diphenylcyclopropene to form vinylcarbenes and that the resulting complexes do indeed react with strained olefins. Unfortunately, due to the bridging nature of the alkylidene, activity toward olefin metathesis is greatly diminished compared to that for 2.

Acknowledgment. We thank Du Pont Chemicals and the NSF for financial support. In addition, we thank Dr. Paul Fagan of Du Pont CR&D for helpful discussions as well as a loan of starting material.

Supplementary Material Available: Text describing the X-ray diffraction study and tables of crystal data and data collection and refinement details, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen positions with isotropic *U* values (15 pages). Ordering information is given on any current masthead page.

OM920518E

An Unexpectedly Strong Chelate Effect in a Cobalt Half-Sandwich Complex with an Intramolecularly Coordinated C–C Double Bond

K. Heinz Zimmermann,[1a] Robert S. Pilato,[1b] István T. Horváth,[1b] and Jun Okuda*,[1a,c]

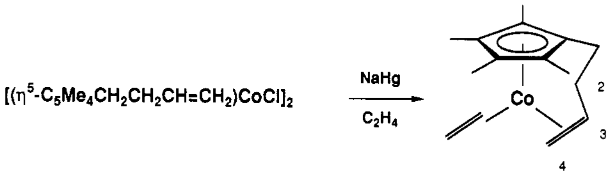
Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4,
D-8046 Garching, Federal Republic of Germany, and Corporate Research Laboratories,
Exxon Research and Engineering Company, Annandale, New Jersey 08801

Received August 20, 1992

Summary: A pronounced chelate effect is observed in the cobalt half-sandwich complex **1**, bearing an intramolecularly coordinated 3-butenyl side chain. The chelating C–C double bond is only slowly cleaved under ethylene pressure of 36 atm to form the bis(ethylene) complex **2**. Two-electron ligands CO, P(OMe)$_3$, and dimethyl fumarate give chelate complexes **3**–**5**, whereas the bidentate ligand 1,5-cyclooctadiene affords the "open-chain" complex **6**.

Polydentate ligands containing two types of inequivalent donors, one firmly bound to a metal center and another weakly bonded, which can temporarily block and protect a metal coordination site, hold promise as a novel class of ligands for homogeneous catalysts.[2] For example, phosphine ligands with tethered functional groups that form labile bonds to a transition-metal center have been reported in the literature.[2,3] Such ligands appear to allow intramolecular control of coordinative unsaturation. We have been investigating the possibility of extending the concept of these so-called "semilabile" ligands[2] to functionally substituted cyclopentadienyl ligands.[4] Due to the lability of the cobalt–ethylene bond, bis(olefin)cobalt complexes of the type $(\eta^5\text{-}C_5R_5)Co(\eta^2\text{-}C_2H_4)_2$ (R = H,[5a] Me[5b]) have been extensively used as a source for the 14-electron fragment $(\eta^5\text{-}C_5R_5)Co$, in particular as catalyst precursors for cobalt-mediated [2 + 2 + 2]-cycloaddition reactions.[6] We therefore sought to combine the anchoring effect of the cyclopentadienyl ligand with the lability of a C–C double bond and had previously described the design and synthesis of the 1-(3-butenyl)-2,3,4,5-tetramethylcyclopentadienyl ligand, in which an alkene functionality is tethered to the five-membered-ring ligand.[4,7,8] Herein, we report the synthesis and reactivity of the ethylene complex $(\eta^5{:}\eta^2\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)Co(\eta^2\text{-}C_2H_4)$ (1) and the observation of an unexpected chelate effect of this ligand system.

Reduction of $[(\eta^5\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)CoCl]_2$[4] by sodium amalgam under an atmosphere of ethylene affords the ethylene complex $(\eta^5{:}\eta^2\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)Co(\eta^2\text{-}C_2H_4)$ (1)[9] in about 80% yield (eq 1). ^1H and ^{13}C NMR



1

(1)

---

(1) (a) Technische Universität München. (b) Exxon Research and Engineering Co. (c) New address: Department of Chemistry, State University of New York at Albany, Albany, NY 12222.

(2) Bader, A.; Lindner, E. *Coord. Chem. Rev.* **1991**, *108*, 27.

(3) Mason, M. R.; Verkade, J. G. *Organometallics* **1992**, *11*, 1514 and references therein.

(4) (a) Okuda, J.; Herdtweck, E.; Zimmermann, K. H. In *Organic Synthesis via Organometallics*; Dötz, K. H., Hoffmann, R. W., Eds.; Vieweg: Braunschweig, Germany, 1991; p 207. (b) Okuda, J.; Zimmermann, K. H.; Herdtweck, E. *Angew. Chem.* **1991**, *103*, 446; *Angew. Chem., Int. Ed. Engl.* **1992**, *30*, 430. (c) Okuda, J.; Zimmermann, K. H. *Chem. Ber.* **1992**, *125*, 637.

(5) (a) Jonas, K.; Deffense, E.; Habermann, D. *Angew. Chem.* **1983**, *95*, 729; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 716; *Angew. Chem., Suppl.* **1983**, 1005. (b) Green, M. L. H.; Pardy, R. B. A. *J. Chem. Soc., Dalton Trans.* **1979**, 355. Beevor, R. G.; Frith, S. A.; Spencer, F. L. *J. Organomet. Chem.* **1981**, *221*, C25. Koelle, U.; Khouzami, F.; Fuss, B. *Angew. Chem.* **1982**, *94*, 132; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 131; *Angew. Chem., Suppl.* **1982**, 232.

(6) (a) Vollhardt, K. P. C. *Angew. Chem.* **1984**, *96*, 525; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539. (b) Boennemann, H. *Angew. Chem.* **1985**, *97*, 264; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 248.

(7) (a) Okuda, J.; Zimmermann, K. H. *J. Organomet. Chem.* **1988**, *344*, C1. (b) Okuda, J.; Zimmermann, K. H. *Chem. Ber.* **1989**, *122*, 1645; **1990**, *123*, 1641.

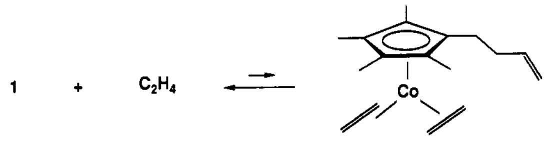
(8) (a) Miguel-Garcia, J. A.; Adams, H.; Bailey, N. A.; Maitlis, P. M. *J. Organomet. Chem.* **1991**, *413*, 427. (b) Lehmkuhl, H.; Naeser, J.; Mehler, G.; Keil, T.; Danowski, F.; Benn, R.; Mynott, R.; Schroth, G.; Gabor, B.; Krüger, C.; Betz, P. *Chem. Ber.* **1991**, *124*, 441. (c) Dötz, K. H.; Rott, J. *J. Organomet. Chem.* **1988**, *338*, C11. For a 3-butenyl-substituted carborane ligand, see: Delaney, M. S.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1981**, *20*, 1341.

(9) $(\eta^5{:}\eta^2\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)Co(\eta^2\text{-}C_2H_4)$ (1): Crude $[(\eta^5\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)CoCl]_2$ (1.46 g, 5.4 mmol) was dissolved in 50 mL of THF and treated at −50 °C with 195 g of sodium amalgam (1% Na, 85 mmol). The reaction mixture was saturated with ethylene, warmed to room temperature, and vigorously stirred for 2 h under an atmosphere of ethylene. Evaporation of all volatiles followed by extraction with pentane, filtration through Kieselguhr, and concentration afforded after recrystallization 2.40 g of red brown crystals (76% based on $Li(C_5Me_4CH_2CH_2CH{=}CH_2)$): mp 83 °C; ^1H NMR (C_6D_6; 25 °C) δ 0.35 [d, ^3J(H,H) = 8.5 Hz, 1 Hz, C_2H_4], 0.50 [dd, ^3J(H,H) = 9.1 Hz, ^3J(H,H) = 13.0 Hz, 1 H, C_2H_4], 0.80 (s, 3 H, CH_3), 1.37 [dd, ^3J(H,H) = 9.1 Hz, ^3J(H,H) = 13.0 Hz, 1 H, C_2H_4], 1.53 [d, ^3J(H,H) = 8.5 Hz, 1 H, C_2H_4], 1.55 (m, 2 H, CH_2-1), 1.64 (s, 3 H, CH_3), 1.84 [d, ^3J(H,H) = 9.2 Hz, 1 H, CH_2-4 (cis)], 1.90 [d, ^3J(H,H) = 12.8 Hz, 1 H, CH_2-4 (trans)], 1.91 (s, 3 H, CH_3), 2.27 (m, 1 H, CH_2-2), 2.41 (s, 3 H, CH_3), 2.67 (m, 1 H, CH-3), 3.23 (m, 1 H, CH_2-2); ^{13}C NMR (C_6D_6; 25 °C) δ 7.13, 10.08 (double intensity), 11.33 [q, ^1J(C,H) = 126 Hz, CH_3], 19.88 [t, ^1J(C,H) = 127 Hz, C-1], 39.52 [t, ^1J(C,H) = 124 Hz, C-2], 43.45 [t, ^1J(C,H) = 153 Hz, C_2H_4], 44.29 [t, ^1J(C,H) = 153 Hz, C_2H_4], 46.01 [t, ^1J(C,H) = 150 Hz, C-4], 68.56 [d, ^1J(C,H) = 155 Hz, C-3], 91.42, 92.67, 92.72, 96.69, 103.23 (ring C); EI MS m/z 262 (11%, M^+), 234 (100%, $M^+ - C_2H_4$), 192 (75%, $M^+ - C_2H_4 - C_3H_6$). Anal. Calcd for $C_{15}H_{23}Co$: C, 68.69; H, 8.84; Co, 22.47. Found: C, 68.61; H, 8.80; Co, 21.80.

0276-7333/92/2311-3935$03.00/0

spectra unambiguously verify the presence of a chelating ligand system with the tethered 3-butenyl group coordinated to the cobalt center. Variable-temperature ^{1}H NMR spectroscopy has revealed that the η^5:η^2-$C_5Me_4CH_2CH_2CH{=}CH_2$ ligand is rigidly bound to the monovalent cobalt center[7b,8] and that the two enantiofaces of the C–C double bond remain fixed (i.e. no racemization of chiral **1** takes place) on the NMR time scale.[10]

When a toluene-d_8 solution of **1** is left standing in a 5-mm sapphire tube[11] under 36 atm of ethylene pressure and at room temperature for 10 days, partial conversion (~50%) of **1** to the bis(ethylene) complex (η^5-$C_5Me_4CH_2CH_2CH{=}CH_2$)Co(η^2-C_2H_4)$_2$ (**2**)[12,13] is observed by ^{13}C NMR. Upon removal of the ethylene pressure, **2** is nearly completely converted to **1** within 24 h. This suggests that under ethylene pressure an equilibrium between **1** and **2** exists, as shown in eq 2. However, it is unfortunately established too slowly to allow a convenient quantitative measurement at this time. This behavior explains why isolation of **2** in the pure state has so far not been successful, although **2** can easily be distinguished from **1** by NMR spectroscopy. In the ^{1}H NMR spectrum of **2** the two rotationally rigid ethylene ligands give rise to two ABB′A′ multiplets centered at δ 0.99 and 1.72, whereas the three vinylic protons of the 3-butenyl chain appear at lower field, clearly indicating that decomplexation of the C–C double bond had taken place. As expected, the ^{13}C NMR spectrum reveals only one triplet at δ 45.00 with J(CH) = 154 Hz for the two ethylene carbon atoms.



(2)

2

The difference between the ligand dissociation enthalpy of C_2H_4 and that of the olefinic side chain is expected to be marginal. It has been shown, by EHMO calculations, that the total energy of CpCo(η^2-C_2H_4) does not significantly vary with the angle at the cobalt center between the Cp centroid and the C–C double bond.[14] Therefore, the apparently sluggish reaction of the olefinic functionality in the $C_5Me_4CH_2CH_2CH{=}CH_2$ ligand at the monovalent cobalt center has to be ascribed to the entropically derived chelate effect.[15]

Scheme I

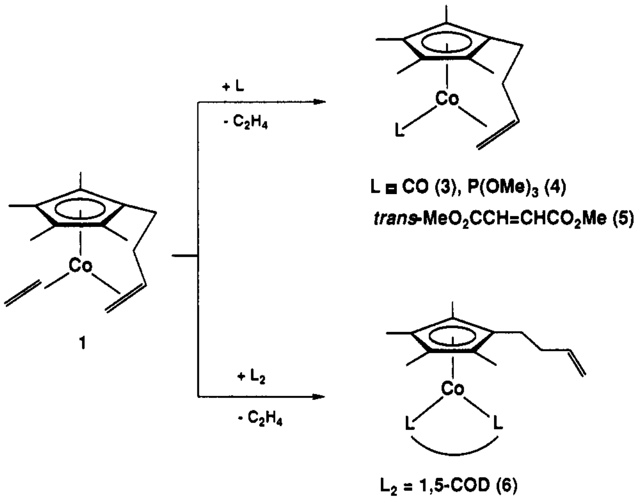
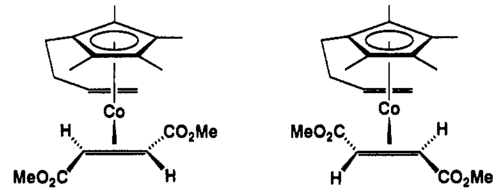


Chart I



In keeping with the above observation, simple two-electron donors such as carbon monoxide and trimethyl phosphite smoothly displace the ethylene ligand of **1** in refluxing hexane with complete preservation of the chelate structure to afford the corresponding complexes **3** and **4** of the type (η^5:η^2-$C_5Me_4CH_2CH_2CH{=}CH_2$)Co(L)[4b,7b] (Scheme I). With dimethyl fumarate[16] **1** gives the monosubstitution product **5** in quantitative yield, which can be shown by NMR spectroscopy to be a mixture of two isomers in the ratio 67:33.[17] We suspect that two diastereomers have been formed due to partial differentiation of the alkene enantioface by the chiral (η^5:η^2-$C_5Me_4CH_2CH_2CH{=}CH_2$)Co fragment during the substitution step (Chart I). In contrast, strongly chelating ligands can compete with the side chain for the coordination site. For example, **6** is readily formed when 1,5-

---

(10) The detection of four separate ^{1}H resonances indicates slow rotation of the ethylene ligand about the cobalt–ligand axis. If fast rotation occurred, an ABA′B′ pattern (exchange of trans protons) would be expected. In the case of a fast dissociation of the chelating 3-butenyl function, an ABB′A′ pattern (exchange of cis protons) should be observed: Benn, R. *Org. Magn. Reson.* **1983**, *21*, 723. For a similar case, see: Curnow, O. J.; Hughes, R. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 3135.

(11) Horvâth, I. T.; Millar, J. M. *Chem. Rev.* **1991**, *91*, 1339. Horvâth, I. T.; Ponce, E. C. *Rev. Sci. Instrum.* **1991**, *62*, 1104.

(12) (η^5-$C_5Me_4CH_2CH_2CH{=}CH_2$)Co(η^2-C_2H_4)$_2$ (**2**): ^{1}H NMR (C_6D_6; 25 °C) δ 0.99 [m, ^3J(H,H) = 12.8 Hz, ^3J(H,H) = 8.7 Hz, 4 H, C_2H_4], 1.34, 1.45 (s, 6 H, CH_3), 1.72 [m, ^3J(H,H) = 12.8 Hz, ^3J(H,H) = 8.7 Hz, 4 H, C_2H_4], 2.07 (m, 2 H, CH_2-2), 2.21 [t, ^3J(H,H) = 7.9 Hz, 2 H, CH_2-1], 4.94 [d, ^3J(H,H) = 10.4 Hz, 1 H, CH_2-4 (cis)], 5.00 [d, ^3J(H,H) = 17.1 Hz, 1 H, CH_2-4 (trans)], 5.75 (m, 1 H, CH-3); ^{13}C NMR (C_6D_6; 25 °C) δ 8.99, 9.31 [q, ^1J(C,H) = 126 Hz, CH_3), 25.07 [t, ^1J(C,H) = 126 Hz, C-1], 32.12 [t, ^1J(C,H) = 135 Hz, C-2], 45.00 [t, ^1J(C,H) = 154 Hz, C_2H_4], 91.74, 96.12, 100.65 (s, ring C), 114.87 [t, ^1J(C,H) = 156 Hz, C-4], 138.51 [d, ^1J(C,H) = 151 Hz, C-3].

(13) When $^{13}C_2H_4$ (99.5%) is employed, the formation of a mixture containing **1**, **1**-$^{13}C_2$, **2**-$^{13}C_2$, and **2**-$^{13}C_4$ is observed. **1**-$^{13}C_2$: ^{13}C{^{1}H} NMR (toluene-d_8, 25 °C) δ 43.57, 44.41 (AB pattern, ^1J(CC) = 44 Hz, C_2H_4). For other examples of reports on ^1J(CC) of an alkene coordinated to a transition metal, see: Fitch, J. W.; Ripplinger, E. B.; Shoulders, B. A.; Sorey, S. D. *J. Organomet. Chem.* **1988**, *352*, C25. Brookhart, M.; Volpe, A. F., Jr.; Lincoln, D. M.; Horvâth, I. T.; Millar, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 5634. Johnson, T. J., Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1992**, *114*, 2725.

(14) Hofmann, P. Unpublished results. See also: Hofmann, P.; Padmanabhan, M. *Organometallics* **1983**, *2*, 1273. For EHMO calculations of CpCo(η^2-C_2H_4)$_2$, see: Benn, R.; Cibura, K.; Hofmann, P.; Jonas, K.; Rufinska, A. *Organometallics* **1985**, *4*, 2214. Albright, T. A.; Geiger, W. E.; Moraczewski, J.; Tulyathan, B. *J. Am. Chem. Soc.* **1981**, *103*, 4787.

(15) Preliminary experiments with the homologous 1-(4-pentenyl)-2,3,4,5-tetramethylcyclopentadienyl ligand system indicate that the reaction analogous to eq 1 gives a 1:1 mixture of the chelate (η^5:η^2-$C_5Me_4CH_2CH_2CH_2CH{=}CH_2$)Co($\eta^2$-$C_2H_4$) and "open chain" complex (η^5-$C_5Me_4CH_2CH_2CH_2CH{=}CH_2$)Co($\eta^2$-$C_2H_4$)$_2$: Okuda, J.; Zimmermann, K. H. Unpublished results. See also ref 8b.

(16) Dimethyl maleate results in the isolation of the same product mixture. Presumably a metal-induced cis–trans isomerization of the alkene takes place prior to the ligand substitution. See: Okuda, J.; Herberich, G. E. *Organometallics* **1987**, *6*, 2331 and references therein.

(17) The ratio of the isomers remains unchanged after 24 h at 110 °C in contrast to the case of the thoroughly studied chiral (alkene)rhenium complexes: Bodner, G. S.; Fernandez, J. M.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 4082. Bodner, G. S.; Fernandez, J. M.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1990**, *9*, 1191. Peng, T.-S.; Arif, A. M.; Gladysz, J. A. *Helv. Chim. Acta* **1992**, *75*, 442. Peng, T.-S.; Gladysz, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 4174.

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 *inter*molecularly.

Acknowledgment. Financial support by the Volkswagen-Stiftung, the Fonds der Chemischen Industrie, and the Leonhard-Lorenz-Stiftung, Technische Universität München, is gratefully acknowledged. We thank Prof. Peter Hofmann for various discussions. J.O. is grateful to the State University of New York at Albany for providing a facility to complete this work.

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.

OM9205152

Palladium-Catalyzed Chemoselective and Site-Selective Reduction of (*Z*)-1,3-Bis(arylseleno)-2-alken-1-ones with *n*-Bu_3SnH

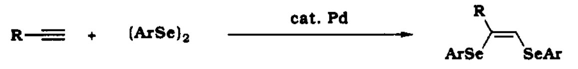
Hitoshi Kuniyasu, Akiya Ogawa,* Keigo Higaki, and Noboru Sonoda*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

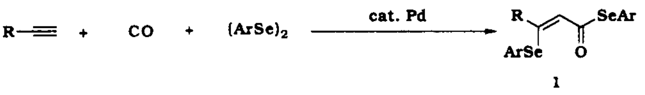
Received September 3, 1992

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.



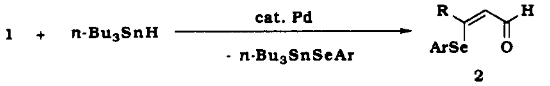
(1)



1

(2)

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]



2

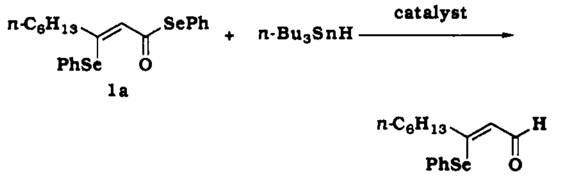
(3)

Table I. Effects of Catalysts on the Reduction of 1a with *n*-Bu_3SnH[a]

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	$Pd(PPh_3)_2Cl_2$ (2.0)	3	85	1:99
7	$Pd(OAc)_2$ (5.0)	3	45	1:99

[a] *n*-Bu_3SnH (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*-Bu_3SnH under several reaction conditions. When the reaction of 1a with *n*-Bu_3SnH was carried out in the presence of 0.4 mol % of $Pd(PPh_3)_4$, 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



1a

(4)

2a

---

(1) Gysling, H. J. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1986; Vol. 1, p 679.

(2) (a) Fukuzawa, S.; Fujinami, T.; Sakai, S. *Chem. Lett.* **1990**, 927. (b) Takahashi, H.; Ohe, K.; Uemura, S.; Sugita, N. *J. Organomet. Chem.* **1987**, *334*, C43. (c) Okamura, H.; Miura, M.; Kosugi, K.; Takei, H. *Tetrahedron Lett.* **1980**, *21*, 87. (d) Cristau, H. J.; Chabaud, B.; Labaudiniere, R.; Christol, H. *J. Org. Chem.* **1986**, *51*, 875. (e) Murahashi, S.-I.; Yano, T. *J. Am. Chem. Soc.* **1980**, *102*, 2456. (f) Hutchins, R. O.; Learn, K. *J. Org. Chem.* **1982**, *47*, 4380.

(3) Kuniyasu, H.; Ogawa, A.; Miyazaki, S.; Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1991**, *113*, 9796.

(4) For an overview of reductions with organotin reagents, see: Pereyre, 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), $Pd(PPh_3)_4$ (4.4 mg, 0.0038 mmol), and benzene (20 mL) under an argon atmosphere. Then, a solution of *n*-Bu_3SnH (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/Et_2O as eluent) to give 270 mg (91%) of 2a as a yellow oil. Data for 2a: yellow oil; ^1H NMR (270 MHz, $CDCl_3$) 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); ^{13}C NMR (68 MHz, $CDCl_3$) 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 $C_{15}H_{20}OSe$: C, 61.01; H, 6.83. Found: C, 60.96; H, 6.81.

0276-7333/92/2311-3937$03.00/0