

cyclooctadiene (1,5-COD) is reacted with 1.

In conclusion, the coordination of the $C_5Me_4CH_2CH_2CH=CH_2$ ligand at monovalent cobalt centers indicates that chelate effects can be unexpectedly strong for supposedly labile metal-ligand interactions. Using this ligand, we are currently exploring the possibility of observing reactions of transition metals with a C-C double bond which would not proceed intermolecularly.

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Supplementary Material Available: Text giving the full experimental procedure for the synthesis of 1 as well as complete analytical and spectroscopic data for 1, 5, and 6 (4 pages). Ordering information is given on any current masthead page.

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Palladium-Catalyzed Chemoselective and Site-Selective Reduction of (Z)-1,3-Bis(arylseleno)-2-alken-1-ones with *n*-Bu₃SnH

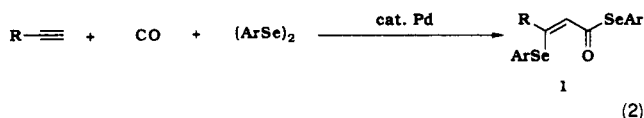
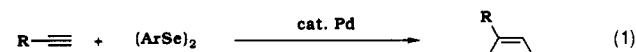
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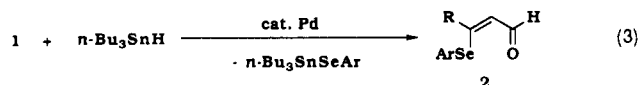
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Summary: Palladium complexes effectively catalyze the reduction of (Z)-1,3-bis(arylseleno)-2-alken-1-ones with tri-*n*-butyltin hydride. The terminal arylseleno group is selectively reduced to afford the corresponding aldehydes in good yields.

It is well-known that selenides serve as ligands for various transition metals;¹ however, transition-metal-catalyzed synthetic reactions using organic selenides as substrates have been scarcely explored.² The lack of investigation in this area is probably due to the widespread prejudice that chalcogen compounds are poisons for transition-metal catalysts. Recently, we have discovered that palladium complexes successfully catalyze the addition (eq 1) and the carbonylative addition (eq 2) of diaryl diselenides to terminal acetylenes.³ These reactions proceed with high stereo- and regioselectivity to give (Z)-1,2-bis(arylseleno)-1-alkenes and (Z)-1,3-bis(arylseleno)-2-alken-1-ones (1), respectively.



We now report the palladium-catalyzed chemoselective and site-selective reduction of 1 with tri-*n*-butyltin hydride to provide the (Z)-3-(arylseleno)-2-alkenals 2 in high yields (eq 3).^{4,5}



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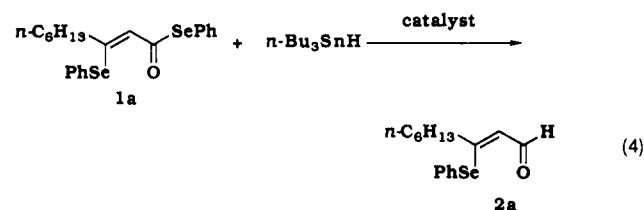
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Table I. Effects of Catalysts on the Reduction of 1a with *n*-Bu₃SnH^c

entry no.	catalyst (amt, mol %)	time of addition, min	yield of 2a, ^b %	E:Z ^b
1	Pd(PPh ₃) ₄ (0.4)	5	91 ^c	only Z
2	PPh ₃ (8.0)		d	
3	none		d	
4	Pd(PPh ₃) ₄ (0.01)	25	94	2:98
5	Pd(PPh ₃) ₄ (0.001)	30	45	1:99
6	Pd(PPh ₃) ₂ Cl ₂ (2.0)	3	85	1:99
7	Pd(OAc) ₂ (5.0)	3	45	1:99

^a *n*-Bu₃SnH (1.0–1.4 equiv) was added to a benzene (or benzene-*d*₆) solution of 1a (0.05–0.1 M) and catalyst at 25 °C. ^b Determined by ¹H NMR. ^c Isolated yield. ^d No reaction.

Table I summarizes the results of the reaction of (Z)-1,3-bis(phenylseleno)-2-nonen-1-one (1a) with *n*-Bu₃SnH under several reaction conditions. When the reaction of 1a with *n*-Bu₃SnH was carried out in the presence of 0.4 mol % of Pd(PPh₃)₄, the reduction took place to give (Z)-3-(phenylseleno)-2-nonenal (2a) in 91% yield (eq 4,



entry 1 in Table I).^{6,7} The carbon-carbon double bond

(4) For an overview of reductions with organotin reagents, see: Perreyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1987.

(5) For an example of the synthetic utility of 2, see: Arrua, E. P.; Comasseto, J. V. *Synth. Commun.* 1991, 21, 1663.

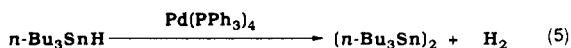
(6) Procedure: Into a two-necked flask equipped with an addition funnel and a magnetic stirring bar were placed 1a (450 mg, 1.0 mmol), Pd(PPh₃)₄ (4.4 mg, 0.0038 mmol), and benzene (20 mL) under an argon atmosphere. Then, a solution of *n*-Bu₃SnH (1.0 mmol in 10 mL of benzene) was added from the addition funnel over a period of 5 min. The reaction mixture was concentrated and subjected to MPLC (hexane/Et₂O as eluent) to give 270 mg (91%) of 2a as a yellow oil. Data for 2a: yellow oil; ¹H NMR (270 MHz, CDCl₃) δ 0.81 (t, *J* = 7.1 Hz, 3 H), 1.01–1.23 (m, 6 H), 1.40 (m, 2 H), 2.27 (t, *J* = 5.6 Hz, 2 H), 6.53 (d, *J* = 4.4 Hz, 1 H), 7.35–7.41 (m, 3 H), 7.62 (d, *J* = 6.8 Hz, 2 H), 9.87 (d, *J* = 4.4 Hz, 1 H) (NOE experiment: irradiation of the methylene triplet at δ 2.27 resulted in a 15% enhancement of the vinyl doublet at δ 6.53); ¹³C NMR (68 MHz, CDCl₃) δ 13.96, 22.36, 28.41, 29.55, 31.27, 38.57, 125.05, 127.39, 129.13, 129.32, 136.39, 166.57, 189.80; IR (NaCl) 3056, 2955, 2928, 2856, 2742, 1671, 1534, 694, 742 cm⁻¹; mass spectrum (EI) *m/e* 296 (M⁺, 97). Anal. Calcd for C₁₅H₂₀OSe: C, 61.01; H, 6.83. Found: C, 60.96; H, 6.81.

Table II. Palladium-Catalyzed Reduction of 1 with *n*-Bu₃SnH^a

entry no.	substrate	product	yield, % ^b	<i>E:Z</i> ^c
1			90	2:98
2			93	2:98
3			90	4:96
4			42 ^d	8:92
5			87	0:100
6 ^e			79	<i>Z,E:Z,Z</i> = 2:98
7 ^f			69 ^e	

^a *n*-Bu₃SnH (1.0 equiv) was added to a benzene solution of 1 and 0.4 mol % of Pd(PPh₃)₄ over a period of 3–17 min at 25 °C; see ref 6. ^b Isolated yield. ^c Determined by ¹H NMR. ^d Besides 2e, a complex mixture was formed. ^e *n*-Bu₃SnH (2.0 equiv) was added over a period of 50 min. ^f 2.4 equiv of *n*-Bu₃SnH was added to a benzene-*d*₆ solution of 1'h over a period of 10 min.

as well as the phenylseleno group attached to the vinylic carbon was scarcely reduced,⁸ and neither decarbonylative product nor ester⁹ was detected. In the absence of catalyst or presence of 8 mol % of PPh₃, the reduction did not occur under similar reaction conditions (entries 2 and 3).¹⁰ The amount of palladium catalyst can be lessened by 0.01 mol % for 1a (entry 4). Further decrease of the catalyst (0.001 mol %) led to a low yield of 2a (entry 5), because the competitive palladium-catalyzed decomposition of tri-*n*-butyltin hydride into hexabutyldistannane (eq 5)



cannot be suppressed.¹¹ Pd(PPh₃)₂Cl₂ and Pd(OAc)₂ also catalyzed the reduction of 1a to 2a (entries 6 and 7).¹² For

(7) For the palladium-catalyzed reduction of acid chloride with tin hydride, see: (a) Four, P.; Guibe, F. *J. Org. Chem.* 1981, 46, 4439. (b) Guibe, F.; Four, P.; Riviere, H. *J. Chem. Soc., Chem. Commun.* 1980, 432.

(8) When 2 equiv of *n*-Bu₃SnH was added to a solution of 1a and Pd(PPh₃)₄, overreduction from 2a took place to produce (*E*)-2-nonenal and nonanal in 10% and 25% yields, respectively. For the palladium-catalyzed reduction of α,β -unsaturated aldehydes, see: Keinan, E.; Gleize, P. A. *Tetrahedron Lett.* 1982, 23, 477.

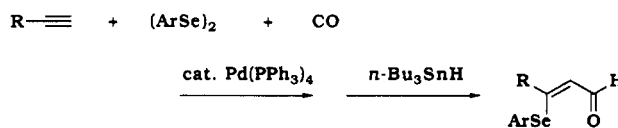
(9) (a) Kuivila, H. G.; Walsh, E. J., Jr. *J. Am. Chem. Soc.* 1966, 88, 571. (b) Walsh, E. J., Jr.; Kuivila, H. G. *J. Am. Chem. Soc.* 1966, 88, 576.

(10) These reactions were carried out using benzene-*d*₆ as a solvent and analyzed by ¹H NMR spectroscopy directly without concentration of the reaction mixture, because the reduction of 1a proceeded even in the absence of catalyst under higher concentrations. For example, the reduction of 1a (1 M solution of benzene-*d*₆) with *n*-Bu₃SnH (1.1 equiv) took place at room temperature for 1 h to give 2a in 39% yield, although the decomposition of *n*-Bu₃SnH into (*n*-Bu₃Sn)₂ occurred competitively. For a detailed investigation about the mechanism of the reduction of acid chloride with tin hydride under high concentration, see: (a) Luszyk, J.; Luszyk, E.; Maillard, B.; Lunazzi, L.; Ingold, K. U. *J. Am. Chem. Soc.* 1983, 105, 4475. (b) Luszyk, J.; Luszyk, E.; Maillard, B.; Ingold, K. U. *J. Am. Chem. Soc.* 1984, 106, 2923.

(11) Gas evolution was confirmed during the addition of *n*-Bu₃SnH.

(12) Pt(PPh₃)₄, Ni(PPh₃)₂Cl₂, Rh(PPh₃)₃Cl, and Ru₃(CO)₁₂ did not exhibit catalytic activity for the reduction of 1a with *n*-Bu₃SnH.

Scheme I



the reduction of selenoesters with *n*-Bu₃SnH to give aldehydes, an AIBN-initiated radical reaction has already been reported.¹³ When the AIBN-initiated reaction system was applied to the reduction of 1a, a similar chemoselective reduction also took place. However, the reaction proceeded sluggishly, accompanied by the isomerization of the C–C double bond.¹⁴

Table II summarizes the results of palladium-catalyzed reduction of some other (*Z*)-1,3-bis(arylseleno)-2-alken-1-ones (1) with *n*-Bu₃SnH. Electron-donating and -withdrawing substituents on the ArSe groups did not have a significant effect on the yields of the products (entries 1 and 2).¹⁵ The reduction of 1e, which has olefinic and ester units, afforded the corresponding enal 2e in 42% yield together with an undetermined complex mixture (entry 4). The reduction of 1'h (synthesized from the reaction of the corresponding acid chloride with PhSeLi) also proceeded to give nonanal in moderate yield with the competitive decomposition of tri-*n*-butyltin hydride to hexabutyldistannane (entry 7). This result suggests the generality of this palladium-catalyzed reduction of sele-

(13) Pfenninger, J.; Heuberger, C.; Graf, W. *Helv. Chim. Acta* 1980, 63, 2328.

(14) After the benzene-*d*₆ solution of 1a (0.025 M), *n*-Bu₃SnH (1.5 equiv), and AIBN (18 mol %) was refluxed for 5 h, the formation of 2a (67%, *E:Z* = 9:91) was confirmed by ¹H NMR.

(15) The competitive reaction of 1b (0.5 mmol) and 1c (0.5 mmol) with 0.2 mmol of *n*-Bu₃SnH under otherwise identical conditions gave a mixture of 2b and 2c in the ratio of 0.34:1.

noesters with tri-*n*-butyltin hydride to give aldehydes, although 1^h is less reactive compared with (*Z*)-1,3-bis(arylseleno)-2-alken-1-ones (1).

The palladium-catalyzed carbonylative addition of terminal acetylene (eq 2) and the reduction of 1 by *n*-Bu₃SnH (eq 3) can be carried out successively without isolation of 1.¹⁶ This one-pot transformation from acetylene to 2 is synthetically equivalent to regio- and stereoselective selenoformylation of acetylene (Scheme I).

The present investigation provides the first example of transition-metal-catalyzed reduction of selenoesters with tin hydride to aldehydes: (*Z*)-1,3-bis(arylseleno)-2-alken-1-ones are converted into (*Z*)-3-(arylseleno)-2-alkenals with excellent chemoselectivity and site selectivity in high yields

under moderate reaction conditions. This paper also reveals the utility of transition-metal catalysts in synthetic reactions using chalcogen compounds.¹⁷

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Supplementary Material Available: Text giving experimental details and analytical and spectroscopic data for the compounds formed (4 pages). Ordering information is given on any current masthead page.

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(17) We have recently reported the transition-metal-catalyzed hydrothiolation and hydroselemination of acetylenes; see: (a) Kuniyasu, H.; Ogawa, A.; Sato, K.; Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* 1992, 114, 5902. (b) Kuniyasu, H.; Ogawa, A.; Sato, K.; Ryu, I.; Sonoda, N. *Tetrahedron Lett.* 1992, 33, 5525.

(16) For example, in a 50 mL stainless steel autoclave were placed 1-octyne (1.0 mmol), (PhSe)₂ (1.0 mmol), Pd(PPh₃)₄ (23 mg, 0.02 mmol), and benzene (0.5 mL). After the mixture was stirred for 18 h at 80 °C under pressurized CO (20 kg/cm²), CO was purged and benzene (15 mL) was added to the reaction mixture. Then *n*-Bu₃SnH (1.0 mmol) was added over a period of 5 min under a flow of argon. The reaction mixture was filtered through Celite and concentrated in vacuo. The formation of 2a was confirmed by ¹H NMR spectroscopy (86%, *E:Z* = 11:89).

Organometallic Molecule–Inorganic Surface Coordination and Catalytic Chemistry. Facile and Selective Alkane Activation by Supported Tetraallylthorium

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Summary: The adsorption of Th(η^3 -allyl)₄ on dehydroxylated alumina yields an active catalyst for the exchange of alkane and cycloalkane C–H bonds with D₂. C–H reactivities fall in the order primary > secondary > tertiary and less sterically hindered > more sterically hindered.

Although significant advances have been made in the activation of C–H bonds by *f*-element/early-transition-element^{1,2} and middle-/late-transition-element^{1,3} complexes, closing cycles which effect the catalytic intermolecular activation of relatively inert alkane molecules with favorable rates and selectivities remains a major challenge. For organo-*f*-element/early-transition-element complexes,

key questions concern whether catalytic processes may be insurmountably constrained by intrinsic electronic, steric, or other factors (e.g., inactivating side reactions) or whether activities higher than heretofore observed^{1,2} are possible. We have recently shown that adsorption of organothorium complexes on Lewis acidic surfaces such as dehydroxylated alumina (DA) affords highly electrophilic molecular surface species⁴ which are active olefin hydrogenation and polymerization catalysts.^{5,6} Activity scales approximately as catalyst precursor coordinative unsaturation, with Th(η^3 -allyl)₄/DA mediating traditionally demanding arene hydrogenation at rates rivaling those of supported platinum metal catalysts.⁷ We now report that Th(η^3 -al-

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