

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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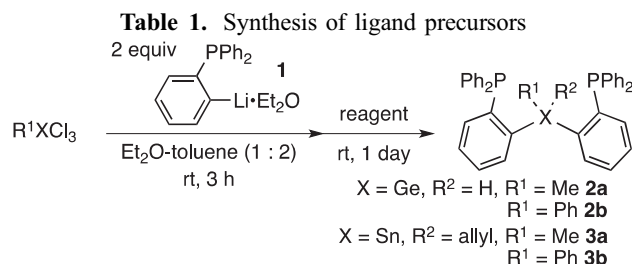
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An efficient method for the synthesis of tridentate PGeP- and PSnP-palladium complexes is developed. Structural analysis revealed that PSiP-ligand exerts the strongest trans influence and electron donation and that PGeP- and PSnP-ligands provide wider 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.

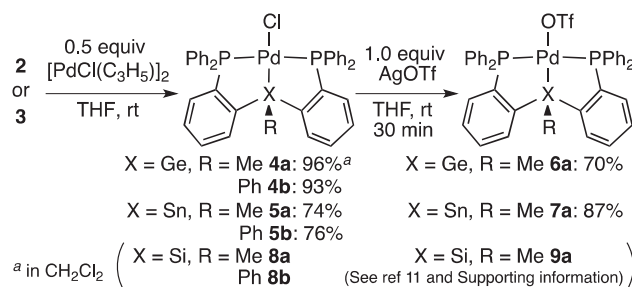
Transition-metal complexes bearing a tridentate PSiP-pincer ligand derived from bis(*o*-phosphinophenyl)silane have been attracting much attention in organometallic chemistry.^{1–3} The features of this type of PSiP-pincer ligand are 1) the strong trans influence of the silicon which enhances nucleophilicity of the *trans* substituent and 2) distorted square-planar structure due to the sp³-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 P₃Ge- or P₃Sn-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 LiAlH₄ 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 (Ar₂MeSnH) 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



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

^aThe reaction was carried out in Et₂O-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).

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).

Complexation of **2** or **3** with [Pd(C₃H₅)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 complexes¹⁰ **4a**, **4b**, **5a**, **5b**, **8a**, and **8b** and ORTEP diagrams of

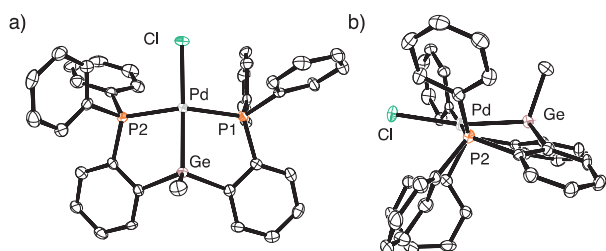


Figure 1. ORTEP drawing of **4a** at 50% probability level (hydrogen atoms are omitted for clarity). a) Top view. b) Side view.

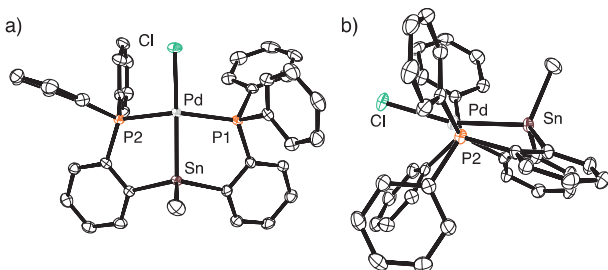


Figure 2. ORTEP drawing of **5a** at 50% probability level (hydrogen atoms are omitted for clarity). a) Top view. b) Side view.

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).

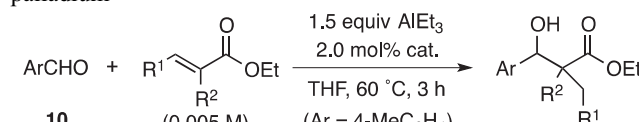
To assess the reactivity of these new PXP–palladium complexes, a reductive aldol-type reaction between α,β -unsaturated esters and aldehydes was investigated using **6a** (X = Ge), **7a** (X = Sn), and **9a** (X = Si) as a catalyst.¹² It was found that not only PSiP–palladium complex **9a**, which was 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**

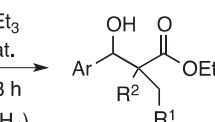
X	R		Pd–Cl/Å	Pd–X/Å	P1–Pd–P2 /degree	^{31}P NMR /ppm
Si	Me	8a	2.4414(17)	2.2858(19)	154.00(6)	46.4 ^a
Ge	Me	4a	2.4219(11)	2.3519(6)	154.01(4)	51.4 ^b
Sn	Me	5a	2.4270(8)	2.5099(3)	154.21(3)	50.2 ^b
Si	Ph	8b ^d	2.4347(15)	2.2832(17)	156.21(6)	47.7 ^c
			2.4291(15)	2.2835(17)	158.87(6)	
Ge	Ph	4b	2.4082(5)	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)	

^aIn CD_2Cl_2 . ^bIn CDCl_3 . ^cIn C_6D_6 . ^dTwo 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



1.5 equiv AlEt_3
2.0 mol% cat.
THF, 60 °C, 3 h
(Ar = 4-MeC₆H₄)



10

1.5 equiv

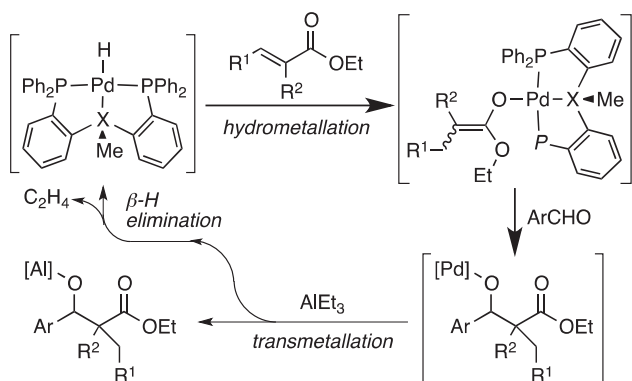
R¹ = H, R² = H **11**
R¹ = Me, R² = H **13**
R¹ = H, R² = Me **15**

R¹ = H, R² = H **12**
R¹ = Me, R² = H **14**
R¹ = H, R² = 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

^ddr = 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}

References and Notes

- 1 a) M. C. MacInnis, D. F. MacLean, R. J. Lundgren, R. McDonald, L. Turculet, *Organometallics* **2007**, *26*, 6522. b) E. E. Korshin, G. Leitus, L. J. W. Shimon, L. Konstantinovski, D. Milstein, *Inorg. Chem.* **2008**, *47*, 7177. c) D. F. MacLean, R. McDonald, M. J. Ferguson, A. J. Caddell, L. Turculet, *Chem. Commun.* **2008**, 5146. d) S. J. Mitton, R. McDonald, L. Turculet, *Angew. Chem., Int. Ed.* **2009**, *48*, 8568. e) E. Morgan, D. F. MacLean, R. McDonald, L. Turculet, *J. Am. Chem. Soc.* **2009**, *131*, 14234. f) S. J. Mitton, R. McDonald, L. Turculet, *Organometallics* **2009**, *28*, 5122. g) M. C. MacInnis, R. McDonald, M. J. Ferguson, S. Tobisch, L. Turculet, *J. Am. Chem. Soc.* **2011**, *133*, 13622. h) H. Fang, Y.-K. Choe, Y. Li, S. Shimada, *Chem.—Asian J.* **2011**, *6*, 2512. i) Y.-H. Li, Y. Zhang, X.-H. Ding, *Inorg. Chem. Commun.* **2011**, *14*, 1306. j) Y.-H. Li, X.-H. Ding, Y. Zhang, W.-R. He, W. Huang, *Inorg. Chem. Commun.* **2012**, *15*, 194.
- 2 a) J. Takaya, N. Iwasawa, *J. Am. Chem. Soc.* **2008**, *130*, 15254. b) J. Takaya, N. Iwasawa, *Organometallics* **2009**, *28*, 6636. c) J. Takaya, K. Sasano, N. Iwasawa, *Org. Lett.* **2011**, *13*, 1698. d) J. Takaya, N. Iwasawa, *Dalton Trans.* **2011**, *40*, 8814. e) J. Takaya, N. Kirai, N. Iwasawa, *J. Am. Chem. Soc.* **2011**, *133*, 12980.
- 3 P. Gualco, T.-P. Lin, M. Sircoglou, M. Mercy, S. Ladeira, G. Bouhadir, L. M. Pérez, A. Amgoune, L. Maron, F. P. Gabbaï, D. Bourissou, *Angew. Chem., Int. Ed.* **2009**, *48*, 9892.
- 4 For examples of other types of Si-containing multidentate phosphine ligands, see: M. S. Balakrishna, P. Chandrasekaran, P. P. George, *Coord. Chem. Rev.* **2003**, *241*, 87.
- 5 Ito and Minato reported the formation of molybdenum complexes bearing a Ge-containing quinquidentate ligand by the reaction of [(dppe)₂MoH₄] with PhGeH₃ or Ph₂GeH₂ (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.
- 6 a) Y. Cabon, H. Kleijn, M. A. Siegler, A. L. Spek, R. J. M. K. Gebbink, B.-J. Deelman, *Dalton Trans.* **2010**, *39*, 2423. b) E. Brendler, E. Wächter, T. Heine, L. Zhechkov, T. Langer, R. Pöttgen, A. F. Hill, J. Wagler, *Angew. Chem., Int. Ed.* **2011**, *50*, 4696, and references cited therein.
- 7 a) H. Kameo, S. Ishii, H. Nakazawa, *Organometallics* **2012**, *31*, 2212. b) H. Kameo, S. Ishii, H. Nakazawa, *Dalton Trans.* **2012**, *41*, 8290.
- 8 N. Selander, K. J. Szabó, *Chem. Rev.* **2011**, *111*, 2048.
- 9 a) H. Nakamura, H. Iwama, Y. Yamamoto, *J. Am. Chem. Soc.* **1996**, *118*, 6641. b) M. Shi, K. M. Nicholas, *J. Am. Chem. Soc.* **1997**, *119*, 5057.
- 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 CH₂Cl₂–Et₂O. **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
- 12 For a review of reductive aldol-type reactions catalyzed by transition-metal catalyst, see: H. Nishiyama, T. Shiomi, in *Metal Catalyzed Reductive C–C Bond Formation: A Departure from Preformed Organometallic Reagents in Topics in Current Chemistry*, ed. by M. J. Krische, Springer-Verlag, Berlin, **2007**, Vol. 279, pp. 105–137. doi:10.1007/128.2007.126.
- 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.