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Probing Stepwise Reaction of NNP−Ligand Copper(I) Complex with Elemental Sulfur by Using *N*-Heterocyclic Carbene as a Trapper

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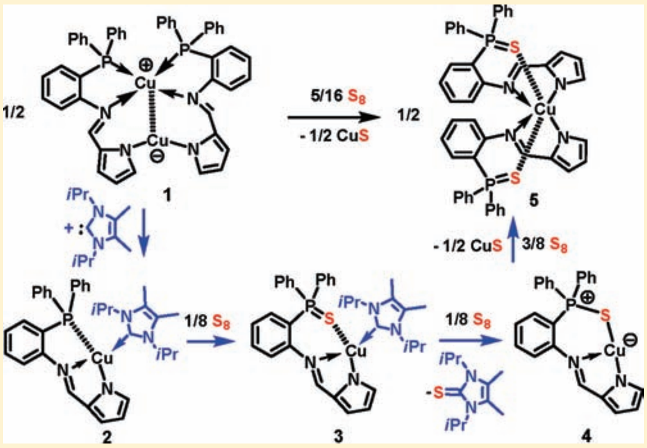
Supporting Information

ABSTRACT: The dinuclear NNP−ligand copper(I) complex [*o*-N=CH(C_4H_3N)−$PPh_2C_6H_4$]$_2$$Cu_2$ (**1**) has been synthesized by the reaction of $(CuMes)_4$ (Mes = 2,4,6-$Me_3C_6H_2$) with *N*-((1*H*-pyrrol-2-yl)-methylene)-2-(diphenylphosphino)benzenamine under an elimination of MesH. Further reaction of **1** with an excess of S_8 produced a mononuclear Cu(II) complex [*o*-N=CH(C_4H_3N)−P(S)$Ph_2C_6H_4$]$_2$Cu (**5**) and CuS. CuS was identified by Raman spectroscopy and **1** and **5** were clearly confirmed by X-ray crystallography. The *N*-heterocyclic carbene was employed to react with **1** to give a mononuclear [*o*-N=CH(C_4H_3N)−$PPh_2C_6H_4$]Cu{C[N(*i*Pr)CMe]$_2$} (**2**). The reactions of **2** were carried out with $^1/_8$, $^2/_8$, and $^5/_8$ equiv of S_8, leading to compounds [*o*-N=CH(C_4H_3N)−P(S)$Ph_2C_6H_4$]-Cu{C[N(*i*Pr)CMe]$_2$} (**3**), [*o*-N=CH(C_4H_3N)−P(S)$Ph_2C_6H_4$]-Cu (**4**), and **5** respectively, in which CuS was generated in the third reaction and S=C[N(*i*Pr)CMe]$_2$ in the latter two reactions. The clean confirmation of **2**−**4** demonstrates a stepwise reaction process of **1** with S_8 to **5** and CuS and the *N*-heterocyclic carbene acts well as a trapping agent.



INTRODUCTION

Reactions of copper(I) complexes with elemental sulfur have been intensively investigated in recent years.[1] This is mainly in focus on synthetic and structural modeling studies of the active sites of the naturally existed copper thiolate- or sulfide-containing biological enzyme systems.[2] Moreover, these reactions exhibit an extensive chemistry with respect to the rich copper−sulfur interactions and result in a number of novel copper sulfide complexes.[1,3] It has been shown that the naked Cu(I) ion, which is paired by weakly coordinating anions (WCAs), reacts with S_8, giving complexes Cu(η^2-S_8)$_2$(AsF_6), [Cu(1,5,9-η^3-S_{12})(η^1-S_8)]-[Al(OR^F)$_4$], and [Cu(1,5,9-η^3-S_{12})(CH_2Cl_2)][Al(OR^F)$_4$] (R^F = C(CH_3)(CF_3)$_2$) in which the metal is still in the oxidation state of +1.[4] On the basis of the stabilization by organic *N*-chelate ligands, the Cu(I) complexes react with S_8, generating Cu(II) complexes [(TMPA)$_2$$Cu_2$($\mu$-1,2-$S_2$)](AN)$_2$ (TMPA = tris[(2-pyridyl)-methyl]amine, AN = ClO_4, or PF_6),[5] [(TMEDA)$_2$$Cu_2$($\mu$-1,2-$S_2$)$_2$](OTF)$_2$ (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, OTF = O_3SCF_3),[6] [(Me_2NPY2)$_2$$Cu_2$($\mu$-$\eta^2$:$\eta^2$-$S_2$)]-[B($C_6F_5$)$_4$]$_2$·2$CH_2Cl_2$ (Me_2NPY2 = *N*,*N*-bis-{2-[2-(*N*′,*N*′-4-dimethylamino)pyridyl]ethyl}methylamine),[7] (HL^{iMe2})$_2$-Cu_2(μ-η^2:η^2-S_2) (HL^{iMe2} = *N*-[2-(2,6-dimethylphenylamino)-benzylidene]-2,6-dimethylaniline),[8] and Cu(II)Cu(III) complexes [L_3Cu_3(μ_3-S)$_2$]X_3 (L = TMEDA, X = SbF_6; L = TMCHD, X = PF_6, TMCHD = *N*,*N*,*N*′,*N*′-tetramethyl-*trans*-1*R*,2*R*-diaminocyclohexane).[9] The *N*-ligands subtly tunable whether in steric hindrance, charge state, or in chelate mode have a great influence on the formation of the different copper sulfides although some of these compounds are produced depending on the reaction conditions.[8b]

It has also been demonstrated by Karlin,[7] Tolman,[8b] and coworkers that the Cu_2(μ-η^2:η^2-S_2) core complexes can occur further by a sulfur atom-transfer reaction from the copper sulfur moiety either to the external substrates or to the intramolecular ligand and the metal is reduced back to the original oxidation state of +1. In the case of PPh_3 as the substrate, S=PPh_3 was formed and detected dissociating from the Cu(I) center. When excessively used, PPh_3 can further coordinatively stabilize the Cu(I) species produced during the reaction.[7,8b] Probably the PPh_3-stabilized Cu(I) compound could react again with S_8 and recover the Cu_2(μ-η^2:η^2-S_2) core complexes. All of these actually show an interesting copper−sulfur−phosphine interaction chemistry, which, however, is studied in a less extent.[3b,7,8b,11] Moreover, because of the formation of the discrete Cu(I) species and S=PPh_3, it seems not facile to draw a picture of such interaction. We now report on the preparation of an NNP-type ligand Cu(I) complex and the further investigation of its reaction

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with S_8. With respect to the NNP ligand character that has an intramolecular phosphine group linkage at the *N*,*N*-chelate, we reason that this reaction could hint the interesting copper—sulfur—phosphine reaction. The NNP ligand, *N*-((1*H*-pyrrol-2-yl)methylene)-2-(diphenylphosphino)benzenamine has recently been employed for synthesizing the Ni, Pd,[12] Y,[13] Cr, and Bi[14] compounds, and, however, it has not been utilized so far for the copper complexes. By this ligand, we prepared a dinuclear copper(I) complex $[o\text{-N=CH}(C_4H_3N){-}PPh_2C_6H_4]_2Cu_2$ (**1**). The reaction of **1** with an excess of the S_8, however, afforded a mononuclear copper(II) compound $[o\text{-N=CH}(C_4H_3N){-}P(S)Ph_2C_6H_4]_2Cu$ (**5**), in which an insoluble CuS was concomitantly produced. This result compares significantly different from those generated by the reactions of the *N*-chelate copper(I) complexes with S_8.[5−8] Herein, we present this result and further report on the use of the *N*-heterocyclic carbene as a trapping agent for detecting the reaction process.

EXPERIMENTAL SECTION

Materials and Methods. All syntheses and manipulations were carried out on a dual-manifold Schlenk line or in an argon-filled MBraun glovebox (typically oxygen and moisture were controlled at less than 1.2 ppm). The organic solvents including toluene, *n*-hexane, tetrahydrofuran, and diethyl ether were predried over fine sodium wires for more than one week and then subjected to reflux with sodium/potassium benzophenone under nitrogen atmosphere prior to use. CH_2Cl_2 and $CHCl_3$ were refluxed with CaH_2 at least for 3 d before use. Benzene-d_6, toluene-d_8, and THF-d_8 were degassed and dried over sodium/potassium alloy, and $CDCl_3$ and CD_2Cl_2 were similarly treated and dried over CaH_2. ^{1}H (400 MHz), ^{13}C (100 MHz), and ^{31}P NMR (160 MHz) NMR spectra were recorded on a Bruker Avance II 400 MHz spectrometer. Melting points were measured in sealed glass tubes using Büchi-540 instrument. EI mass spectra were measured on Esquire HCT spectrometer. Fluorescence data were obtained on a Hitachi F-7000 spectrometer. Magnetic measurements were carried out with the Quantum Design SQUID MPMS-XL instrument, and EPR ones on the Bruker ER200D-SRC spectrometer. Elemental analysis was performed on a Thermo Quest Italia SPA EA 1110 instrument. Commercially available reagents were purchased from Aldrich, Acros, Alfa-Assar, or Lvyin Chemical Co. and used as received. $o\text{-N=CH}(C_4H_3NH){-}PPh_2C_6H_4$,[12] $(CuMes)_4$ (Mes = 2,4,6-$Me_3C_6H_2$),[15] and $C[N(i\text{Pr})CMe]_2$[16] were prepared according to published procedures.

$[o\text{-N=CH}(C_4H_3N){-}PPh_2C_6H_4]_2Cu_2$ (1). At room temperature a solution of $(CuMes)_4$ (0.65 g, 0.75 mmol) in THF (10 mL) was added to a solution of $o\text{-N=CH}(C_4H_3NH){-}PPh_2C_6H_4$ (1.06 g, 3.0 mmol) in THF (40 mL). The mixture was stirred for 4 h, and a red solution was formed. All volatiles were removed under vacuum followed by washing with *n*-hexane (2 mL) to give a red crystalline solid of **1** (1.18 g, 95%). Mp: 258 °C. ^{1}H NMR (400 MHz, C_6D_6, 298 K, ppm): δ = 6.51−6.54 (m, 2 H), 6.69−6.77 (m, 4 H) (NC_4H_3), 6.82−6.89 (m, 8 H), 6.92−6.97 (m, 8 H), 7.00−7.10 (m, 10 H), 7.15 (m, 2 H) (C_6H_4, C_6H_5), 7.96 (s, 2 H, N=C*H*). ^{13}C NMR (100 MHz, C_6D_6, 298 K, ppm): δ = 113.39, 120.36, 122.94, 123.81, 125.44, 128.40, 128.45, 128.49, 129.10, 131.45, 133.15, 133.30, 133.42, 133.50, 133.59, 139.13, 140.39, 155.58, 156.87, 156.96, 157.05. ^{31}P NMR (160 MHz, C_6D_6, 298 K, ppm): δ = −16.87. ESI-MS: *m*/*z* (%) 835.5 (5, $[M + H]^+$), 355.2 (100, $[L + H]^+$) (L = $o\text{-N=CH}(C_4H_3NH){-}PPh_2C_6H_4$). Anal. Calcd for $C_{46}H_{38}Cu_2N_4P_2$ (M_r = 834.12): C, 66.10; H, 4.58; N, 6.70. Found: C, 65.92; H, 4.46; N, 6.78. X-ray quality single crystals of **1**·THF were obtained by recrystallization in THF/*n*-hexane (1:1) solvent mixture at −30 °C.

$[o\text{-N=CH}(C_4H_3N){-}PPh_2C_6H_4]Cu\{C[N(i\text{Pr})CMe]_2\}$ (2). At room temperature, a solution of $C[N(i\text{Pr})CMe]_2$ (0.36 g, 2.0 mmol) in toluene (10 mL) was added to a solution of **1** (0.83 g, 1.0 mmol) in toluene (15 mL). The mixture was stirred for 2 h. After workup, toluene was removed under vacuum and an orange-yellow crystalline solid of **2** was obtained (1.15 g, 96%). Mp: 176 °C. ^{1}H NMR (400 MHz, C_6D_6, 298 K, ppm): δ = 1.29 (d, 12 H, $^{3}J_{HH}$ = 6.8 Hz, CH*Me*$_2$), 1.55 (s, 6 H, C*Me*), 4.64 (sept, 2 H, $^{3}J_{HH}$ = 6.8 Hz, C*H*Me$_2$), 6.83−6.88 (m, 2 H), 6.94−6.98 (m, 1 H) (NC_4H_3), 6.99−7.04 (m, 8 H), 7.17−7.23 (m, 1 H), 7.36−7.42 (m, 4 H), 7.74 (s, br, 1 H) (C_6H_4, C_6H_5), 7.93 (s, 1 H, N=C*H*); ^{13}C NMR (100 MHz, C_6D_6, 298 K, ppm): δ = 9.09 (CH*Me*$_2$), 22.90 (C*Me*), 51.56 (CHMe$_2$), 111.89, 117.62, 119.08, 122.79, 123.05, 128.22, 128.26, 128.29, 130.12, 132.68, 133.02, 133.06, 133.92, 134.11, 136.76, 137.74, 137.68, 141.07, 154.50, 154.52, 156.70, 156.90 (C_6H_4, C_6H_5, NC_4H_3, CMe), 179.88 (N=*C*), 180.18 (Cu−C_{carbene}); ^{31}P NMR (160 MHz, C_6D_6, 298 K, ppm): δ = −20.75. ESI-MS: *m*/*z* (%) 598.2 (6, $[M + H]^+$), 355.2 (16, $[L + H]^+$), 181.1 (100, $[C[N(i\text{Pr})CMe]_2 + H]^+$) (L = $o\text{-N=CH}(C_4H_3NH){-}PPh_2C_6H_4$). Anal. Calcd for $C_{34}H_{38}CuN_4P$ (M_r = 597.19): C, 68.38; H, 6.41; N, 9.38. Found: C, 68.52; H, 6.56; N, 9.28. X-ray quality single crystals of **2** were obtained by recrystallization in toluene at −30 °C.

$[o\text{-N=CH}(C_4H_3N){-}P(S)Ph_2C_6H_4]Cu\{C[N(i\text{Pr})CMe]_2\}$ (3). At −20 °C, a solution of S_8 (2.5 mL, 0.0625 mmol, 0.025 M THF solution) was added to a solution of **2** (0.30 g, 0.50 mmol) in toluene (40 mL). The mixture was warmed to room temperature and stirred for 12 h. An orange-red solution was formed. All solvents were removed under vacuum and the residue was washed with cold *n*-hexane (5 mL) to give an orange-yellow solid of **3** (0.27 g, 90%). Mp: 159 °C. ^{1}H NMR (400 MHz, C_6D_6, 298 K, ppm): δ = 1.32 (d, 12 H, $^{3}J_{HH}$ = 6.8 Hz, CH*Me*$_2$), 1.56 (s, 6 H, C*Me*), 4.62 (sept, 2 H, $^{3}J_{HH}$ = 6.8 Hz, C*H*Me$_2$), 6.72−6.83 (m, 3 H, NC_4H_3), 6.91−7.00 (m, 7 H), 7.11−7.19 (m, 1 H), 7.45−7.65 (br, 3 H), 7.80−7.94 (m, 4 H) (C_6H_4, C_6H_5, N=C*H*); ^{13}C NMR (100 MHz, C_6D_6, 298 K, ppm): δ = 9.17 (CH*Me*$_2$), 23.16 (C*Me*), 51.52 (CHMe$_2$), 111.37, 118.00, 121.49, 121.68, 122.28, 123.04, 130.58, 130.59, 132.49, 132.60, 132.88, 133.26, 133.55, 133.61, 134.02, 134.09, 136.55, 139.80, 154.53, 158.12 (C_6H_4, C_6H_5, NC_4H_3, CMe), 176.93 (N=*C*), 178.66 (Cu−C_{carbene}); ^{31}P NMR (160 MHz, C_6D_6, 298 K, ppm): δ = 38.19. ESI-MS: *m*/*z* (%) 630.4 (2, $[M + H]^+$), 387.2 (100, $[L(S) + H]^+$) (L(S) = $o\text{-N=CH}(C_4H_3NH){-}P(S)Ph_2C_6H_4$). Anal. Calcd for $C_{34}H_{38}CuN_4PS$ (M_r = 629.25): C, 64.89; H, 6.09; N, 8.90. Found: C, 64.84; H, 6.22; N, 8.75. X-ray quality single crystals of **3** were obtained by recrystallization in toluene at room temperature.

$[o\text{-N=CH}(C_4H_3N){-}P(S)Ph_2C_6H_4]Cu$ (4). At −20 °C, a solution of S_8 (5 mL, 0.125 mmol, 0.025 M of THF solution) was added to a solution of **2** (0.30 g, 0.50 mmol) in toluene (40 mL). The mixture was warmed to room temperature and stirred for 12 h. A deep-red solution was formed. All solvents were removed under vacuum and the residue was extracted with toluene (20 mL). The extract was concentrated (ca. 10 mL) and to it *n*-hexane (10 mL) was layered on the top. After keeping at −20 °C for 3 d, red-black crystals of **4** were yielded (0.15 g, 64%). The mother lique was concentrated (ca. 3 mL) and kept at −20 °C for one week, colorless crystals were produced and identified as $S{=}C[N(i\text{Pr})CMe]_2$. All the analytic data is for **4**. Mp: 223 °C. ^{1}H NMR (400 MHz, C_6D_6, 298 K, ppm): δ = 6.64−6.69 (m, 2 H), 6.82−6.90 (m, 1 H) (NC_4H_3), 6.91−6.99 (m, 7 H), 7.04 (dd, 1 H), 7.06−7.14 q(m, 1 H), 7.48 (s, br, 1 H), 7.59 (q, br, 4 H) (C_6H_4, C_6H_5,), 8.01 (s, br, 1 H, N=C*H*); ^{13}C NMR (100 MHz, C_6D_6, 298 K, ppm): δ = 114.59, 117.78, 117.84, 118.34, 119.26, 121.74, 121.77, 121.91, 128.49, 128.62, 130.66, 131.53, 131.85, 131.87, 132.26, 132.36, 134.07, 134.18, 134.23, 141.08, 141.58, 150.12, 151.79 (C_6H_4, C_6H_5, NC_4H_3), 182.6 (N=*C*); ^{31}P NMR (160 MHz, C_6D_6, 298 K, ppm): δ = 30.22. ESI-MS: *m*/*z* (%) 449.3 (10, $[M + H]^+$), 387.2 (100, $[L(S) + H]^+$) (L(S) = $o\text{-N=CH}(C_4H_3NH){-}P(S)Ph_2C_6H_4$). Anal. Calcd for $C_{23}H_{18}CuN_2PS$ (M_r = 448.99): C, 61.53; H, 4.04; N, 6.24. Found: C, 61.91; H, 4.30; N, 6.23. Note: When this reaction was carried out under similar conditions but

Table 1. Crystal Data and Structure Refinement for 1−5[a]

	1·THF	2	3	4·5	5·*n*-hexane
formula	$C_{50}H_{44}Cu_2N_4OP_2$	$C_{34}H_{38}CuN_4P$	$C_{34}H_{38}CuN_4PS$	$C_{69}H_{54}Cu_2N_6P_3S_3$	$C_{52}H_{50}CuN_4P_2S_2$
fw	905.91	597.19	629.25	1283.35	920.56
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic	orthorhombic
space group	*P*2(1)/*c*	*Pbca*	*P*2(1)	*P*2(1)/*c*	*Pbca*
a/Å	12.2441(3)	15.9968(7)	11.1838(8)	13.0045(10)	14.2716(6)
b/Å	13.6298(4)	17.4056(7)	8.8057(8)	21.9160(14)	17.6685(9)
c/Å	13.6298(4)	22.3356(10)	16.4636	21.3005(18)	35.8182(16)
α/deg					
β/deg	96.909(2)		97.681(7)	98.395(7)	
γ/deg					
V/Å^3	4640.2(2)	6219.0(5)	1606.8(2)	6005.7(8)	9031.8(7)
Z	4	8	2	4	8
ρ_{calcd}/g·cm^{-3}	1.297	1.276	1.301	1.419	1.354
μ/mm^{-1}	1.025	0.783	0.823	0.941	0.688
F(000)	1872	2512	660	2644	3848
cryst size/mm^3	0.40 × 0.40 × 0.10	0.25 × 0.20 × 0.18	0.10 × 0.06 × 0.04	0.20 × 0.15 × 0.08	0.40 × 0.40 × 0.20
θ range/deg	2.30−26.00	2.34−26.00	2.90−26.00	2.71−26.00	2.16−26.00
index ranges	$-15 \le h \le 15$	$-19 \le h \le 19$	$-10 \le h \le 13$	$-16 \le h \le 15$	$-17 \le h \le 17$
	$-16 \le k \le 16$	$-19 \le k \le 21$	$-10 \le k \le 10$	$-24 \le k \le 27$	$-21 \le k \le 21$
	$-34 \le l \le 34$	$-23 \le l \le 27$	$-20 \le l \le 20$	$-23 \le l \le 26$	$-44 \le l \le 43$
collected data	47 999	47 761	14 042	54 732	91 351
unique data	9088 (R_{int} = 0.0373)	6101 (R_{int} = 0.1325)	5908 (R_{int} = 0.0753)	11780 (R_{int} = 0.1453)	8866 (R_{int} = 0.1094)
completeness to θ	99.7%	100.0%	99.8%	99.9%	99.9%
data/restraints/params	9088/20/567	6101/0/367	5908/5/376	15 358/0/748	8866/10/545
GOF on F^2	0.968	0.802	0.687	0.788	1.177
final R indices [$I > 2\sigma(I)$]	R_1 = 0.0418	R_1 = 0.0472	R_1 = 0.0451	R_1= 0.0568	R_1 = 0.0933
	wR_2 = 0.1187	wR_2 = 0.0612	wR_2 = 0.0389	wR_2 = 0.0821	wR_2 = 0.2131
R indices (all data)	R_1 = 0.0604	R_1 = 0.1234	R_1 = 0.1029	R_1= 0 0.1643	R_1 = 0.1181
	wR_2 = 0.1242	wR_2 = 0.0714	wR_2 = 0.0453	wR_2 = 0 0.0975	wR_2 = 0.2262
largest diff peak/hole (e·Å^{-3})	0.735/−0.309	0.764/−0.466	0.720/−0.406	0.998/−0.624	1.109/−0.712

[a] All data were collected at 173(2) K using Mo K$_\alpha$ (λ = 0.71073 Å) radiation. $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2/\Sigma[w(F_o{}^2)^2]]^2\}^{1/2}$, GOF = $\{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/(N_o - N_p)\}^{1/2}$.

using ca. 2.2/8 equiv of S_8, cocrystals of **4** and **5** was produced during crystallization under similar conditions.

[*o*-N═CH(C_4H_3N)−P(S)$Ph_2C_6H_4$]$_2$Cu (5). *Method A.* At room temperature, an excess of S_8 (16 mg, 0.0625 mmol) was added to a solution of **1** (0.083 g, 0.10 mmol) in toluene (40 mL). The mixture was stirred for 12 h, and a dark-brown solution was formed together with insoluble black solids. The black solids were collected by filtration and washed with THF (20 mL) to remove unreacted S_8. The filtrate was concentrated (ca. 15 mL) and kept at −20 °C. Three days later, dark-brown crystals of **5** were yielded (0.043 g, 50%). Mp: 238 °C. ^{1}H NMR (400 MHz, C_6D_6, 298 K, ppm): δ = 7.70 (br), 8.30 (br); ^{31}P NMR (160 MHz, C_6D_6, 298 K, ppm): no resonances were observed. ESI-MS: *m*/*z* (%) 835.3 (66, [M + H]$^+$), 387.2 (100, [L(S) + H]$^+$) (L(S) = *o*-N═CH(C_4H_3NH)−P(S)$Ph_2C_6H_4$). Anal. Calcd for $C_{46}H_{36}CuN_4P_2S_2$ (M_r = 834.43): C, 66.21; H, 4.35; N, 6.71. Found: C, 66.88; H, 4.41; N, 6.94.

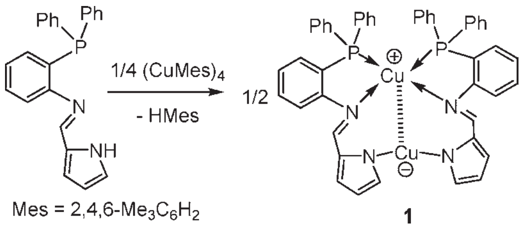
Method B. At −20 °C, an excess of S_8 (0.16 g, 0.625 mmol) was added to a solution of **2** (0.60 g, 1.0 mmol) in toluene (30 mL). The mixture was warmed to room temperature and stirred for 12 h. A brown solution was formed together with insoluble black solids. The black solids were collected and washed with large amount of THF to remove unreacted S_8. Raman spectral measurement indicates the black solids of CuS. The filtrate was concentrated (ca. 10 mL) and to it *n*-hexane (5 mL) was layered on the top again. The solution was kept at −20 °C. One week later, dark-brown crystals of **5** were grown and collected by filtration. The mother liquor was concentrated again (ca. 4 mL) and to it *n*-hexane (5 mL) was layered on the top. After keeping at −20 °C for one week, a second crop of **5** together with colorless crystals of S═C[N(*i*Pr)CMe]$_2$ were obtained. Total yield of **5**, 0.32 g, 76% (based on **2**).

X-ray Crystallographic Analyses of 1−5. The crystallographic data of **1**−**5** were collected on an Oxford Gemini S Ultra system. In all cases, graphite-monochromated Mo−K$_\alpha$ radiation (λ = 0.71073 Å) was used. Absorption corrections were applied using the spherical harmonics program (multiscan type). The structures were solved by direct methods (SHELXS-96)[17] and refined against F^2 using SHELXL-97.[18] In general, the non-hydrogen atoms were located by difference Fourier synthesis and refined anisotropically, and hydrogen atoms were included using the riding model with U_{iso} tied to the U_{iso} of the parent atoms unless otherwise specified. In **1**·THF and **5**·*n*-hexane, the THF and *n*-hexane solvent molecules were both disclosed in disorder and refined in split positions with non-hydrogen atoms in isotropic model. In **3**, one of the *i*Pr groups from the *N*-heterocyclic carbene was similarly found and treated in the same way. A summary of cell parameters, data collection, and structure solution and refinement is given in Table 1.

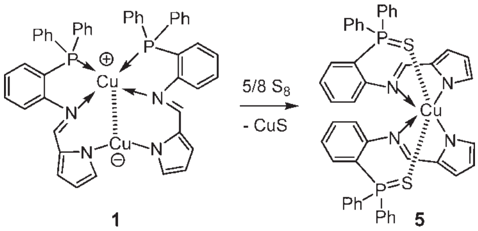
RESULTS AND DISCUSSION

Synthesis and Characterization of a Dinuclear NNP Copper(I) Complex and Its Reaction with Elemental Sulfur.

Scheme 1. Synthesis of 1



Scheme 2. Reaction of 1 with S_8 to 5 and CuS



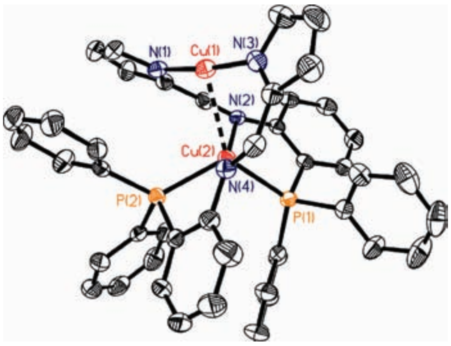


Figure 1. X-ray crystal structure of **1** with thermal ellipsoids drawn at the 50% probability. Selected bond lengths [Å] and angles [°]: Cu(1)−N(1) 1.856(3), Cu(1)−N(3) 1.856(3), Cu(2)−N(2) 2.112(2), Cu(2)−N(4) 2.187(2), Cu(2)−P(1) 2.2506(8), Cu(2)−P(2) 2.2559(8), Cu(1)$\cdots$Cu(2) 2.6399(5); N(1)−Cu(1)−N(3) 173.95(11), N(2)−Cu(2)−N(4) 151.82(9), P(1)−Cu(2)−P(2) 117.58(3).

The reaction of $(CuMes)_4$ (Mes = 2,4,6-$Me_3C_6H_2$) with *o*-N═H(C_4H_3NH)−$PPh_2C_6H_4$ in a molar ratio of 0.25:1 proceeded smoothly in THF at room temperature, and afforded under an elimination of MesH a dinuclear compound [*o*-N═CH(C_4H_3N)−$PPh_2C_6H_4$]$_2$Cu$_2$ (**1**, Scheme 1). **1** was isolated as a red crystalline solid in an almost quantitative yield (95%) by removal of all volatiles and washing with *n*-hexane (2 mL). It is air-sensitive and changes the color to brown when exposed to air whether in the solid state or in solution. However, it is stable in an inert gas atmosphere and also thermally stable as indicated by a clear melting temperature at 258 °C. **1** has a good solubility in chlorohydrocarbons, such as CH_2Cl_3 and $CHCl_3$, and aromatic hydrocarbons such as toluene and benzene as well as in donor solvents like THF and Et_2O. The ^{31}P NMR spectrum of **1** recorded in C_6D_6 shows one resonance at δ −16.87 ppm and this resonance compares a little upfielded from that of the free NNP ligand (δ −12.8 ppm).[12] The ^{1}H NMR spectrum exhibits one resonance at δ 7.96 ppm as a singlet corresponding to the imine N═CH proton, and the resonances at δ 6.51−6.54 and 6.69−6.77 ppm respectively as multiplets assignable to the pyrrol ring protons, whereas the ones at a separated wide range of δ 6.82−7.15 ppm to the phenyl protons due to the combination of the two different types of the aryl groups (C_6H_5 and C_6H_4). The exact structure of **1** was disclosed based on the X-ray single crystal diffraction study.

The crystal structural analysis clearly proves **1** a dinuclear compound (Figure 1), and the two copper centers, however, are located into different coordination environments. The Cu(1) is linearly ligated by the two anionic pyrrolide groups, whereas the Cu(2) tetrahedrally coordinated by the two neutral phosphido and two neutral imido groups. **1** can be actually ascribed as an ion pair with the Cu(1) as the anionic center, whereas the Cu(2) the cationic center. Compound $[(phen)_2Cu]^+[Cu(NPh_2)_2]^-$ (phen = 1,10-phenanthroline) has recently been reported as a common separated ion pair and thought to be predominantly double salt in both polar and less polar solvents.[19] Compound **1**, in comparison, represents one of the examples with the two ionic parts in one molecule[20] and shows little difference in solubility either in polar or in nonpolar organic solvents. The Cu(1)−N(1) and Cu(1)−N(3) bond lengths (1.856(3) Å) are similar to those in the anionic $[Cu(NPh_2)_2]^-$ (1.860(2)−1.879(2) Å),[19] whereas the Cu(2)−N(2) (2.112(2) Å) and Cu(2)−N(4) (2.187(2) Å) as well as the Cu(2)−P(1) (2.2506(8) Å) and Cu(2)−P(2) (2.2559(8) Å) bond distances appear close to those in a cationic $[Cu(1,10\text{-pp-}N_2P_2)]^+$ (Cu−N, 2.173(7) and 2.185(7) Å; Cu−P, 2.251(2) and 2.255(2) Å; 1,10-pp-N_2P_2 = 1,10-bis(diphenylphosphino)-4,7-dimethyl-4,7-diazadecane).[21] It is interesting to find that the Cu(1)$\cdots$Cu(2) separation is 2.6399(5) Å. This distance can be comparable to those in a cluster compound $Cu_{24}O_{24}Si_8R_8$ (R = (2,6-*i*$Pr_2C_6H_3$)N($SiMe_3$), 2.6296(8)−2.7204(8) Å),[22] suggesting a weak Cu(I)$\cdots$Cu(I) $d^{10}\cdots d^{10}$ attractive interaction.[23] Further emission spectra measurement of **1** in the solid state at room temperature shows a peak at 683 nm band, indicating a tentative Cu(I)$\cdots$Cu(I) interaction (Figure 2s of the Supporting Information). This has been commonly discussed in M$\cdots$M interaction-containing group 9 metal complexes.[24]

The reaction of **1** with an excess of S_8 was conducted in toluene at room temperature (Scheme 2). After workup, a black insoluble solid was formed, which was collected and washed with a large amount of THF to remove unreacted S_8. This solid was analyzed by Resonance Raman spectroscopy (Figure 1s of the Supporting Information) and identified as CuS with the characteristic band at 474 nm similar to those reported in references[25] and literature databases.[26] The concentration of the filtrate followed by keeping at −20 °C for three days afforded brown crystals of [*o*-N═CH(C_4H_3N)−P(S)$Ph_2C_6H_4$]$_2$Cu (**5**) in moderate yield (50%). The ^{1}H NMR spectrum showed broad resonances centered at δ 7.70 and 8.30 ppm respectively, whereas no resonances were able to be observed in the ^{31}P NMR spectrum. This implies a paramagnetic ground state of **5** having the Cu(II) center. Further SQUID and EPR measurements prove this property of **5** (Figures 4s and 6s of the Supporting Information). The exact composition and structure of **5** were determined by X-ray single crystal diffraction.

The crystal structure of **5** shown in Figure 2 unambiguously confirmed a formation of a mononuclear Cu(II) compound incorporating two phosphine sulfide NNP(S) ligands. The copper center is four-coordinated by two pyrrolide and two imido groups with the Cu−$N_{pyrrolide}$ bond lengths (Cu(1)−N(1), 1.953(4) and Cu(1)−N(3), 1.965(5) Å) relatively shorter than

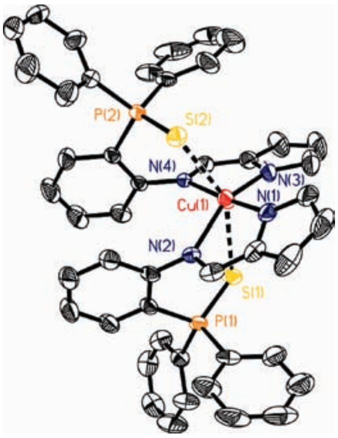


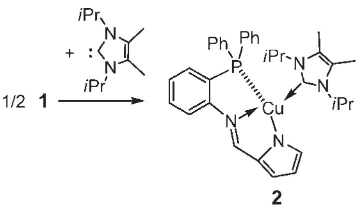
Figure 2. X-ray crystal structure of **5** with thermal ellipsoids drawn at the 50% probability. Selected bond lengths [Å] and angles [°]: Cu(1)−N(1) 1.953(4), Cu(1)−N(2) 2.077(4), Cu(1)−N(3) 1.965(5), Cu(1)−N(4) 2.039(4), P(1)−S(1) 1.9557(18), P(2)−S(2) 1.9642(18), Cu(1)···S(1) 3.310, Cu(1)···S(2) 2.836; N(1)−Cu(1)−N(2) 81.55(18), N(1)−Cu(1)−N(3) 98.6(2), N(2)−Cu(1)−N(4) 100.60(16), N(3)−Cu(1)−N(4) 81.89(18).

those of the Cu−N_{imido} bond (Cu(1)−N(2), 2.077(4) and Cu(1)−N(4), 2.039(4) Å). The Cu(1)(N(1)N(2)N(3)N(4) least-squares plane is calculated by Δ = 0.2475 Å, and is a little deviated from the ideal plane. This indicates a distortedly square-planar geometry around the Cu(II) center fitting to an orbital hybridization of the dsp^2-type. The different Cu···S separations are observed by 3.310 (S(1)···Cu(1)) and 2.836 Å (S(2)···Cu(1)), respectively, so it is with the different P−S bond lengths ((P(1)−S(1), 1.9557(18) and (P(2)−S(2), 1.9642(18) Å), which are of double bond character, however, are a little longer than those found in free S═PPh_3 (1.950(3) Å)[27] and *o*-NH(Ph)NH−P(S)$Ph_2C_6H_4$ (1.9477(7) Å).[28] This suggests the two unbalanced weak Cu···S interactions, which may give rise to a little elongation of the P−S bond lengths and the further deviated square planar geometry over the Cu(II) center.

Obviously, the conversion of **1** with S_8 to **5** and CuS may imply a multiple reaction process including the degradation of **1** by a dinuclear to a mononuclear form, sulfur abstraction by the phosphine, and the oxidation state change of the copper center accompanying with the NNP(S) ligand redistribution. This result appears different when compared to those by the reactions of the *N*-chelate Cu(I) complexes with S_8 especially in the formation of the Cu(II) or Cu(II)Cu(III) sulfide complexes with the S_n^{2-} (n = 1 or 2) linkage as well as of the sulfur-to-ligand transfer compounds $Cu^I_4(SR)_4$ (SR = SCH[(CMe)(NAr)]$_2$, Ar = 2,6-R′$_2C_6H_3$, R′ = Me or Et),[5−9] and also different from that by a disproportionation partially occurred during the reaction of [(tmeda)Cu^I(CH_3CN)](O_3SCF_3) (tmeda = $Me_2NCH_2CH_2NMe_2$) and S_8 to [(tmeda)$_2Cu^{II}_2$(μ-1,2-S_2)$_2$](O_3SCF_3)$_2$ and metallic copper,[6] although the sulfur abstraction by phosphine compounds is well-known.[3b,27,28] This prompts us a further investigation on this reaction detail.

Synthesis and Characterization of a Mononuclear NNP *N*-Heterocyclic Carbene Copper(I) Complex and Its Stepwise Reactions with Elemental Sulfur. More recently, we have shown a reaction of *N*-heterocyclic carbene, 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene with a $L_2Cu_8Br_6$ cluster compound, smoothly giving a mononuclear LCu{C[N(*i*Pr)CMe]$_2$} (L = 2,6-(RN═CH)$_2$-4-*t*BuC_6H_2, R = 2,6-*i*$Pr_2C_6H_3$), which can be used as a good precursor for an interesting conjugated addition to the organic azide molecule.[29] Following this similar way, we successfully prepared a mononuclear NNP *N*-heterocyclic carbene Cu(I) compound [*o*-N═CH(C_4H_3N)−PPh_2-C_6H_4]Cu{C[N(*i*Pr)CMe]$_2$} (**2**, Scheme 3).

Scheme 3. *N*-Heterocyclic Carbene Degradation of 1 to 2



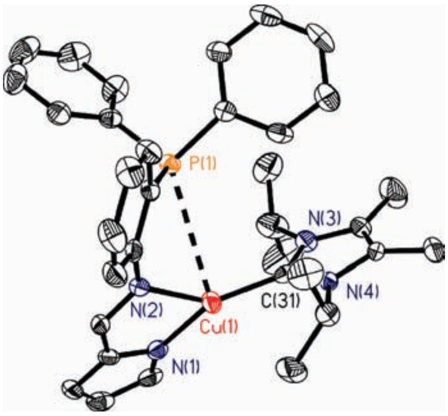
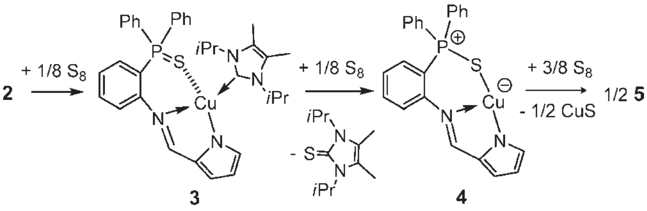


Figure 3. X-ray crystal structure of **2** with thermal ellipsoids drawn at the 50% probability. Selected bond lengths [Å] and angles [°]: Cu(1)−N(1) 1.940(2), Cu(1)−N(2) 2.211(2), Cu(1)−C(31) 1.882(3), Cu(1)···P(1) 3.500; N(1)−Cu(1)−N(2) 80.96(10), C(31)−Cu(1)−N(1) 151.09(12), C(31)−Cu(1)−N(2) 127.62(11).

The reaction of **1** with two equiv of C[N(*i*Pr)CMe]$_2$ was accomplished in toluene at room temperature, affording **2** in almost quantitative yield (96%). **2** has been characterized by multinuclear NMR (^{1}H, ^{13}C, and ^{31}P) spectroscopy, X-ray crystallography, and elemental analysis. As shown in Figure 3, the Cu center is three-coordinated by the NNP ligand and C[N(*i*Pr)CMe]$_2$ in an ideal trigonal-planar geometry ($\Delta_{Cu(1)C(31)N(1)N(2)}$ = 0.0207 Å). The Cu(1)−N(1) bond length (1.940(2) Å) is shorter than that of the Cu(1)−N(2) (2.211(2) Å). This difference has also been observed in **5** mostly on account of a bonding of the metal to the anionic *N*-pyrrolide donor for the former while to the neutral *N*-imido one for the latter. The Cu(1)−C(31) bond distance (1.882(3) Å) locates in those for Cu(I) *N*-heterocyclic carbene compounds (1.862(10)−1.911(4) Å).[11d,29] The separation of the Cu(1)···P(1) is 3.500 Å within van der Waals distance and is much longer than those in **1**, indicating of a very weak donor−acceptor interaction. In the ^{31}P NMR spectrum the phosphorus resonance is observed at δ −20.75 ppm.

The reaction of **2** was first carried out with $^1/_8$ equiv of S_8 in toluene from −20 °C to room temperature, producing a phosphine sulfide compound [*o*-N═CH(C_4H_3N)−P(S)$Ph_2C_6H_4$]Cu{C[N(*i*Pr)CMe]$_2$} (**3**) in high yield (90%). Under similar reaction conditions but using $^2/_8$ equiv of S_8 instead compound [*o*-N═CH(C_4H_3N)−P(S)$Ph_2C_6H_4$]Cu{C[N(*i*Pr)CMe]$_2$} (**4**)

Scheme 4. Stepwise Reaction of 2 with S_8 to 3−5



was afforded (70%) and in the meantime S═C[N(*i*Pr)CMe]$_2$[30] was isolated too. And then we tried the reaction of **2** with a little excess ($^5/_8$ equiv) of S_8 and **5** (76%), CuS, and S═C[N(*i*Pr)CMe]$_2$ were all able to be isolated. This result seems almost the same as that from the reaction of **1** and an excess of S_8 except for the formation of S═C[N(*i*Pr)CMe]$_2$. Obviously, under the control of the S_8 amount, the generation of **5** from **2** indicates a stepwise reaction process (Scheme 4).

3 and **4** both have been definitely confirmed by multinuclear NMR (^{1}H, ^{13}C, and ^{31}P) spectroscopy as well as by X-ray crystallography. The ^{31}P NMR spectra show the resonance at δ 38.19 ppm for **3** and at δ 30.22 ppm for **4** and these chemical shifts are significantly downfielded when compared to those for compounds **1** and **2**, indicating a formation of the phosphine sulfide moiety. Similar example is observed in *o*-NH(Ph)NH−P(S)Ph$_2$C$_6$H$_4$ (δ 42.6 ppm).[28] The ^{1}H NMR spectrum of **3** shows the presence of the carbene ligand proton resonances at a range of δ 1.30−4.70 (δ 1.32, doublet, CH*Me*$_2$; 1.56, singlet, C*Me*; 4.62, septet, C*H*Me$_2$); however, these resonances are not observed in that of **4**.

When compared to the structure of **2**, in **3** (Figure 4) the S atom is bonded to the P with the P−S bond length of 1.9517(15) Å a little longer than that in the similar free ligand *o*-NH(Ph)NH−P(S)Ph$_2$C$_6$H$_4$ (1.9477(7) Å).[28] The Cu(1)···S(1) distance is 2.6420(12) Å, suggesting a weak Cu···S interaction like those found in **5**. The Cu(1) center keeps three-coordinated. However, it is worthy to note that the Cu(1)C(31)N(1)N(2) least-squares plane is calculated by 0.1521 Å and thus the Cu(1) center is away from the C(31)N(1)N(2) plane by 0.4187 Å. Moreover, the peripheral angle around the Cu(1) (344.22°) significantly deviates from ideal 360°. These data indicate a distorted trigonal-planar geometry over the Cu(1) center in **3** markedly different from the one featured in **2**, suggesting a relatively strong Cu···S interaction although the P−S bond length is not seriously changed. In **4** (Figure 5), the P(1)−S(1) distance (2.0089(17) Å) becomes longer and locates between the P−S double and single bonds,[31] whereas the corresponding Cu(2)−S(1) distance (2.1705(15) Å) much shorter when compared to those in **3** and **5**, indicative of a covalent bond character. Similar cases are observed in compounds (Ph$_3$P)$_2$Cu[(SPPh$_2$)(O$_2$SMe)N] and (Ph$_3$P)$_2$Cu[(SPPh$_2$)(O$_2$SC$_6$H$_4$-Me-4)N]·0.5toluene (P−S and Cu−S bond lengths, 1.9886(14) and 2.3912(11) Å for the former; 1.995(2) and (2.3761(18) Å for the latter).[32] Thus, **4** is better described as a zwitterionic compound with positive charge at the P while negative charge at the Cu center. Temperature-dependent molar magnetic susceptibility (χ_m·T) versus temperature (T) measurement for **4** from 2 to 300 K at a magnetic field of 1000 Oe showed that at room temperature the χ_m·T value was 0.44 cm^3·K·mol^{-1}, and with the decrease of the T, this value gradually decreased to 0.03 cm^3·K·mol^{-1} (Figure 5s of the Supporting Information).

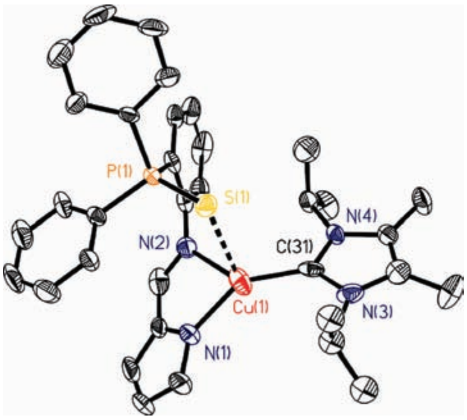


Figure 4. X-ray crystal structure of **3** with thermal ellipsoids drawn at the 50% probability. Selected bond lengths [Å] and angles [°]: Cu(1)−C(31) 1.913(4), Cu(1)−N(1) 1.968(3), Cu(1)−N(2) 2.326(3), P(1)−S(1) 1.9517(15), Cu(1)···S(1) 2.6420(12); C(31)−Cu(1)−N(1) 142.86(15), C(31)−Cu(1)−N(2) 124.11(15), N(1)−Cu(1)−N(2) 77.25(15).

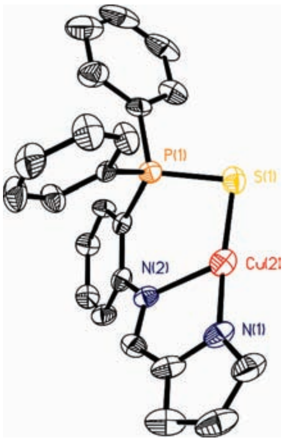
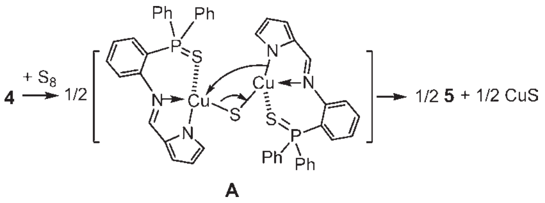


Figure 5. X-ray crystal structure of **4** with thermal ellipsoids drawn at the 50% probability. Selected bond lengths [Å] and angles [°]: Cu(2)−N(1) 1.913(4), Cu(2)−N(2) 2.170(4), Cu(2)−S(1) 2.1705(15), P(1)−S(1) 2.0089(17); N(1)−Cu(2)−N(2) 82.55(17), N(1)−Cu(2)−S(1) 172.36(14), N(2)−Cu(2)−S(1) 104.37(12), P(1)−S(1)−Cu(2) 91.57(7).

This may indicate a paramagnetic ground state of **4** and a probable temperature-dependent antiferromagnetic interaction occurred. However, the EPR of **4** is silent (Figure 3s of the Supporting Information). These data suggest that an electron charge is in great what transferred from the P to the Cu center via the S bridge, giving rise to the significant bond parameter changes of the P−S and Cu−S when compared to those in **2**, **3**, and **5**. The copper center in **4** is three-coordinate with a closely linear N(1)−Cu(2)−S(1) bond angle (172.36(14)°) and a perfectly planar Cu(2)N(1)N(2)S(1) plane (Δ = 0.0187 Å), revealing a T-shaped geometry over the copper center.

On the basis of the disclosure of the structures of **2**−**4**, it is pictured to us that the bonding of the carbene to the Cu(I) center in **2** weakens the Cu−P bond and then a weak Cu···P interaction is shown. This significantly changes the structural modes of the original two coppers in **1** despite that the metal is located either in the cationic or in the anionic center. The initial

Scheme 5. Plausible Reaction of 4 with S_8 to 5 and CuS



reaction of **2** with S_8 could be considered as an insertion of the sulfur atom into the Cu···P weak bond and the further reaction with S_8 might be believed to occur by an insertion of the sulfur into the Cu−$C_{carbene}$ bond. S=C[N(*i*Pr)CMe]$_2$ was formed and dissociated from the copper center. This makes the copper center more Lewis acidic[33] and then the S atom of the P=S bond triggers the Cu(I) by the strong donor−acceptor interaction resulting in the formation of the covalent Cu−S bond.

Now, we can find that it is **4** that directly undergoes the reaction of the Cu(I) to Cu(II) species with S_8 to form **5** and CuS. We treated a C_6D_6 solution of **4** at varied temperatures (room temperature to 80 °C) without an addition of S_8, the ^1H NMR spectra detected showed almost no changes of the proton resonances (Figures 7s−10s of the Supporting Information). Moreover, **4** was measured to exhibit a good thermal stability in the solid state in an inert atmosphere (mp, 223 °C). This implies no disproportionation reaction occurred for **4** in the absence of S_8, even upon heat treatment. We further performed a reaction using **2** and 2.2/8 equiv of S_8 to see if the presence of the excess of S_8 as an initiator would lead to the disproportionation of **4**. As a result, CuS was still produced rather than the copper metal and in the meantime cocrystals of **4** and **5** were isolated, which are structurally confirmed (Figure 11s of the Supporting Information). An attempt to isolate the copper sulfide compounds by a direct reaction of **4** with S_8 under varied conditions was yet not successful, and **5** and CuS were always generated.[34] Accordingly, we assume that the formation of **5** and CuS from the reaction of **4** with S_8 or even **1** and **2** respectively, with an excess of S_8 might proceed through a transient state **A** followed by the ligand redistribution (Scheme 5).

CONCLUSIONS AND REMARKS

In summary, we have reported on the synthesis of the NNP−ligand copper(I) complex **1** and its further reaction with S_8. The formation of the copper(II) compound **5** and CuS shows a stepwise reaction process including the degradation of **1**, sulfur abstraction by the phosphine, and the oxidation state change of the copper center accompanying with the NNP(S) ligand redistribution. This result appears different from those reported by the reactions of the *N*-chelate ligand-stabilized copper(I) species with S_8.[5−9] This reaction process has been further detected by the introduction of the *N*-heterocyclic carbene as a trapping agent through the formation of the mononuclear carbene-coordinated **2** and **3** and S=C[N(*i*Pr)CMe]$_2$-dissociated **4** and **5**, respectively, based on the strong Lewis donor character of the carbene in the former two compounds and the noted sulfur abstraction ability in the latter two ones.[3a,11d,16,29] Moreover, the presence of the intramolecular phosphine group linkage at the *N,N*-chelate in the NNP ligand allows to reveal such varied interactions as P···Cu, P=SCu, and P^+−S−Cu^-, and these interactions bring the significant structural changes of the corresponding copper compounds. This may reflect a complexity of this stepwise reaction process. The current endeavor is to isolate the transient $Cu_2(\mu\text{-S})$ core compound, and this work is underway.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Resonance Raman spectrum of CuS, emission spectra of the NNP ligand and **1**, X-band EPR spectra of **4** and **5**, temperature-dependent molar susceptibility versus temperature plot of **4** and **5**, proton NMR spectra of **4** detected at varied temperatures, structure of **5** in cocrystal of **4**·**5**, and CIF data for **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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