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Synthesis, Structure, and Catalytic Activity of Palladium Complexes Bearing a Tridentate PXP-Pincer Ligand of Heavier Group 14 Element (X = Ge, Sn)

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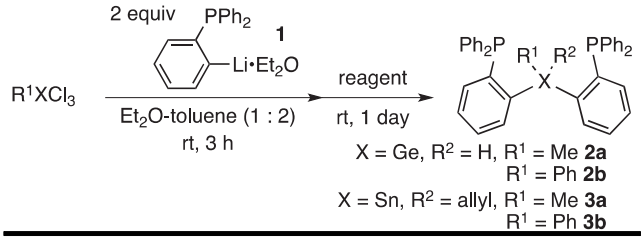
An efficient method for the synthesis of tridentate PGeP– and PSnP–palladium complexes is developed. Structural analysis revealed that PSiP-ligand exerts the strongest trans influence and electron donation and that PGeP- and PSnP-ligands provide wider coordination sphere around the palladium. Preliminary studies demonstrated that both PGeP– and PSnP–palladium complexes work as an efficient catalyst for reductive aldol-type reaction, indicating promising utility in synthetic organic chemistry.

Transition-metal complexes bearing a tridentate PSiP-pincer ligand derived from bis(*o*-phosphinophenyl)silane have been attracting much attention in organometallic chemistry.[1–3] The features of this type of PSiP-pincer ligand are 1) the strong trans influence of the silicon which enhances nucleophilicity of the *trans* substituent and 2) distorted square-planar structure due to the sp^3-Si atom which induces facile structural change.[2b] Contrary to the well-developed chemistry of Si-containing multidentate ligands,[4] multidentate ligands containing a heavier group 14 element such as Ge and Sn have rarely been developed despite their unique characteristics different from Si.[5,6] Recently Nakazawa reported synthesis and structural analysis of new rhodium and iridium complexes bearing a tetradentate P_3Ge- or P_3Sn-ligand and their unique reactivity in ligand dissociation and substitution reaction.[7] However, there has been no report on the synthesis and reactivity of metal complexes bearing an anionic, tridentate PXP-pincer type ligand (X = Ge, Sn). Such tridentate pincer complexes of divalent group 10 metals are expected to be an active catalyst for molecular transformation since similar PCP–palladium(II) complexes have been widely utilized in synthetic organic chemistry.[8] Herein we report the synthesis and structural analysis of palladium complexes bearing a tridentate PGeP- or PSnP-pincer ligand and their catalytic activity in reductive aldol-type reaction between α,β-unsaturated esters and aldehydes.

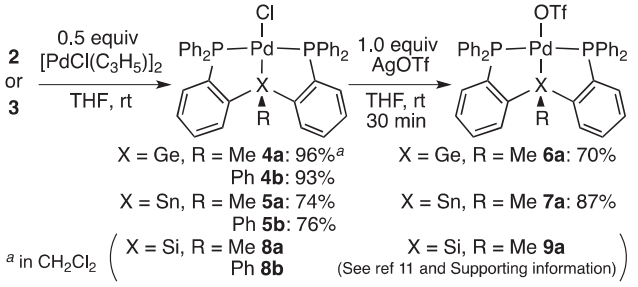
Based on the synthesis of the PSiP-pincer palladium(II) complex,[1a,2a] bis[*o*-(diphenylphosphino)phenyl]methylgermane (**2a**) was synthesized as a ligand precursor for the synthesis of the corresponding PGeP–palladium complex. Treatment of commercially available methyltrichlorogermane with 2 equiv of *o*-(diphenylphosphino)phenyllithium (**1**) afforded diarylmethylchlorogermane, which was successively reduced in one pot by $LiAlH_4$ to give desired **2a** in 75% yield (Table 1, Entry 1). Germane **2b** bearing a phenyl group instead of methyl on germanium was also obtained in good yield by the same procedure using phenyltrichlorogermane as a starting material (Entry 2). However, the synthesis of the corresponding stannane derivative (Ar_2MeSnH) by the same procedure was unsuccessful probably due to its instability under the reaction conditions. Therefore, the possibility of using allylstannane derivative **3** as a more stable ligand precursor was examined with the expectation that the reactive C–Sn bond of allylstannane would be cleaved easily by palladium to form a Pd–Sn bond.[9] Allylstannane derivatives **3a** (R = Me) and **3b** (R = Ph) were synthesized from commercially available methyl- or phenyltrichlorostannane **1** and allylmagnesium chloride (Entries 3 and 4).

Table 1. Synthesis of ligand precursors



Entry	X	R^1	R^2	Reagent		Yield/%
1[a]	Ge	Me	H	1.5 equiv $LiAlH_4$	**2a**	75
2		Ph			**2b**	89
3[b]	Sn	Me	allyl	2 equiv allylMgCl	**3a**	16
4[b]		Ph			**3b**	40

[a]The reaction was carried out in Et_2O–toluene (2:1). [b]**1** was added at 0 °C and the mixture was stirred for 1 h at rt.



Scheme 1. Synthesis of PXP–palladium complexes (X = Ge, Sn).

Complexation of **2** or **3** with $[Pd(C_3H_5)Cl]_2$ proceeded smoothly at room temperature to give PXP–palladium(II) chloride complexes **4** or **5** (X = Ge, Sn) in high yield (Scheme 1). The reaction of the Ph-substituted germane and stannane derivatives also proceeded without problem. It should be noted that the allylstannanes **3** successfully worked as a ligand precursor via C–Sn bond cleavage. Triflate complexes **6a** and **7a** were also prepared by treatment of **4a** or **5a** with AgOTf. Thus, an efficient method for the synthesis of tridentate PGeP- and PSnP-pincer type palladium complexes was realized for the first time.

X-ray analyses were performed for all palladium chloride complexes[10] **4a**, **4b**, **5a**, **5b**, **8a**, and **8b** and ORTEP diagrams of

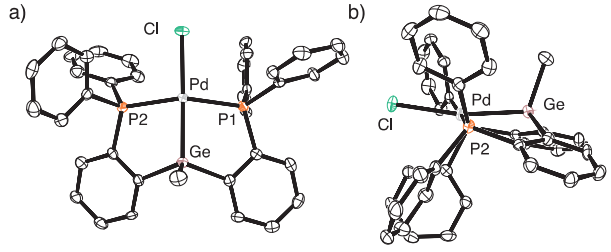


Figure 1. ORTEP drawing of **4a** at 50% probability level (hydrogen atoms are omitted for clarity). a) Top view. b) Side view.

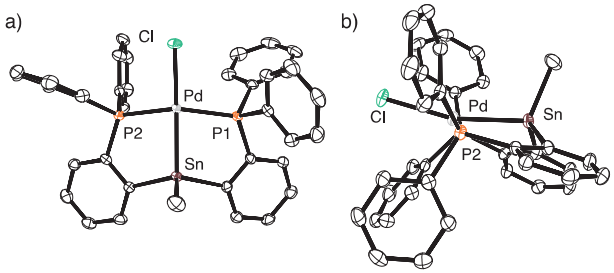
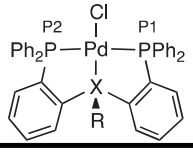


Figure 2. ORTEP drawing of **5a** at 50% probability level (hydrogen atoms are omitted for clarity). a) Top view. b) Side view.

4a and **5a** are depicted in Figures 1 and 2. The geometry around the metal center was distorted square planar in all cases where phosphine atoms slightly bended from 180°. To compare the effect of the central group 14 element on the structure and electronic properties of palladium complexes, selected bond lengths, angles, and ^{31}P NMR data of **3**, **4**, and corresponding PSiP–palladium complexes **8a** and **8b**[11] are listed in Table 2. The Pd–Cl bond length of PSiP-complexes are 2.4414(17) Å for **8a** and 2.4347(15) Å for **8b**. These values are slightly longer than those of PGeP- and PSnP-complexes. The ^{31}P NMR of **8a** and **8b** exhibited upfield shift of the phosphorous atoms at $\delta = 46.4$ for **8a** and $\delta = 47.7$ for **8b** whereas those of PGeP- and PSnP-complexes **4** and **5** appeared in almost the same region over $\delta = 50$. These data suggest that PSiP-pincer complexes exhibit the strongest trans influence and electron-donating ability among these PXP-pincer palladium complexes (X = Si, Ge, Sn). On the other hand, PGeP- and PSnP-complexes **4** and **5** possess wider coordination sphere around the palladium than PSiP-complex due to their longer bond length of the Pd–X bond (Pd–Si^{Me} = 2.2858(19) Å, Pd–Ge^{Me} = 2.3519(6) Å, Pd–Sn^{Me} = 2.5099(3) Å).

To assess the reactivity of these new PXP–palladium complexes, a reductive aldol-type reaction between α,β-unsaturated esters and aldehydes was investigated using **6a** (X = Ge), **7a** (X = Sn), and **9a** (X = Si) as a catalyst.[12] It was found that not only PSiP–palladium complex **9a**, which was reported to work as an excellent catalyst for reductive carboxylation reaction of allene and 1,3-dienes,[2a,2c] but also PGeP- and PSnP-complexes efficiently catalyzed this reaction. Thus, treatment of *p*-tolualdehyde (**10**), ethyl acrylate (**11**), and 1.5 equiv of $AlEt_3$ in the presence of 2.0 mol % of PSiP– or PSnP–palladium complex **9a** or **7a** in THF at 60 °C afforded β-hydroxyester **12** in good yield (Table 3, Entries 1 and 3), while the reaction by

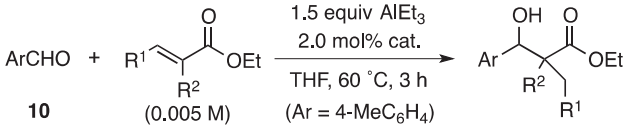
Table 2. Selected bond lengths, angles, and ^{31}P NMR data of **4**, **5**, and **8**



X	R		Pd–Cl/Å	Pd–X/Å	P1–Pd–P2 /degree	^{31}P NMR /ppm
Si	Me	**8a**	2.4414(17)	2.2858(19)	154.00(6)	46.4[a]
Ge	Me	**4a**	2.4219(11)	2.3519(6)	154.01(4)	51.4[b]
Sn	Me	**5a**	2.4270(8)	2.5099(3)	154.21(3)	50.2[b]
Si	Ph	**8b**[d]	2.4347(15)	2.2832(17)	156.21(6)	47.7[c]
			2.4291(15)	2.2835(17)	158.87(6)	
Ge	Ph	**4b**	2.4082(5)	2.3572(3)	161.49(2)	52.2[b]
Sn	Ph	**5b**[d]	2.4097(14)	2.5244(5)	160.54(5)	52.9[c]
			2.4150(14)	2.5212(5)	163.21(6)	

[a]In CD_2Cl_2. [b]In $CDCl_3$. [c]In C_6D_6. [d]Two independent molecules are present in the unit cell, and values for both molecules are listed.

Table 3. Reductive aldol-type reaction catalyzed by PXP–palladium



10 (0.005 M)
1.5 equiv

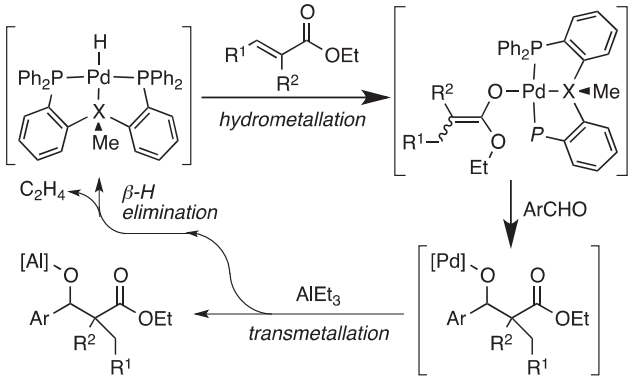
R^1 = H, R^2 = H **11**
R^1 = Me, R^2 = H **13**
R^1 = H, R^2 = Me **15**

R^1 = H, R^2 = H **12**
R^1 = Me, R^2 = H **14**
R^1 = H, R^2 = Me **16**

Entry	Cat.	X	Substrate	Product	Yield[a]/%
1	**9a**	Si	**11**	**12**	86
2	**6a**	Ge	**11**	**12**	49
3	**7a**	Sn	**11**	**12**	82
4	**9a**	Si	**13**	**14**	94
5	**6a**	Ge	**13**	**14**	54
6	**7a**	Sn	**13**	**14**	95
7	**9a**	Si	**15**	**16**	52
8	**6a**	Ge	**15**	**16**	47
9	**7a**	Sn	**15**	**16**	93

[a]dr = 65:35–72:28 for product **12** and **14**.

PGeP–palladium **6a** resulted in diminished yield (49%, Entry 2). The reaction was applicable to ethyl crotonate **13** as an enolate precursor to give aldol adduct **14** with the same trend of catalytic activity (Entries 4–6). Diastereoselectivity of **12** and **14** was moderate and was scarcely affected by the kind of the pincer ligand (Entries 1–6, dr = 65:35–72:28). Furthermore, it is noteworthy that PSnP–palladium **7a** showed higher activity than PSiP–palladium in the reaction of ethyl methacrylate (**15**) (PSiP-: 52%, PSnP-: 93%, Entries 7 and 9). Although further detailed mechanistic studies are necessary, these preliminary results may suggest that the wider coordination sphere around the palladium of the PSnP-complex facilitates hydrometallation and/or nucleophilic addition steps more efficiently in spite of the



Scheme 2. Proposed reaction mechanism.

stronger electron donation of the PSiP-ligand (Scheme 2). This is the first example of utilization of Ge- or Sn-containing multidentate ligand for a catalytic synthetic reaction.

In conclusion, we have developed an efficient method for the synthesis of tridentate PGeP– and PSnP–palladium complexes. Structural analysis revealed that PSiP-ligand exerts the strongest trans influence and electron donation and that PGeP- and PSnP-ligands provide wider coordination sphere around the palladium. Preliminary studies demonstrated that both PGeP– and PSnP–palladium complexes worked as an efficient catalyst for the reductive aldol-type reaction, indicating promising utility in synthetic organic chemistry. Further studies on the origin of difference of reactivity and synthetic application of these new PXP-pincer palladium complexes are ongoing in our laboratory.[13,14]

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5 Ito and Minato reported the formation of molybdenum complexes bearing a Ge-containing quinquidentate ligand by the reaction of $[(dppe)_2MoH_4]$ with $PhGeH_3$ or Ph_2GeH_2 (dppe: 1,2-bis(diphenylphosphino)ethane). See: M. Minato, D.-Y. Zhou, L.-B. Zhang, R. Hirabayashi, M. Kakeya, T. Matsumoto, A. Harakawa, G. Kikutsuji, T. Ito, *Organometallics* **2005**, *24*, 3434, and references cited therein.

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10 Crystallographic Data have been deposited with Cambridge Crystallographic Data Center as Supplementary Publication No. CCDC-892419 (for **4a**), 892420 (for **4b**), 892421 (for **5a**), 892422 (for **5b**), 892423 (for **8a**), and 892424 (for **8b**). Copies of the data can be obtained free of charge on application to CCDC, 12, Union Road, Cambridge, CB2 1EZ, U.K. (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

11 Synthesis of **8a** was previously reported in ref 1a; however, its structural analysis by X-ray has not been reported. Fine crystals of **8a** suitable for X-ray crystallography were obtained by recrystallization from CH_2Cl_2–Et_2O. **8b** was synthesized by the same procedure for the synthesis of **8a** using commercially available dichlorophenylsilane as a starting material. See Supporting Information for details.[13]

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13 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

14 After submission of this manuscript, synthesis of rhodium and iridium complexes bearing a PEP-type ligand (E = Ge or Sn) via E–C bond cleavage was reported by Nakazawa. See: H. Kameo, S. Ishii, H. Nakazawa, *Dalton Trans.* **2012**. Advance Article. doi:10.1039/C2DT30996C.

