phosphine oxide  $p_2O_2$  deactivated the Co catalyst, probably due to the poor π accepting ability resulting in destabilization of the Co(I) active species.

Two different reaction mechanisms for the catalytic cycle were proposed recently [4]. One is an oxidative addition driven mechanism (Scheme 2) in which the oxidative addition of a Co(I) species with an alkyl halide gives the alkyl Co(III) intermediate, followed by coordination of an alkene. The alkene is then inserted into the Co-alkyl bond, protonation gives the final reductive coupling product and reduction of the Co(III) species by zinc powder regenerates the active Co(I) species. The other is a radical generation mechanism (Scheme 3) in which electron transfer from a low-valent Co(I) species to an alkyl halide generates an alkyl radical, followed by radical addition to the acrylate, trapping by the Co(II) species to give the Co(III) intermediate. Subsequent protonation gives the final product, and reduction of Co(III), similar to the oxidative addition driven mechanism, regenerates the Co(I) species. It is obvious that the active catalyst is the Co(I) complex, generated by reduction of the Co(II) species with zinc powder, because the coupling product, *n*-butyl-4-methylhexanoate, was stoichiometrically formed by the reaction of the Co(I) complex **7** without zinc powder. Deactivation of complex **4** with the tetradentate  $pp_3$  compared to the bis(p<sub>2</sub>) complex **1** may be attributed to blocking the formation of the alkyl halide adduct and subsequent coordination of an alkene by the robust coordination structure with the tetradentate ligand. On the other hand, the tetradentate phosphine sulfides pp<sub>3</sub>S<sub>2</sub> and pp<sub>3</sub>S<sub>4</sub> do not interfere with the substrate coordination, probably due to partial dissociation of the weakly  $\sigma$ -donating phosphine sulfide groups on Co(III). These results are consistent with an oxidative addition driven mechanism with alkene coordination to the alkyl halide adduct.

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#### Appendix A. Supplementary data

CCDC 923329 and 923330 contain the supplementary crystallographic data for **1** and **2**, respectively. These 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 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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