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Sulfur transfer reaction from phosphine sulfides to phosphines assisted by metal ions

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The sulfur transfer reaction from phosphine sulfides to various phosphines in the presence of metal ion was studied; in the presence of Cu(I), a sulfur transfer reaction from $dppmS_2$ (bis(diphenylphosphino)methane disulfide) to dppm (bis(diphenylphosphino)methane) or to dppa (bis(diphenylphosphino)amine) occurs and the product $[Cu(dppmS)_2]^+$ (**1**) and $[Cu(dppmS)(dppaS)]^+$ (**2**) was obtained quantitatively. In the presence of Zn(II), sulfur transfer to various phosphines can be carried out catalytically. The reaction mechanism has been proposed from the difference in the reactivity of diphosphines and metal ions.

1. Introduction

Over the past several decades, diphosphine disulfide ligands (Scheme 1, above), which can be considered to be inorganic analogues of β-diketonate, have been studied extensively in the coordination chemistry of both main group and transition metals [1]. The widespread interest in their complexes arises from a number of potential use, *e.g.*, as lanthanide shift reagents [2], in metal extraction processes [3], or as sulfur source for the production of nano-scale semiconducting metal sulfides [4]. In addition, since phosphine sulfides containing pentavalent phosphorus atoms are more stable toward oxidation than trivalent phosphine derivatives and sulfur atoms can function as soft donors like phosphorus ones, phosphine sulfides are useful as the alternatives of phosphine ligands in order to form stable functional materials. Reigle et al. and our group have reported the luminescence of several complexes with phosphine sulfides [5,6].

Though the phosphine sulfide group is not a strong σ-donor, the unoccupied π^* orbital is positioned in a moderately low energy-level and thus can effectively accept electrons to stabilize metals in the low oxidation state, *e.g.*, Pd(0). Aizawa et al. reported catalytic activity of Pd(0) complexes bearing phosphine sulfides for some coupling reactions [7]. In their work, it was also shown that Pd(0) promotes chalcogen atom replacement of phosphine chalcogenides ($R_3P{=}X$, X = O, S, and Se). As for similar chalcogen transfer reactions, it has been reported that phosphine telluride is decomposed into the corresponding phosphine and elemental tellurium in the presence of Lewis acid and reversible chalcogen transfer from phosphine telluride or selenide to free phosphines occurs [8]. In addition, sulfur transfer reactions from thiophosphates or metal sulfides also have been reported [9].

Previously, it has been reported that the mixed-ligand dinuclear Cu(I) complex, $[Cu_2(phen)_2(dppm)_2](PF_6)_2$, which is bridged by dppm, is readily obtained by treatment of Cu(I) ion and 1,10-phenanthroline (phen) with an equimolar amount of dppm [10]. Therefore we expected that the use of diphosphine disulfide instead of the phen ligands would give the mixed-ligand Cu(I) complexes, such as $[Cu_2(dppmS_2)_2(dppm)_2]^{2+}$. Attempt to prepare such mixed-ligand Cu(I) complexes failed. Instead, we found novel sulfur transfer reactions mediated by copper(I) and zinc(II) complexes. In this report, sulfur transfer reactions from phosphine sulfides to free phosphines (as shown in Scheme 1, below) in the presence of Cu(I) or Zn(II) ion have been described and the mechanism of the reactions have been discussed. Reaction of copper complexes affords quantitative production of phosphine sulfides; on the other hand, the use of Zn(II) ion gives catalytic reactions.

2. Experimental

2.1. General

All reactions were carried out under Ar atmosphere by using Schlenk technique. Diphosphines (Scheme 1, below) and zinc salts

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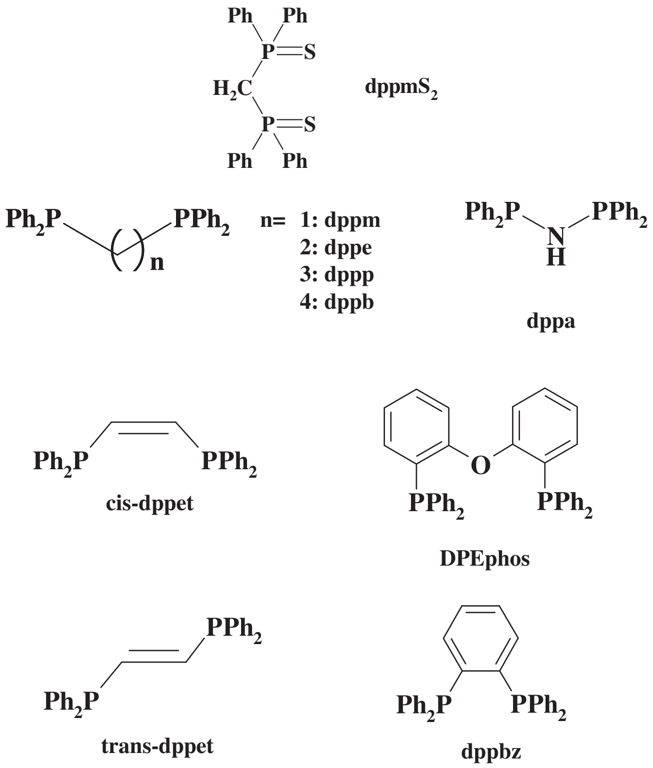


Scheme 1.

were purchased by WAKO Co. Ltd. and Aldirich Co. Ltd., and used without further purification. Bis(diphenylphosphino)methane disulfide (dppmS$_2$) [11] and [Cu(CH$_3$CN)$_4$]PF$_6$ [12] were obtained according to the procedures described. NMR spectra were obtained using a JEOL Λ-400 spectrometer, and chemical shifts are referenced by using tetramethylsilane (^{1}H; as internal) or 85% H$_3$PO$_4$ (^{31}P{^{1}H}; as external).

2.2. Reaction of dppm with dppmS$_2$ in the absence of metal ions

Dppm (76 mg, 0.2 mmol) and dppmS$_2$ (90 mg, 0.2 mmol) was dissolved in acetone (5 ml). After stirring the mixture for a day, the solution was evaporated to dryness under reduced pressure. The ^{31}P NMR spectrum of the obtained white powder dissolved in CDCl$_3$ was measured.

2.3. Stoichiometric reactions in the presence of Cu(I) ion

Each diphosphine (dppm, dppa or dppp: 0.2 mmol) and dppmS$_2$ (90 mg 0.2 mmol) was added to the solution of [Cu(CH$_3$CN)$_4$]PF$_6$ (75 mg, 0.2 mmol) in acetone (5 ml) at room temperature. After stirring the mixture for 1 h, diethyl ether (ca. 15 ml) was added to the solution. The white powder precipitated was collected by filtration. [Cu(dppmS)$_2$]PF$_6$ (140 mg, 67%) was obtained using dppm as starting diphosphine, *Anal.* Calc. for [C$_{50}$H$_{44}$P$_4$S$_2$Cu]PF$_6$: C, 57.66; H, 4.26. Found: C, 57.01; H, 4.57%.

[Cu(dppaS)(dppmS)]PF$_6$: 130 mg was obtained by using dppa. *Anal.* Calc. for [C$_{49}$H$_{43}$NP$_4$S$_2$Cu]PF$_6$·(CH$_3$)$_2$CO: C, 56.75; H, 4.49; N, 1.27. Found: C, 56.39; H, 4.86; N, 1.43%. [Cu(dppmS$_2$)(dppp)]PF$_6$: 168 mg (79%) was obtained by using dppp. *Anal.* Calc. for [C$_{52}$H$_{48}$P$_4$S$_2$Cu]PF$_6$: C, 58.40; H, 4.52. Found: C, 58.67; H, 4.00%.

Recrystallization can be carried out for these complexes in acetone/diethyl ether.

2.4. Catalytic reaction in the presence of Zn(II) ion

2.4.1. Initial screening of the catalytic activity of zinc salt

Dppm (2.0 mmol) and dppmS$_2$ (0.81 g 1.8 mmol) was dissolved in acetone (50 ml), and then zinc salt (2.5 mol%, Zn(CF$_3$SO$_3$)$_2$, Zn(BF$_4$)$_2$, ZnCl$_2$, ZnBr$_2$ or ZnF$_2$) was added to the solution. The mixture was continuously stirring for 24 h at room temperature under dark conditions to prevent oxidation of phosphine moieties by a trace amount of oxygen dissolved in the solution. The solution was evaporated to dryness. The semi-quantitative product yields were estimated from the integrated area of the corresponding ^{31}P NMR signals assigned to dppm(δ −22.1), dppmS(δ 41.2 and −27.8) and dppmS$_2$ (δ 35.8) of the resultant powder dissolved in acetone-d_6.

2.4.2. Quantitative analysis of the reactivity of diphosphine and dppmS$_2$

First, the solutions of the accurately weighed amount of dppmS or dppmS$_2$ (5, 10 and 15 mg) was put into NMR sample tube including a capillary in which a small amount of 85% H$_3$PO$_4$ as standard was encapsulated, and then the relative sensitivity of the two compounds was calculated from the ratio of an integrated areas of the signals assigned to dppmS or dppmS$_2$ to that at δ 0 in ^{31}P NMR spectra. Diphosphine (2.0 mmol) and dppmS$_2$ (0.81 g 1.8 mmol) were dissolved in acetone (50 ml), and then Zn(CF$_3$SO$_3$)$_2$ (65 mg, 10 mol%) was added to the solution. After stirring for 24 h at room temperature under dark conditions, the solution was evaporated to dryness. A weighed amount of the obtained white mixture (ca. 10 mg) was dissolved in acetone-d_6 and then measurement of ^{31}P NMR was carried out. Since no signals were observed except the unreacted reactants and products (*i.e.*, diphosphine monosulfide), the sum of molar amounts of dppmS or dppmS$_2$ estimated from each integrated value should be almost equal to the amount of initial dppmS$_2$. So conversion yield was estimated by the ratio of the amount of dppmS to that of initial dppmS$_2$.

2.5. X-ray measurements

Single crystals suitable for X-ray analysis for 1, 2 and 3 are obtained by slow diffusion of diethyl ether in acetone solution. X-ray crystallographic measurements were made on a Rigaku Saturn 70 CCD area detector with graphite-monochromated Mo Kα radiation. The crystal-to-detector distance was 54.90 mm. The data were collected at a temperature of 150 ± 1 K and processed by using CrystalClear software [13]. Absorption corrections were made by numerical methods. The structures were solved by direct methods (SIR-92 [14] or SIR 2004 [15]) and were refined by full matrix least squares procedures (SHELXL-97 [16]). The non-hydrogen atoms are refined anisotropically and the positions of all hydrogen atoms were fixed at calculated positions. All calculations were performed by using the CrystalStructure crystallographic software package [17].

3. Results and discussion

3.1. Reactions of dppmS$_2$ with several diphosphines in the presence of Cu(I) ion

Treatment of [Cu(I)(CH$_3$CN)$_4$] ion and dppmS$_2$ with equimolar amounts of dppm at room temperature gave an unexpected homoleptic product, [Cu(dppmS)$_2$]PF$_6$ (**1**), in which a sulfur atom of dppmS$_2$ was transferred to a dppm ligand. The transfer reaction occurs almost quantitatively, therefore complex **1** can be isolated in good yield (67%). The ^{31}P{^{1}H} NMR spectrum of complex **1** in

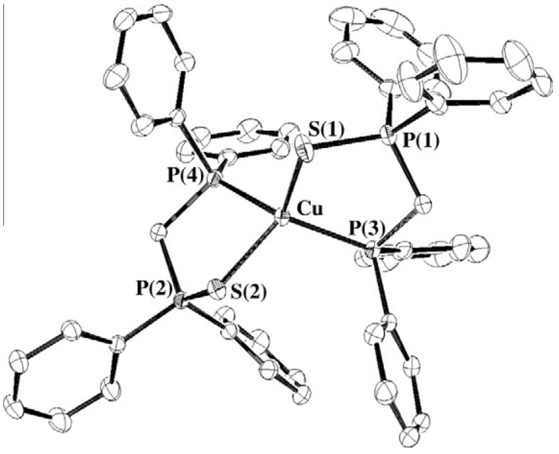


Fig. 1. ORTEP structure of the diphosphine monosulfide complex cation, $[Cu(dppmS)_2]^+$ (**1**).

Table 1
Crystallographic data for **1** and **3**.

	1	3
Formula	$C_{52}H_{47}CuF_6P_5S_2O$	$C_{53}H_{50}CuF_6P_5S_2Cl_2$
Formula weight	1057.42	1154.41
Crystal size	0.35 × 0.23 × 0.20	0.20 × 0.12 × 0.12
T (K)	123	123
Crystal system	triclinic	monoclinic
Space group	P-1 (#2)	Cc (#9)
a (Å)	11.069 (4)	26.137 (2)
b (Å)	11.900 (4)	12.7462 (9)
c (Å)	19.200 (6)	17.707 (2)
α (°)	91.804 (4)	90
β (°)	105.228 (5)	110.792 (1)
γ (°)	91.062 (4)	90
V (Å^3)	2438.1 (13)	5515.0 (8)
Z	2	4
D_{calc} (g/cm^3)	1.440	1.390
μ (cm^{-1})	7.58	7.685
R_1	0.045	0.085
wR_2	0.121	0.248

$CDCl_3$ exhibits two signals at δ 50.0 (dd, J = 60 and 34 Hz) and -10.9(br) (Fig. S1(a)). The signal broadening in the higher field resonance assigned to a trivalent phosphine group may be caused by quadrapolar relaxation of the copper nucleus on direct coordination of phosphine, which has been observed for some Cu(I)–phosphine complexes [18]. The signal lying in the lower field, which is typical of the pentavalent phosphorus in P═S groups, shows doublet of doublet splitting by coupling with two phosphorus atoms; one is on the same ligand and the other is on the ligand coordinating on the opposite site. Treatment of $dppmS_2$ and dppm in the absence of Cu(I) ion gave the solution, the $^{31}P\{^1H\}$ NMR of which showed only two distinct singlet signals assigned to each compound (δ 35.8 and -20.2), whereas no signal assigned to dppmS was observed even after a day. This shows that the sulfur transfer reaction from $dppmS_2$ to dppm does not occur in the absence of the Cu(I) ion.

The structural details of **1** were determined by single crystal X-ray diffraction (Fig. 1). Actually, two dppmS ligands are coordinated to the copper center in a five-membered chelate fashion. The complex of the perchlorate salt was already obtained by a treatment of $[Cu_2(CH_3CN)_4(dppm)_2]^{2+}$ with CS_2 as previously reported [19], however, disorder of one phenyl group was observed in the previous crystal structure analysis. The R factor in our result (R_1 = 4.5%) is considerably smaller than that of the previous report (R_1 = 9.1%). Crystallographic data are shown in Table 1 and selected bond distances and angles are summarized in Table 2. The P–S bond lengths ranging from 1.9769(9) to 1.9862(9) Å show that the bonds almost have double bond character [6,20]. The five-membered chelate angles of P(1)–Cu(1)–S(3) and P(2)–Cu(1)–S(4) are 97.39(3)° and 94.49(2)°, respectively.

The use of dppa, in which diphenylphosphino groups are bridged by an amino group instead of a methylene group, gave a heteroleptic complex, $[Cu(dppmS)(dppaS)]^+$ (**2**), in which sulfur transfer reaction from $dppmS_2$ to dppa also occurs and thus the structure of complex **2** should be similar to that of complex **1**. In the ^{31}P NMR spectrum of the products (*Fig.* S1(b)), a multiplet signal at δ 50.0 and a broad signal at δ -11 are assigned to the dppmS moiety from a comparison with the spectrum of complex **1**. In addition, the spectrum exhibits another couple of a multiplet signal and a broad signal occurring at δ 67.8 and δ 32, respectively. The signals are assigned to dppaS. The multiple splitting of the lower-field signals shows the presence of the coupling to the other three phosphorus atoms in different environments and thus it shows the presence of heteroleptic cation **2** even in solution.

On the other hand, treatment of dppp with $dppmS_2$ and Cu(I) ion gave a heteroleptic complex, $[Cu(dppp)(dppmS_2)]^+$ (**3**), in which transfer of sulfur from $dppmS_2$ to dppp does not occur. Unlike the case of complex **1** and **2**, the $^{31}P\{^1H\}$ NMR spectrum of complex **3** in $CDCl_3$ exhibits a triplet signal at δ 35 (J = 17 Hz) assigned to the pentavalent phosphorus on $dppmS_2$ and a broad signal at δ -16 assigned to trivalent phosphorus directly coordinated to the Cu(I) ion (Fig. S1(c)). The crystal structure obtained by X-ray analysis also shows the formation of the heteroleptic complex. Structural details are shown in Fig. 2 and selected bond

Table 2
Selected bond lengths (Å) and angles (°) and torsion angles (°) for **1**.

Cu–S(1)	2.3813(8)	Cu–S(2)	2.4041(6)
Cu–P(3)	2.2526(7)	Cu–P(4)	2.2618(8)
S(1)–P(1)	1.9769(9)	S(2)–P(2)	1.9862(9)
S(1)–Cu–S(2)	104.26(3)	P(3)–Cu–P(4)	135.35(3)
S(1)–Cu–P(3)	97.39(3)	S(1)–Cu–P(4)	109.68(3)
S(2)–Cu–P(3)	112.82(3)	S(2)–Cu–P(4)	94.49(2)
Cu–S(1)–P(1)	95.32(3)	Cu–S(2)–P(2)	91.49(3)
Cu–P(3)–C(1)	105.70(9)	Cu–P(4)–C(2)	106.0(1)
Cu–S(1)–P(1)–C(1)	−43.2(1)	Cu–S(2)–P(2)–C(2)	−53.33(8)
S(1)–P(1)–C(1)–P(3)	43.7(2)	S(2)–P(2)–C(2)–P(4)	46.2(1)
Cu–P(3)–C(1)–P(1)	−18.2(2)	Cu(1)–P(4)–C(2)–P(2)	−10.7(1)

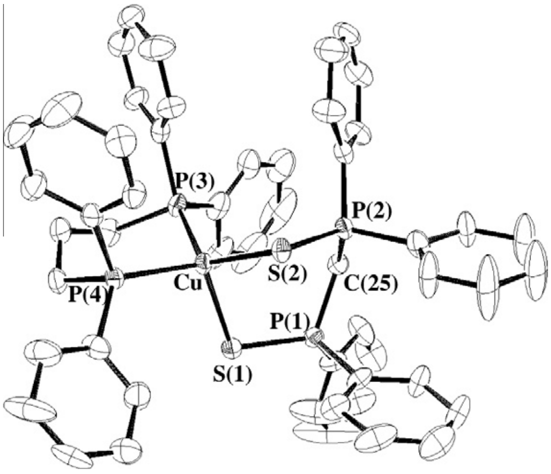


Fig. 2. ORTEP structure of the heteroleptic complex cation, $[Cu(dppmS_2)(dppp)]^+$ (**3**).

Table 3
Selected bond lengths (Å) and angles (°) and torsion angles (°) for **3**.

Cu(1)–S(1)	2.3933(19)	Cu(1)–S(2)	2.3266(18)
Cu(1)–P(3)	2.266(2)	Cu(1)–P(4)	2.248(2)
S(1)–P(1)	1.973(2)	S(2)–P(2)	1.977(3)
S(1)–Cu–S(2)	102.64(6)	P(3)–Cu–P(4)	100.67(8)
S(1)–Cu–P(3)	102.90(7)	S(1)–Cu–P(4)	110.15(8)
S(2)–Cu–P(3)	127.82(8)	S(2)–Cu–P(4)	111.85(8)
Cu–S(1)–P(1)	103.01(10)	Cu–S(2)–P(2)	100.44(9)
Cu–P(3)–C(50)	105.4(3)	Cu–P(4)–C(52)	105.7(3)
Cu–S(1)–P(1)–C(25)	−22.9(3)	Cu–S(2)–P(2)–C(25)	−35.0(2)
S(1)–P(1)–C(25)–P(2)	73.6(4)	S(2)–P(2)–C(25)–P(1)	−35.6(4)

lengths and angles are shown in Table 3. Each dppp and dppmS$_2$ ligand was coordinated to the Cu(I) ion in a chelate fashion. The P-S bond lengths of the complexes range from 1.973(2) to 1.977(3) Å, which are consistent with double bond character of the P=S bonds. However, the bond lengths are slightly longer than those in a free dppmS$_2$ ligand (1.941(1) and 1.948(1) Å) [21], suggesting that the P=S bonds are somewhat weakened. The six-membered chelate angles of P(1)–Cu(1)–P(2) and S(1)–Cu(1)–S(2) are 102.64(6)° and 100.67(8)°, respectively. The reaction of dppe or dppbz instead of dppp gave similar results; *i.e.*, the sulfur transfer reaction does not occur (Fig. S2).

Sulfur transfer reaction of dppmS$_2$ with monophosphine in the presence of Cu(I) ion hardly occurred. ^{31}P NMR spectra of the products after the reaction of 3 h at room temperature shows that little transformation of Ph$_3$P to PPh$_3$P=S is observed and that the utilization of Ph$_2$Ppy leads to no sulfur transfer reaction (Fig. S3).

3.2. Catalytic reaction of dppmS$_2$ with several diphosphines in the presence of Zn(II) ion

The use of Zn(II) ion instead of Cu(I) ion also gave dppmS by sulfur transfer reaction from dppmS$_2$ to dppm. However, the transfer reaction can be carried out catalytically unlike the case of the Cu(I) ion. Even in the presence of a small amount of Zn(CF$_3$SO$_3$)$_2$ (2.5 mol%) at room temperature, dppmS produced by the sulfur transfer reaction was readily obtained by the reaction of dppm and dppmS$_2$ (Fig. S4). After the reaction for 20 h in the presence of 10 mol% Zn(CF$_3$SO$_3$)$_2$, the ^{31}P NMR spectrum of the reaction solution shows that the catalytic reaction has been completed quantitatively (entry 1 in Table 4) and the dppmS was isolated in 58% yield after recrystallization. Using Zn(BF$_4$)$_2$ instead of Zn(CF$_3$SO$_3$)$_2$ also gave dppmS in a comparable yield. However, zinc halides did not act as good catalysts. In the presence of ZnCl$_2$ or ZnBr$_2$, only about a half amount of dppmS was obtained even by reaction for three days as compared with the triflate, and no sulfur transfer reaction occurs in the presence of ZnF$_2$ (Fig. S5).

Table 4
Conversion yields on catalytic sulfur transfer reaction of dppmS$_2$ to various phosphines in the presence of 10 mol% Zn(CF$_3$SO$_3$)$_2$ at room temperature.

Entry	Diphosphine	Conversion yield (%)[a]
1	dppm	96
2	dppe	87
3	dppp	45
4	dppb	16
5	DPEphos	47
6	*cis*-dppet	16
7	*trans*-dppet	0
8	dppbz	0

[a] Estimated yields by integral values in ^{31}P NMR.

In addition, unlike the case of copper(I) ion, the reaction of dppmS$_2$ with various phosphines in the presence of the zinc salts also afforded the corresponding diphosphine monosulfide (Table 1). The conversion yield of dppe was estimated to be 87% (Table 4, entry 2 and Fig. S6). The increase in the length of the carbon chain bridging the two phosphorus atoms leads to a decrease of the yield of monophosphine sulfide (entry 3–4). In the reaction with dppb, the conversion yield decreases to 16%. However, DPEphos, which is bridged by four carbons and one oxygen between the two phosphorus atoms, gave a moderate conversion yield (47%, Table 4, entry 5 and Fig. S6(b)). The use of *cis*-dppet results in further decrease of the yield compared with the case of dppe (16%, entry 6). No transfer reaction to *trans*-dppet or dppbz occurred (Table 4, entry 7, 8 and Fig. S6(c)). Reaction of dppmS$_2$ with two equivalent of Ph$_3$P readily produces Ph$_3$P=S (Fig. S6(d)). However, production of a small amount of dppm shows sulfur transfer reaction from dppmS can occur slightly.

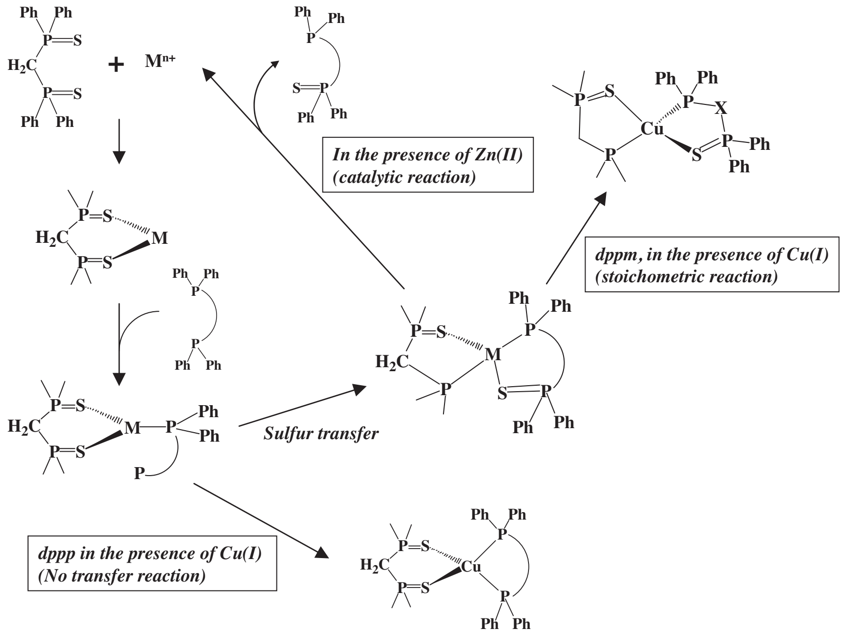
3.3. Mechanism for sulfur transfer reaction of dppmS$_2$ with several diphosphines in the presence of metal ion

As described above, sulfur transfer reaction from the phosphine sulfides, dppmS$_2$, to free phosphines can be carried out in the presence of Cu(I) and Zn(II) ions, whereas no reaction occurs on treatment of the substrates without metal ions. Interestingly, it was found that the reaction mode of the sulfur transfer depends not only on the metal ions used but also on the phosphines. When dppm or dppa is used as phosphine, sulfur transfer reaction always occurs. In the presence of Cu(I), phosphine monosulfide complex **1** and **2** are obtained quantitatively. In the presence of Zn(II), catalytic sulfur transfer reactions have been observed. However, in the cases of dppe, dppp or dppbz, the results depends on the metal ions: the mixed-ligand Cu(I) complexes have been isolated without causing sulfur transfer. In the presence of Zn(II) ion, the transfer reaction from dppmS$_2$ to the diphosphines bridged by methylene groups proceeds catalytically. In the cases of dppbz, no sulfur transfer reactions have been observed in the presence of either Cu(I) or Zn(II) ion.

The trend in the reactivity of the sulfur transfer seems to show that the use of diphosphines which can readily coordinate to a metal center in a chelate fashion prevents the sulfur transfer reaction. The dppm ligand is known to have less ability to make a chelate. On the other hand, dppbz is likely to coordinate only in a chelate fashion.

For the chalcogen transfer reactions from phosphine chalcogenides to phosphines, the associative mechanism involving the attack of the phosphorous atom on the sulfur atom to give a P–S–P intermediate has been proposed by means of theoretical calculations and kinetic measurements (Scheme S1) [9,22]. The mechanism requires an uncoordinated phosphorus atom of a diphosphine ligand in the intermediate of the sulfur-transfer reaction. This seems to be consistent with the trend of the reactivity of the phosphines described above.

The tentative reaction mechanism is shown in Scheme 2. The diphosphine disulfides and diphosphines successively coordinate to the metal ion. At this stage, if Cu(I) and chelating phosphines are used, simple heteroleptic complexes are obtained. If the diphosphines do not seem to form stable chelates, sulfide transfer occurs to give complexes coordinated by two diphosphine monosulfides. In the presence of Cu(I), the phosphine monosulfide complex is thus readily obtained. On the other hand, the harder Zn(II) ion coordinates to the phosphine monosulfide ligands more weakly, thus the free diphosphine monosulfides are released from the complex. It is well known that the coordination bond between zinc and phosphorus atoms has a greater tendency to dissociate in solution [23].



Scheme 2.

4. Conclusion

It has been found that sulfur transfer reactions from a phosphine sulfide (dppmS_2) bridging by a methylene group to various phosphines occur in the presence of metal ions. In the presence of Cu(I), dppmS_2 and diphosphine bridged by a methylene or an amino group (dppm or dppa), underwent quantitative formation of four-coordinate complexes coordinated by two diphosphine monosulfides. Sulfur transfer reaction from dppmS_2 to dppp did not occur in the presence of Cu(I), but a simple heteroleptic complex, $[Cu(dppp)(dppmaS_2)]^+$, was obtained. In the presence of Zn(II) ion, the transfer reaction from dppmS_2 to many diphosphines except dppbz and *trans*-dppet proceeds catalytically. The difference in the reactivity of the diphosphines suggests that the tendency to make chelates is one of the key factors to accept a sulfur atom for diphosphine ligands.

Another important result in this study is the quantitative formation of $[Cu(dppmS)_2]$. This may be due to the fact that the product has stable five-membered chelates as compared to the starting ligands dppmS_2 and dppm, which potentially make less stable seven- and four-membered chelates. The Cu(I) complex is also of importance from the point of view that the complexes can be regarded as an intermediate in the catalytic system mediated by the Zn(II) ion.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.11.049.

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