Preparation of Alkylthio- and Phenylthio(triphenylphosphine)copper(I) Complexes and Their Catalytic Activity for Transesterification of *S*-Alkyl Ethanethioates and Thiols

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Alkylcopper complexes, $RCu(PPh_3)_2$ (R=methyl, ethyl, propyl, isobutyl)reacted with sulfur smoothly at low temperatures to produce dialkyl disulfides. This indicates the insertion of sulfur to alkyl-Cu bond taking place followed by coupling of the two alkylthio–Cu bonds. Methylcopper complex, $CH_3Cu(PPh_3)_2 \cdot 0.5Et_2O$ reacted with thiols to produce alkylthio- and phenylthiocopper complexes having one or two triphenylphosphine ligands. The reactions of these alkylthiocopper complexes with acyl halides and acid anhydrides produced *S*-alkyl ethanethioates in high yields, whereas the reactions of alkylthiocopper complexes with alkyl halides produced dialkyl sulfides. Alkylthio- and phenylthiocopper complexes were found to catalyze the transesterification reactions between *S*-alkyl ethanethioates and thiols. The exchange reactions also take place between the alkylthiocopper complex and benzenethiol producing phenylthiocopper complex with liberation of alkanethiol.

As part of the project for studying the chemistry of organic copper complexes we have been investigating the properties of alkylcopper and alkoxocopper complexes containing tertiary phosphine ligands.[1-9] Natural extension of our study of alkoxocopper complexes[8,9] has led us to investigation of the chemistry of copper complexes containing organic sulfur moiety. Survey of the literature revealed that the chemistry of organic sulfur-copper complexes has been scarcely explored. Copper(I) alkanethiolates have been prepared by the reaction of copper(II) sulfate and thiols,[10] from copper(II) acetoacetate and sulfocyanate,[11] and from copper(II) acetate and thiols.[12] Phenylthiocopper complex also has been prepared from $ClCu(PPh_3)_3$ and NaSPh.[13] The copper(I) alkane- and benzenethiolates thus obtained are insoluble except for copper(I) alkanethiolates of higher secondary thiols in organic solvents, but their characterization is far from satisfactory.

Some reactions of the copper(I) alkane- and benzenethiolates have been examined sporadically, including the reactions of the complexes with carbon disulfide,[12] alkenyl halides,[14] phenyl acetylene,[15] sulfur dioxide.[16] Since most of the works concerning the copper(I) alkanethiolates have been done in rather old days and in none of the works the well defined copper(I) alkanethiolates have been prepared and their behavior examined, we consider it worthwhile to prepare a series of alkylthiocopper and phenylthiocopper complexes and examine their properties as chemical reagents which might be used for organic syntheses, particularly for catalytic reactions.

Our previous work on alkylcopper and alkoxocopper complexes having tertiary phosphine ligands[1-9] revealed the remarkable stabilizing effects of the tertiary phosphine ligands and employment of the tertiary phosphine ligands led to isolation of various well-characterized organic copper complexes. This paper deals with the preparation of new alkylthio- and phenylthiocopper complexes starting from the methylcopper complex having triphenylphosphine ligands and their properties including catalytic transesterification reactions of *S*-alkyl ethanethioate with thiols.

Results and Discussion

Preparation of Alkylthio- and Phenylthiocopper Complexes with Triphenylphosphine Ligands. As our previous studies on the properties of alkylcopper complexes having tertiary phosphine show, they have some similarities to Grignard reagents. Grignard reagents are known to react with sulfur giving magnesium alkanethiolates which on hydrolysis yield thiols.[17] Therefore we first attempted to prepare the alkylthiocopper complexes by reactions of sulfur with alkylcopper complexes having triphenylphosphine ligands in tetrahydrofuran below −10 °C. The reaction did not give isolable alkylthiocopper complexes but yielded dialkyl disulfides accompanied by small amounts of dialkyl sulfides as shown in Table 1. As our later study showed the alkylthiocopper complex once formed can be readily converted into dialkyl disulfide in high yields on reaction with sulfur. The small amount of dialkyl sulfide may have been produced by the reaction of alkylthiocopper

TABLE 1. REACTION OF ALKYLCOPPER COMPLEXES WITH SULFUR[a]

$$RCu(PPh_3)_2 \xrightarrow[\text{in THF}]{\text{Sulfur}} R\text{–}S\text{–}S\text{–}R + R\text{–}S\text{–}R$$

Alkylcopper complex (mmol)	Sulfur (g)	Products (yield %)[b] RSSR	RSR
$CH_3Cu(PPh_3)_2 \cdot 0.5Et_2O$ (1.00)	2.00	43	1
$CH_3CH_2Cu(PPh_3)_2$ (0.45)	1.50	30	7
$CH_3CH_2CH_2Cu(PPh_3)_2$ (0.89)	2.00	31	3
$(CH_3)_2CHCH_2Cu(PPh_3)_2$ (3.02)	2.50	48	2

a) The reactions were carried out in tetrahydrofuran for 5 h at −40 to −10 °C in a vacuum or under N_2 atmosphere. b) Yields were calculated based on alkyl group in alkylcopper complexes. Alkanes were also evolved in these reactions.

Table 2. Characterization data of alkylthio- and phenylthiocopper complex

Complex	Yield (%)	Mp[b] (°C)	Molecular weight (Calcd)	Elemental analyses Found (Calcd) (%) C	H	S	^{1}H-NMR (r.t., C_6D_6)
$CH_3CH_2SCu(PPh_3)_2$ **1**	78	139 (dec)	—[a]	70.4 (70.4)	5.3 (5.4)	5.1 (4.9)	δ 1.2 (t, 3H), δ 2.8 (q, 2H) δ 7.1 (m, 18H, *m,p*-phenyl) δ 7.5 (m, 12H, *o*-phenyl)
$CH_3CH_2CH_2SCuPPh_3$ **2**	84	57—58 (dec)	455±10 (400.5)	63.0 (62.9)	5.0 (5.5)	8.3 (8.0)	δ 0.75 (t, 3H), δ 1.7 (m, 2H) δ 2.8 (t, 2H), δ 7.1 (m, 9H, *m,p*-phenyl) δ 7.6 (m, 6H, *o*-phenyl)
$(CH_3)_2CHSCuPPh_3$ **3**	86	135—136 (dec)	448±10 (400.5)	63.0 (62.9)	5.2 (5.5)	7.7 (8.0)	δ 1.46 (d, 6H), δ 3.4 (m, 2H) δ 7.1 (m, 9H, *m,p*-phenyl) δ 7.6 (m, 6H, *o*-phenyl)
$(CH_3)_2CHCH_2SCu(PPh_3)_2$ **4**	81	75 (dec)	603±10 (676.5)	71.2 (71.0)	5.7 (5.8)	4.7 (4.7)	δ 1.0 (d, 6H), δ 1.8 (m, 1H) δ 2.7 (d, 2H), δ 7.1 (m, 18H, *m,p*-phenyl) δ 7.6 (m, 12H, *o*-phenyl)
$PhSCu(PPh_3)_2$ **5**	92	148—149 (dec)	620±10 (696.5)	72.0 (72.3)	4.8 (5.0)	4.5 (4.6)	δ 6.7 (m, 5H) δ 7.0 (m, 18H, *m,p*-phenyl) δ 7.5 (m, 12H, *o*-phenyl)

a) Complex **1** is not satisfactorily soluble in benzene to allow the molecular weight measurement.
b) Measured in vacuum-sealed capillaries.

complexes with remaining alkylcopper complexes or by the reaction of the dialkyl disulfide with triphenylphosphine which was present in the reaction mixture by dissociation from the copper complex.

Upon failure of our attempts to prepare an alkylthiocopper complex using sulfur powder we have tried reactions of thiols with a methylcopper complex having triphenylphosphine ligands and found that the reactions at 0 °C in diethyl ether gave a series of alkylthiocopper complexes and phenylthiocopper complex in considerably high yields evolving one mole of methane per mol of the copper complex.

$$CH_3Cu(PPh_3)_2\cdot 0.5Et_2O + RSH \xrightarrow[Et_2O]{0\,^\circ C} RSCu(PPh_3)_n + CH_4$$

$n=1$ for R=*n*-Pr (**2**), *i*-Pr (**3**)
$n=2$ for R=Et (**1**), *i*-Bu (**4**), Ph (**5**)

The phenylthiocopper complex could be also prepared by the reaction of PhSH with Cu_2O in the presence of PPh_3 in a high yield (92%) as well as from the methylcopper complex with PhSH. The alkylthio- and phenylthiocopper complexes were characterized by elemental analysis, molecular weight determination (cryoscopic in benzene), chemical reactions, and IR and NMR spectroscopy. Table 2 shows relevant data for characterization together with yields and melting points with decomposition of alkylthio- and phenylthiocopper complexes. Infrared spectra of the alkylthiocopper complexes (shown in Experimental section) showed a band in the range of 1220 to 1260 cm^{-1} which may be related to alkylthio group, in addition to other bands due to triphenylphosphine. The molecular weights of the alkylthiocopper complexes having one triphenylphosphine ligand (complexes **2** and **3**) were found to be slightly higher than the theoretical values, whereas those of complexes having two triphenylphosphine ligands were slightly lower. The possible explanation for the former cases is the association of the alkylthiocopper complexes whereas in the latter the partial dissociation of the triphenylphosphine ligands might be taking place as have been observed in other alkylcopper complexes.[1-2,6] The melting points (with decomposition) of the isolated alkylthiocopper complexes showed a considerable variance and no reasonable explanation for this was found. Although the complexes have relatively high thermal stabilities and are relatively insensitive to air when heated rapidly, they are gradually decomposed at room temperature even under nitrogen.

Reactions of Alkylthiocopper Complexes. Pyrolysis of the ethylthiocopper complex at 150 °C liberated diethyl sulfide (54%), diethyl disulfide (31%) and a

Table 3. Reactions of alkylthiocopper complexes with various reagents[a]

Alkylthiocopper complex (mmol)	Reagent (quantity)	Product (yield % per Cu)
$CH_3CH_2CH_2SCuPPh_3$ **2** (0.72)	$CH_3CH_2CH_2Br$ (2 ml)	$CH_3CH_2CH_2SCH_2CH_2CH_3$ (39)
$CH_3CH_2CH_2SCuPPh_3$ **2** (0.38)	CH_3COCl (1.15 mmol)	$CH_3COSCH_2CH_2CH_3$ (92)
$CH_3CH_2SCu(PPh_3)_2$ **1** (0.20)	$(CH_3CO)_2O$ (0.5 ml)	$CH_3COSCH_2CH_3$ (95) $CH_3COOCu(PPh_3)_2$ (90)
$(CH_3)_2CHSCuPPh_3$ **3** (0.36)	$CH_3COOCH=CH_2$ (2 ml)	polyvinylacetate
$CH_3CH_2CH_2SCuPPh_3$ **2**	PhSH (1 ml)	$PhSCuPPh_3$ (88)

a) For reaction conditions see Experimental section.

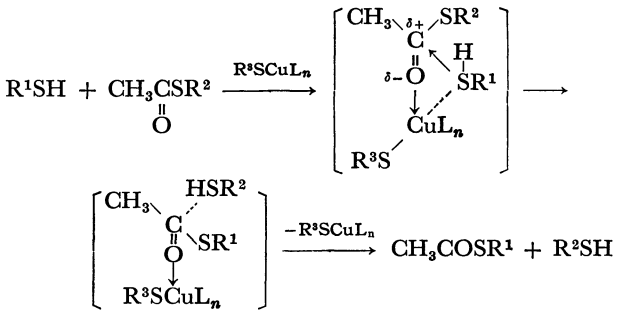
TABLE 4. TRANSESTERIFICATION REACTIONS OF *S*-ALKYL ETHANETHIOATES WITH THIOLS USING ALKYLTHIOCOPPER COMPLEXES[a)]

Starting ester (mmol)	Thiol (quantity)	Catalyst (mmol)	Product (yield % starting ester)
$CH_3COSCH_2CH_3$ (4.86)	$CH_3CH_2CH_2SH$ (11 mmol)	**2** (0.25)	$CH_3COSCH_2CH_2CH_3$ (64)
$CH_3COSCH_2CH_2CH_3$ (1.19)	$(CH_3)_2CHSH$ (2.5 mmol)	**3** (0.25)	$CH_3COSCH(CH_3)_2$ (40)
$CH_3COSCH(CH_3)_2$[b)] (8.06)	CH_3CH_2SH (5 ml)	**1** (0.25)	$CH_3COSCH_2CH_3$ (11)
$CH_3COSCH_2CH(CH_3)_2$ (10.7)	$CH_3CH_2CH_2SH$ (5 ml)	**2** (0.50)	$CH_3COSCH_2CH_2CH_3$ (66)
CH_3COSPh (5.51)	$(CH_3)_2CHSH$ (5 ml)	**3** (0.25)	$CH_3COSCH(CH_3)_2$ (22)
$CH_3COSCH_2CH_3$[c)] (4.86)	$CH_3CH_2CH_2SH$ (22 mmol)	**5** (0.25)	$CH_3COSCH_2CH_2CH_3$ (41)

a) These reactions were carried out at room temperature for 12 h. b) At 32 °C for 2 h.
c) In 2 ml of THF.

small amount of ethane (7%) and a trace of ethylene, the yields being based on the ethyl group. Pyrolysis of the phenylthiocopper complex at 150 °C similarly gave diphenyl sulfide (43%), diphenyl disulfide (52%), and benzene (2%). The formation of disulfides may be accounted for by assuming the homolytic splitting of the RS–Cu bond yielding RS radicals which are known to give the disulfide on recombination. On the other hand, the sulfide may have been formed either from the disulfide on reaction with triphenylphosphine which is known to convert the disulfide into sulfide with concomitant conversion of the triphenylphosphine to triphenyl phosphine sulfide,[18,19)] or by the recombination of R radical and RS radical produced on pyrolysis of these complexes. The small amount of RH (ethane and benzene) seems to be produced by the abstraction of *o*-hydrogen of the PPh_3 ligand by the R radical. A part of the ethyl radical seems to participate into the disproportionation to afford ethylene. For further characterizing the alkylthiocopper complexes and for getting information of their chemical properties the alkylthiocopper complexes were subjected to various chemical reactions. The main features of the chemical properties of the alkylthiocopper complexes parallel with those of the alkoxocopper complexes as shown in Table 3. They afford *S*-alkyl ethanethioate on reaction with acetic anhydride and acetyl chloride, dialkyl sulfide on treatment with alkyl halide under mild conditions, whereas vinyl acetate was polymerized with the alkylthiocopper complex. Propylthiocopper complex **2** reacts with benzenethiol at 0 °C to produce the more thermally stable phenylthiocopper complex **6** in a high yield.

Catalytic Transesterification Reactions Promoted by the Alkylthiocopper Complexes. Our previous study on the alkoxocopper complexes revealed their excellent catalytic activities for transesterification of carboxylic esters with alcohols under mild conditions. In the light of the importance of the thiol esters such as exemplified by coenzyme A in biosynthesis, the catalytic transesterification reactions of *S*-alkyl ethanethioates with thiols promoted by the alkylthiocopper complexes under mild conditions were examined. As Table 4 shows, the alkylthiocopper complexes were found to serve as the transesterification catalyst in a similar manner to the alkoxocopper complexes which catalyzed the transesterification of carboxylic esters with alcohols.[9)] In view of the reluctane for the exchange of the alkylthio group bound to copper with that in the other alkanethiol, a stepwise mechanism involving the exchange of RSCu entity with R'SH is not likely and attack of an ester carbonyl group, which is polarized on coordination to copper, by thiol in a nucleophilic manner as shown below seems to provide a reasonable explanation for the transesterification catalyzed by the copper complexes:



A similar S_N2 type mechanism has been proposed for the transesterification of carboxylic esters with alcohols catalyzed by alkoxocopper and phenoxocopper complexes.[9)]

Whereas the transesterification between the *S*-alkyl ethanethioates and thiols were catalyzed by the alkylthiocopper complexes, attempted transesterification of carboxylic esters with thiols has been so far unsuccessful. On the other hand transesterification of *S*-*t*-butyl ethanethioate with ethanol was found to be catalyzed by the ethoxocopper complex, $EtOCu(PPh_3)_2$. A related activation of thiol esters by copper, silver, and mercury compounds have been examined by Masamune and utilyzed for organic synthesis.[20,21)]

Experimental

General. All preparations and reactions of copper complexes were carried out in Schlenk type flasks under deoxygenated nitrogen, argon or in a vacuum. Solvents were dried by usual procedures, distilled, and stored under argon or nitrogen. IR spectra were recorded on a Hitachi Model

295 using KBr discs under nitrogen. ^{1}H-NMR spectra were recorded with a Japan Electron Optics Lab. JNM-PS-100 spectrometer. Evolved gas was analyzed with a Hitachi RMU 5B mass-spectrometer and a Shimadzu GC 5B gas chromatograph, and its volume was measured with a Toepler pump. The microanalysis of carbon, hydrogen, and nitrogen was performed by Mr. T. Saito of our labolatory with a Yanagimoto CHN Autocorder Type MT-2.

Reactions of Alkylcopper Complexes with Sulfur. Sulfur (2.0 g) was added into a Schlenk-type flask containing methylcopper complex, $CH_3Cu(PPh_3)_2 \cdot 0.5Et_2O$ (1 mmol) in THF (5 ml) and the yellow emulsion was stirred at -40 °C to -10 °C for 5 h to give a red solution. Analysis of the products in the solution by means of gas chromatography showed that dimethyl disulfide (yield 43%) and dimethyl sulfide (yield 1%) were produced (yields are based on the methyl group of the methylcopper complex). The other reactions between alkylcopper complexes and sulfur were carried in a similar way to the above reaction.

Preparation of Ethylthiobis(triphenylphosphine)copper (1). Ethanethiol (0.28 ml, 3.62 mmol) was added to a yellow suspension of $CH_3Cu(PPh_3)_2 \cdot 0.5Et_2O$ (1.932 g, 3.02 mmol) in 5 ml of Et_2O at -10 °C, and the mixture was stirred at -10 °C for about 10 min until the yellow emulsion turns to white. A quantative amount of methane (yield 98% on the basis of Cu) was evolved. The white complex produced was separated and recrystallized from toluene to give white crystals of $CH_3CH_2SCu(PPh_3)_2$ (**1**) (1.535 g, yield 78%). IR(KBr): 2950 w, 2900 w, 2840 w, 1235 w, 1235 m and other absorption bands due to PPh_3.

Preparation of Propylthiotriphenylphosphinecopper (2). The reaction of $CH_3Cu(PPh_3)_2 \cdot 0.5Et_2O$ (2.085 g, 3.26 mmol) with propanethiol (3.26 mmol) in 10 ml of Et_2O at -10 °C to 0 °C for 1 h produced a light yellow precipitate and methane (0.99 mol per Cu). The yellow precipitate was recrystallized from a mixture of Et_2O and toluene. Light yellow crystals of **2** (1.095 g, yield 84%) were obtained. IR(KBr): 2950 w, 2900 w, 2860 w, 1200 m cm^{-1} and other absorption bands due to PPh_3.

Preparation of Isopropylthiotriphenylphosphinecopper (3). The reaction of $CH_3Cu(PPh_3)_2 \cdot 0.5Et_2O$ (1.475 g, 2.3 mmol) with 1-methyl-ethanethiol (2.76 mmol) in 5 ml of Et_2O at -10 °C to 0 °C for 1 h produced a white precipitate from the yellow emulsion. Methane (0.94 mol per Cu) was evolved. The white precipitate was recrystallized from a mixture of Et_2O and toluene to give white crystals of **3** (0.795 g, yield 86%). IR(KBr): 2930 w, 2900 w, 2840 w, 1220 w, 1140 w cm^{-1} and other absorption bands due to PPh_3.

Preparation of Isobutylthiobis(triphenylphosphine)copper (4). To a yellow suspension of the methylcopper complex (1.832 g, 2.86 mmol) in Et_2O (5 ml) at -20 °C 2-methylpropanethiol (3.44 mmol) was added. After stirring the mixture at -20 to 0 °C for 3 h a yellow solution was produced. On concentrating the solution, a white complex precipitated and it was recrystallized from a mixture of Et_2O and hexane to give white crystals of **4** (1.572 g, yield 81%). IR(KBr): 2950w, 2920w, 2900w, 2860w, 1370w, 1350w, 1225w cm^{-1} and other absorption bands due to PPh_3.

Preparation of Phenylthiobis(triphenylphosphine)copper (5). The reaction of the methylcopper complex (0.941 g, 1.31 mmol) with benzenethiol (1.57 mmol) in diethyl ether (5 ml) at -10 °C for 10 min produced a white precipitate from a yellow heterogeneous system. The precipitate was recrystallized from a mixture of diethyl ether and toluene and was dried in a vacuum to give crystals of **5** (0.835 g, yield 92%). IR(KBr): 1570s, 1260w, 1075m cm^{-1} and absorption bands due to PPh_3.

Thermal Decomposition of Complex 1 and 5. Complex **1** (0.5 mmol) was decomposed by heating at 150 °C under nitrogen atmosphere and diethyl ether (2 ml) was added to the cooled thermolysis residue. After stirring the solution the amount of products formed on thermolysis was measured by means of gas chromatography.

Reactions of Alkylthiocopper Complexes with Alkyl Halide, Acyl Halide, Acid Anhydride, Vinyl Acetate, and Benezenethiol. Propyl bromide (2 ml) was introduced into a Schlenk type flask containing **3** (0.722 mmol) by a trap-to-trap distillation in a vacuum. After stirring the white emulsion at room temperature for 1 h a yellow solution was produced and finally a colorless supernatant and a white precipitate of bromocopper(I) complex were produced with further stirring the solution for 11 h. The mixture was filtered and the filtrate was introduced into another flask by distillation to remove copper compounds. The distillate was analyzed by means of gas chromatography to confirm the formation of dipropyl sulfide (yield 39% on the basis of Cu). Other products in the reactions of alkylthiocopper complexes with reagents were analyzed similarly.

Acetyl chloride (1.15 mmol) was added to a white emulsion of **3** (0.382 mmol) in diethyl ether (2 ml) and the mixture was stirred at room temperature overnight under nitrogen atmosphere to give *S*-propyl ethanethioate (yield 92% on the basis of Cu).

Acetic anhydride (0.5 ml) was added to a white emulsion of **2** (0.204 mmol) in diethyl ether (2 ml) and the mixture was stirred at room temperature overnight to produce *S*-propyl ethanethioate (yield 95% on the basis of Cu) and a white precipitate of $CH_3CO_2Cu(PPh_3)_2$ (yield 90%).

Vinyl acetate (2 ml) was introduced into a Schlenk type flask containing **4** (0.355 mmol) by a trap-to-trap distillation in a vacuum. The yellow solution was stirred at -10 to 0 °C for a day to give polyvinylacetate.

One ml of benzenethiol was added to complex **2** (0.20 g, 0.5 mmol) in diethyl ether (3 ml) and the mixture was stirred at 10 min to give a yellow solution. Further stirring it for 20 min gave a white precipitate. The precipitate was crystallized from toluene to give white crystals identified as PhSCu-PPh_3 (**6**) (191 mg, yield 88%). Complex **6**, mp 115—117 °C (dec.). Found: C, 67.0; H, 4.91; S, 7.27%. Calcd for $C_{24}H_{20}PSCu$: C, 66.3; H, 4.60; S, 7.36%. IR(KBr): 1570s, 1260w, 1075s cm^{-1} and absorption bands due to PPh_3. ^{1}H-NMR (C_6D_6): δ 6.7 (m, 5H, phenyl); δ 7.0 (m, 9H, *m,p*-phenyl of PPh_3); δ 7.5 (m, 6H, *o*-phenyl of PPh_3).

Transesterification Reactions between S-Alkyl Ethanethioates and Thiols with Alkylthiocopper Catalysts. *S*-Ethyl ethanethioate (4.86 mmol) was added into a flask containing propanethiol (11 mmol) and **2** (0.25 mmol). The yellow solution was stirred at room temperature overnight and the mixture was passed through a column of Wakogel C-200 (5 g) with diethyl ether to remove copper compounds. The solution was condensed under reduced pressure and the condensate was analyzed by means of gas chromatography to confirm the formation of *S*-propyl ethanethioate (yield 64% on the basis of starting *S*-ethyl ethanethioate) and thiol. The other transesterification reactions were carried in a similar way.

Reaction between S-Alkyl Ethanethioate and Alcohol with Alkoxocopper Catalyst. *S-t*-Butyl ethanethioate (10 mmol) was added to a solution containing ethanol (40 mmol) and EtOCu-$(PPh_3)_2$ (0.3 mmol). The mixture was stirred at room temperature overnight to produce ethyl acetate (yield 14% on the basis of thiol ester) and 1,1-dimethylethanethiol (yield 13%).

References

1) A. Miyashita and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **50**, 1102 (1977).
2) A. Miyashita, T. Yamamoto, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **50**, 1109 (1977).
3) T. Ikariya and A. Yamamoto, *J. Organomet. Chem.*, **72**, 145 (1975).
4) A. Miyashita and A. Yamamoto, *J. Organomet. Chem.*, **113**, 187 (1976).
5) A. Yamamoto, A. Miyashita, T. Yamamoto, and S. Ikeda, *Bull. Chem. Soc. Jpn.*, **45**, 1583 (1972).
6) M. Kubota, A. Miyashita, S. Komiya, and A. Yamamoto, *J. Organomet. Chem.*, **139**, 111 (1977).
7) T. Yamamoto, M. Kubota, A. Miyashita, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **51**, 1835 (1978).
8) M. Kubota and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **51**, 2909 (1978).
9) M. Kubota, T. Yamamoto, and A. Yamamoto, submitted to *Bull. Chem. Soc. Jpn.*
10) P. Klason, *Ber.*, **20**, 3412 (1887).
11) E. Kohler, *Am. Chem. J.*, **22**, 72 (1899).
12) W. E. Duncan, E. Ott, and E. E. Reid, *Ind. Eng. Chem.*, **23**, 381 (1931).
13) W. T. Reichle, *Inorg. Chim. Acta*, **5**, 325 (1971).
14) A. Commercon, J. Normant, and J. Villieras, *J. Organomet. Chem.*, **93**, 415 (1975).
15) W. T. Reichle, *Inorg. Nucl. Chem. Lett.*, **1969**, 981.
16) P. G. Eller and G. J. Kubas, *J. Am. Chem. Soc.*, **99**, 4346 (1977).
17) N. Rabjohn, Editor-in-Chief, "Organic Syntheses" collective Vol. 4, page 667.
18) M. B. Evans, G. M. C. Higgins, C. G. Moore, M. Porter, S. Savile, J. F. Smith, B. R. Trego, and A. A. Watson, *Chem. & Ind.*, **1960**, 88.
19) "Chemistry of Organosulfur Compounds," ed by S. Oae, Kagakudojin, Kyoto (1968), p. 80.
20) S. Masamune, Y. Hayase, W. Schilling, W. K. Chan, and G. S. Bates, *J. Am. Chem. Soc.*, **99**, 6756 (1977).
21) S. Masamune, S. Kamata, and W. Schilling, *J. Am. Chem. Soc.*, **97**, 3515 (1975).