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1,2-Migration of Phosphorus-Centered Anions on Ate-type Copper Carbenoids and Its Application for the Synthesis of New Potent Phosphine Ligands

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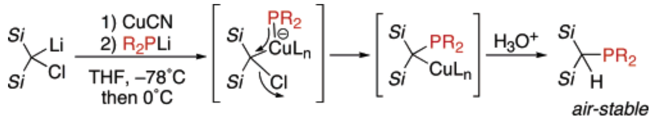
ABSTRACT

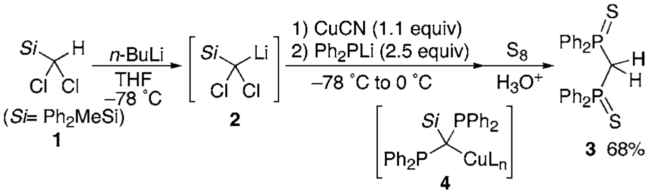


Diorganophosphide anions, which usually function as nontransferable ligands on mixed cuprates, undergo smooth 1,2-migration on ate-type copper carbenoids. Phosphinodisilylmethylcoppers prepared by this protocol are converted into the corresponding phosphines, which can be used as bulky, highly basic and air-stable ligands.

Organocopper reagents are an extremely valuable family of organometallic compounds that are widely used in organic synthesis.[1] Among them, mixed cuprates have been developed to improve the reactivity and thermal stability by introducing "dummy" ligands. These reagents often employ cyano, silylmethyl, alkynyl, 2-thienyl, and mesityl groups as the carbon-based dummy groups.[1] Heteroatom-based ones include phenylsulfanyl, *N*-imidazolyl, dialkylamino, and dialkylphosphino groups.[2,3] However, in the course of our recent study on 1,2-migration of various groups via ate-type copper carbenoids, we have found that nontransferable carbon-based anionic ligands transfer efficiently.[4] Here we wish to report the 1,2-migration of phosphorus-centered anions, such as Ph_2P^- or $(c\text{-}C_6H_{11})_2P^-$, which are generally expected to exhibit no migratory aptitude on cuprates in other conventional reactions.[3] The migratory phosphination afforded new phosphines useful in transition-metal-catalyzed reactions.[5]

Initially, we chose dihalosilylcarbenoid as a test case to examine the feasibility of the phosphination via 1,2-migration on cuprates (Scheme 1). An addition of *n*-BuLi to a THF solution of $Ph_2MeSiCHCl_2$ (**1**) provided dichlorosilylmethyllithium **2** with the quantitative deprotonation. Lithium

Scheme 1. Diphosphination via Double 1,2-Migration of Phosphorus-Centered Anion on Ate-type Copper Carbenoid



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(1) (a) *Modern Organocopper Chemistry*; Krause, N., Ed.; Wiley-VCH: Weinheim, Germany, 2000. (b) *Organocopper Reagents*; Taylor, R. J. K., Ed.; Oxford University Press: Oxford, 1994. (c) Lipshutz, B. H. In *Organometallics in Synthesis*; Schlosser, M., Ed.; Wiley: Chichester, 2002; p 665.

(2) (a) Phenylsulfanyl: Posner, G. H.; Whitten, C. E.; Sterling, J. J. *J. Am. Chem. Soc.* **1973**, *95*, 7788. (b) *N*-Imidazolyl: Lipshutz, B. H.; Fatheree, P.; Hagen, W.; Stevens, K. L. *Tetrahedron Lett.* **1992**, *33*, 1041.

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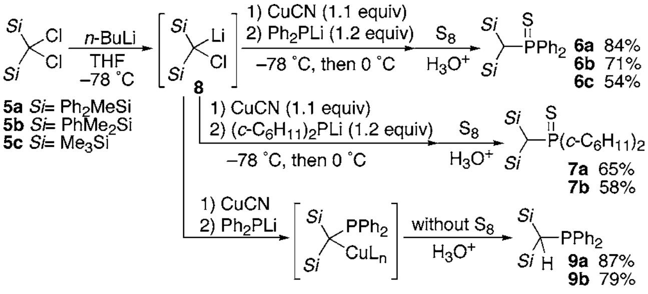
carbenoid **2** was sequentially treated with CuCN•2LiCl (1.1 equiv in THF) and lithium diphenylphosphide (2.5 equiv in THF) at −78 °C, and the mixture was allowed to warm gradually to 0 °C. After quenching with sulfur and dilute HCl aq., extractive workup followed by purification afforded the pentavalent phosphorus compound **3**. This result indicates the generation of copper species **4** through the double 1,2-migrations of diphenylphosphino groups on ate-type copper carbenoid. Desilylation of **4** took place upon hydrolysis to yield **3**.

Next, we attempted the monophosphination of chlorodisilylcarbenoid **8a**, which was instantly prepared by mixing $(Ph_2MeSi)_2CCl_2$ (**5a**) with *n*-BuLi (1.0 equiv) in THF at −78 °C (Scheme 2). In a similar way as described above, lithium carbenoid **8a** was treated with 1.1 equiv of CuCN and 1.2 equiv of Ph_2PLi. The mixture was stirred at 0 °C and quenched with sulfur and aqueous NH_4Cl. Disilylmethylphosphine sulfide **6a** was obtained in 84% yield as a sole product.[6] The reactions of **5b** and **5c** having two other silyl groups, $PhMe_2Si$ and Me_3Si, respectively, proceeded in the same manner. $(c\text{-}C_6H_{11})_2PLi$ was also applicable to this reaction protocol and furnished the corresponding phosphine sulfides despite slight decreases in yields. Furthermore, we could isolate the trivalent phosphines **9a** and **9b** in good yields without sulfurization.[7]

Scheme 2. Monophosphination of Chlorodisilylcarbenoids



Importantly, these (disilylmethyl)diphenylphosphines **9a** and **9b** show much higher air-stability than the parent PPh_2Me. The structure of the phosphine sulfide **6b** was unambiguously elucidated by X-ray crystallographic analysis, as shown in Figure 1. Clearly, two large silyl groups sterically hinder the environment of the phosphorus center. In addition, DFT calculations at the B3LYP/6-31G* level show that **9a** is expected to have a large cone angle (Supporting Information, Figure S1).[8d,9] The electron-donating silylmethyl group should enhance the basicity of **9a**. $^1J(^{77}Se-^{31}P)$ coupling constants of the phosphine selenides $Se{=}PR_3$ are commonly used to estimate the relative basicities of the parent phosphines PR_3. In our case, the selenide of **9a** marked 690 Hz, which indicates that **9a** has a comparable basicity to $P(t\text{-}Bu)_3$ ($Se{=}P(t\text{-}Bu)_3$, 686 Hz) and stronger basicity than PPh_3 ($Se{=}PPh_3$, 735 Hz).[8]

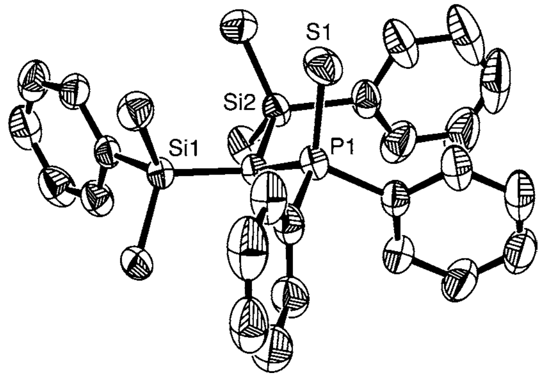
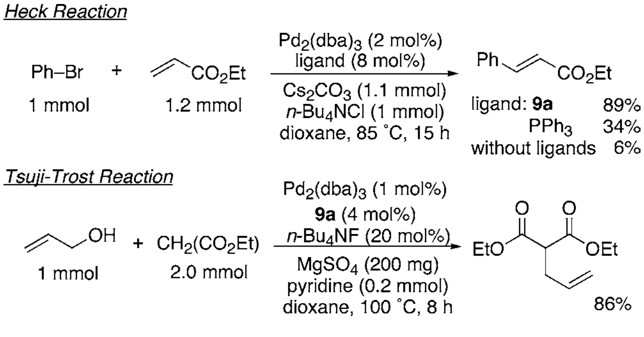


Figure 1. ORTEP drawing of the phosphine sulfide **6b**. Hydrogen atoms were omitted for clarity. The thermal ellipsoids were at the 50% probability level.

Scheme 3. Ligand **9a** in Transition-Metal-Catalyzed Reactions



The phosphine **9a** is expected to have some unique chemical properties due to its steric and electronic effects, which are induced by silyl substitution at the α-position. Consequently, we have examined the use of this silicon-bearing phosphine **9a** as a ligand of two typical transition-metal-catalyzed reactions.[10] Scheme 3 shows the preliminary results of the Heck reaction with aryl bromide and ethyl acrylate to exploit the basicity and bulkiness of **9a**.[11] We were pleased to find that the desired Heck product was obtained in good yield at 85 °C in the presence of tetrabutylammonium chloride with ligand **9a**. In contrast, the same transformation with PPh_3 or under ligandless conditions resulted in diminished yield (34 or 6% yield, respectively). The Heck reaction with aryl bromide generally needs high reaction temperatures over 120 °C,[12] and these milder

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(5) We recently described new methods for the synthesis of organophosphorus compounds. See: (a) Hirano, K.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2004**, *6*, 4873. (b) Sato, A.; Yorimitsu, H.; Oshima, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 1694. (c) Ohmiya, H.; Yorimitsu, H.; Oshima, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 2368.

(6) We could not detect the byproduct, α,α-bis(methyldiphenylsilyl)-acetonitrile, which was derived via 1,2-migration of the cyano group.

reaction conditions can be attributed to the bulky and highly basic nature of **9a**.[11,12b]

We also attempted to utilize this phosphine **9a** for Tsuji−Trost reaction with the direct use of allylic alcohol.[13] Tsuji−Trost reaction with allyl alcohol as the allyl source usually requires acidic activators for the hydroxy group, such as inorganic acids or Lewis acids. Several other catalytic examples have been recently reported which utilize π-allylpalladium complexes bearing diphosphinidenecyclobutene ligands[13a] or water-soluble palladium complex in an aqueous−organic biphasic system.[13b] These precedent works stimulated us to find a new way to prepare π-allylpalladium species with a combination of $Pd_2(dba)_3$, **9a**, and tetrabutylammonium fluoride. This was indeed the case, and the reaction of diethyl malonate with allyl alcohol exclusively afforded monoallylated product in 86% yield without formation of the diallylated product. Both crotyl alcohol and its regioisomer, 3-buten-2-ol, provided the corresponding linear and branched products in comparable ratios (linear/branched = 59:41 and 56:44, respectively). The comparable ratios suggest the formation of the π-allylpalladium intermediate.

In conclusion, we have demonstrated 1,2-migration of phosphorus-centered anions on ate-type copper carbenoids. Additionally, we have applied (disilylmethyl)diphenylphosphine as a bulky and electron-rich ligand to transition-metal-catalyzed reactions. Further studies are now underway to elucidate the effects of (disilylmethyl)diphenylphosphines in transition-metal-catalyzed reactions.

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Supporting Information Available: Detailed experimental procedures, characterization data of compounds, and X-ray crystallographic data for **6b** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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