Highlight Review

Transition Metal-catalyzed Carbochalcogenation of Alkynes

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Abstract

The progress of transition metal-catalyzed carbochalcogenation of alkynes, which can be performed by using readily available catalysts, is reviewed. It has been proposed that stereo- and regioselective insertion of alkynes into the metal complexes is involved in the catalytic cycles. These reactions clearly demonstrate the synthetic versatility of organochalcogen compounds in transition metal-catalyzed reactions.

♦ Introduction

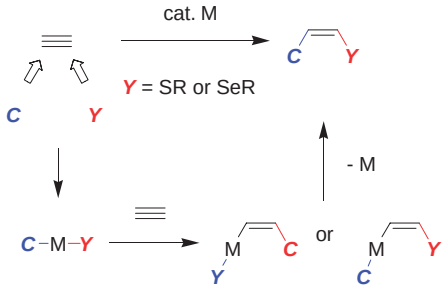
Building desired compounds by introducing functional groups at will has been one of the most challenging topics in chemistry. Development of new reaction systems, selection of reagents, solvents, catalysts, and reaction conditions are critical to achieve this goal. Simultaneous introduction of carbon and heteroatom moieties to C–C unsaturated compounds with the aid of transition-metal complexes has provided such sophisticated methodologies; carbosilylation and carbostannylation have been among the most important examples.[1,2] Here, we review the development of transition metal-catalyzed carbochalcogenation of alkynes, which provides convenient methods for the simultaneous introduction of carbon and sulfur (or selenium) functional groups to C–C triple bonds.[3,4] Carbothiolation,[5] carboselenation,[6] and carbotelluration[7] under radical conditions and reactions employing stoichiometric amounts of a Cu^{I} salt[8] are beyond the scope of this review; other X–S and X–Se bond activations (X: non-carbon element or group) by transition-metal catalysts have already been reviewed elsewhere.[9]

♦ General Concept

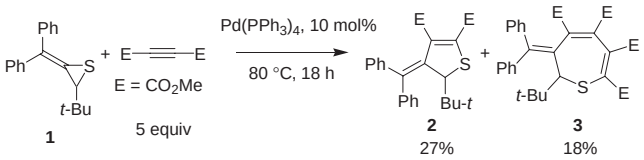
Scheme 1 shows a representative reaction route of transition metal-catalyzed carbochalcogenation of alkynes, which includes (1) generation of a metal complex with a *C*–M–*Y* (*C*: carbon functional group, *Y*: chalcogen functional group) unit through the reaction of a *C*–*Y* bond with a low-valent metal complex M, (2) incorporation of an alkyne into either *C*–M or M–*Y* bond to give a vinyl metal complex, and (3) vinyl-*Y* or vinyl-*C* bond-forming reductive elimination of the product with regeneration of a metal catalyst. Some reactions can be accompanied by carbonylation, decarbonylation, transmetalation, and so on during the process. In this highlight review, the reactions are classified by the metal of the catalysts.

♦ Pd-catalyzed Carbochalcogenation

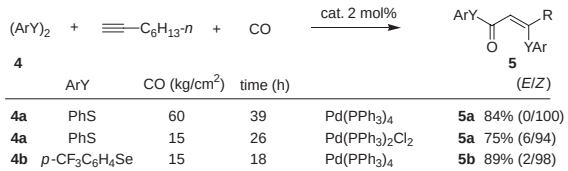
In 1991, two papers describing Pd-catalyzed carbochalcogenation were reported. To our knowledge, these are the first examples of transition metal-catalyzed carbochalcogenation of C–C unsaturated compounds. Ando et al. showed that the reaction of episulfide **1** with DMAD in the presence of $Pd(PPh_3)_4$ gave a mixture of **2** and **3**, albeit in low yield (Scheme 2).[10] When the Pd-catalyzed addition of diphenyl disulfide (**4a**) to 1-octyne to afford (*Z*)-1,2-bis(phenylthio)-1-octene was performed under pressurized CO (60 kg/cm^2), regio- and stereo-selective thiocarbonylthiolation, simultaneous introduction of PhSC(O) and PhS groups, took place to afford *Z*-**5a** in 84% yield (Scheme 3).[11] Not only $Pd(PPh_3)_4$ but also $Pd(PPh_3)_2Cl_2$, which did not exhibit any catalytic activity for the simple addition of **4a** to alkynes, can be used as the catalyst. Selenocarbonylselenation was also achieved using diaryl diselenide **4b** to give **5b** in 89% yield with high Z-selectivity. In the mechanism, successive insertion of an alkyne and CO into the Y–Pd bond of $Pd(YAr)_2$ (**6**, PPh_3 omitted) to afford acyl palladium **8** via vinyl palladium **7** is conceivable (path **A** of Scheme 4). An alternative is the insertion of CO into the Y–Pd bond of **6** to yield **9**, into which the alkyne is inserted to



Scheme 1.



Scheme 2.



	ArY	CO (kg/cm^2)	time (h)		(*E*/*Z*)
4a	PhS	60	39	$Pd(PPh_3)_4$	**5a** 84% (0/100)
4a	PhS	15	26	$Pd(PPh_3)_2Cl_2$	**5a** 75% (6/94)
4b	*p*-$CF_3C_6H_4Se$	15	18	$Pd(PPh_3)_4$	**5b** 89% (2/98)

Scheme 3.

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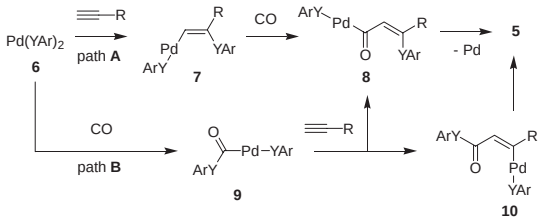
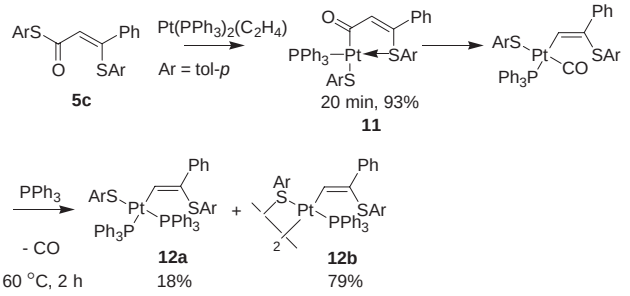


Scheme 4.



Scheme 5.

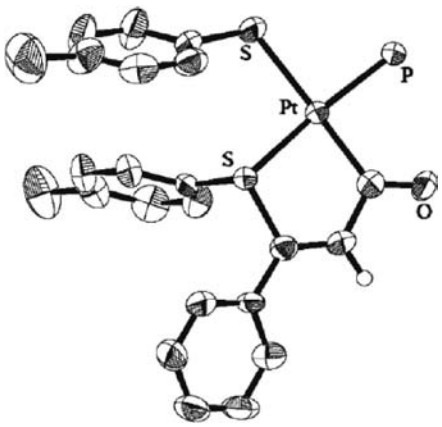
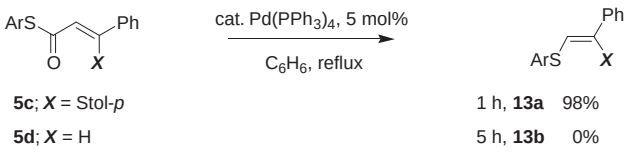


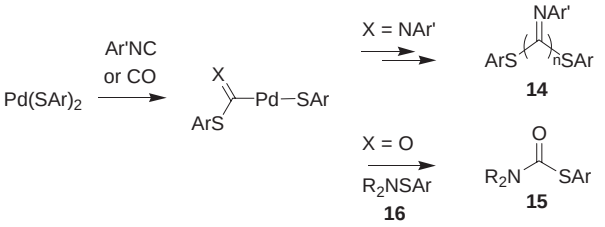
Figure 1. ORTEP drawing of **11**.

afford **8** or **10**. The subsequent reductive elimination of **5** regenerates the Pd^0-complex (path **B**).

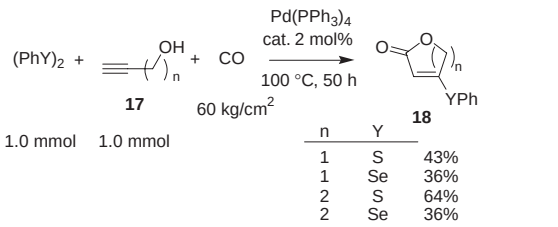
A recent study involving the stoichiometric reaction of **5c** with $Pt(PPh_3)_2(C_2H_4)$ demonstrated that acyl platinum **11** was produced in 93% yield after 20 min at room temperature (Scheme 5).[12] The structure of **11**, which was determined by X-ray crystallographic analysis, has a *cis*-β-SAr unit intramolecularly coordinated to the Pt center, and its five-membered ring is almost coplanar with the Pt^{II} square plane (Figure 1). It became evident that decarbonylation to afford vinyl platinum **12a** and **12b** (dimeric form of **12a**) was facilitated by the *cis*-β-SAr coordination. The *cis*-β-SAr moiety also promoted catalytic decarbonylation. While decarbonylation using $Pd(PPh_3)_4$ as a catalyst yielded **13a** quantitatively, decarbonylation of thioester **5d**, which does not have a *cis*-β-SAr, did not take place even with prolonged reaction times (Scheme 6). Based on microscopic reversibility,[13] the formation of **8** in path **A** of Scheme 4 can be facilitated by a similar *cis*-β-SAr moiety. Considering that insertions of isocyanide and CO into the S–Pd bond of $Pd(SAr)_2$ eventually afford **14** and **15** in the Pd-catalyzed reaction of



Scheme 6.



Scheme 7.



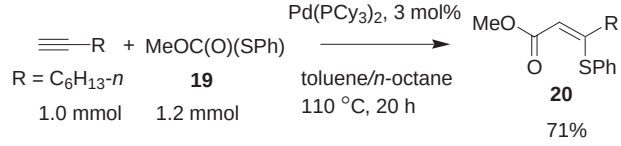
Scheme 8.

$(ArS)_2$ with isocyanide[14] and azathiolation of CO with sulfenamide (R_2NSAr, **16**) (Scheme 7),[15] path **B** in Scheme 4 cannot be completely ruled out.

The reactions using propargyl and homopropargyl alcohols (**17**) provided lactones **18** in moderate yields (Scheme 8).[16]

Tanaka and co-workers revealed that the reaction of a terminal alkyne with a thiocarbonate, MeOC(O)(SPh) (**19**) in the presence of $Pd(PCy_3)_2$ as a catalyst furnished compound **20**, the product of methoxycarbonylthiolation.[17] Again, the PhS group is introduced at the internal position together with *cis*-C(O)OMe at the terminal carbon (Scheme 9). The oxidative addition of **19** to $Pd(PCy_3)_2$ was confirmed to give $Pd(SPh)(CO_2Me)(PCy_3)_2$, which reacted with 1-octyne to afford **20**. No clear information about a possible vinyl palladium intermediate was provided in the paper, implying that reductive elimination was faster than insertion of the alkyne into the Pd–S bond.[18]

Meyer and Knapton disclosed carbamoylselenation using Me_2NSPh (**16a**), $(PhSe)_2$ (**4c**) and CO as reagents with $Pd(PPh_3)_4$ as a catalyst (Scheme 10).[19] As to the mechanism, there were more than one reaction route for the formation of **21a**. They included the reaction of acyl palladium **8** with **16** and the reaction of **5** with **16**. The authors proposed that the intramolecular coordination of selenium to Pd to form **22** or **23**, the



Scheme 9.

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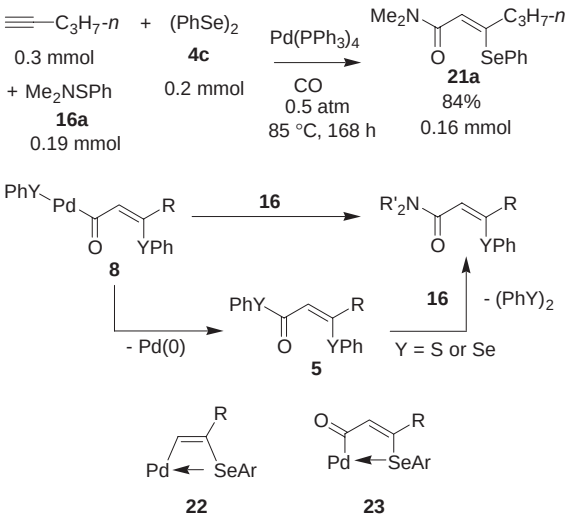
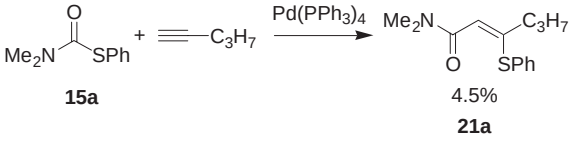
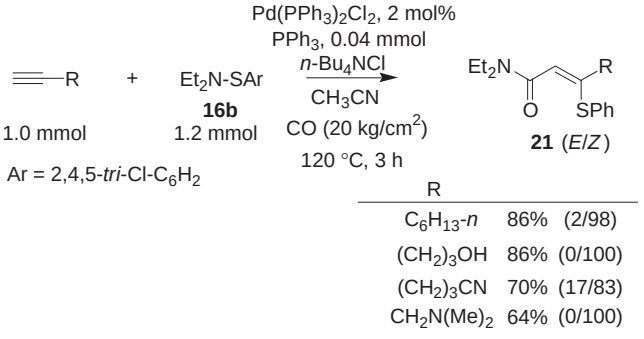


Scheme 10.



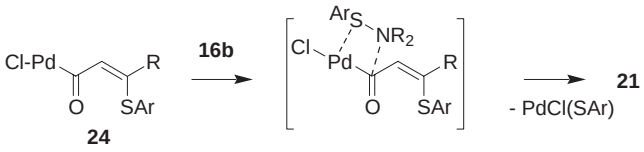
Scheme 11.



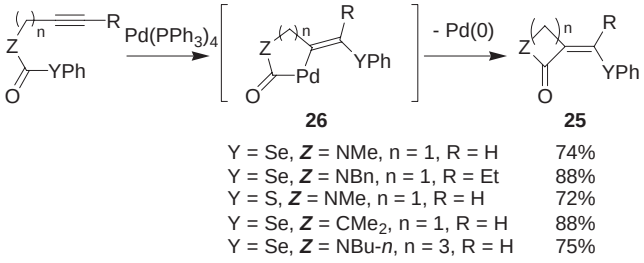
Scheme 12.

latter of which is related to complex **11** in Scheme 5, facilitated the insertion of CO. Although the reaction of thiocarbamate **15a** with alkynes produced **21a**, which is a carbamoylthiolation product, the yield was low (Scheme 11). On the other hand, carbamoylthiolation was more efficiently achieved by utilizing Et_2N-SAr (Ar = 2,4,5-tri-Cl-C_6H_2) (**16b**) and CO as the reagents and $Pd(PPh_3)_2Cl_2/PPh_3/n$-Bu_4NCl as a catalyst system to produce the corresponding **21** in good yield with high Z-selectivity (Scheme 12).[20] Because the formation of a C–Cl bond by reductive elimination from complex **24** may not be thermodynamically favored, **21** was selectively afforded. σ-Bond metathesis between the N–S bond of **16b** and the C–Pd bond of **24** was proposed as a crucial step in the catalytic cycle (Scheme 13).

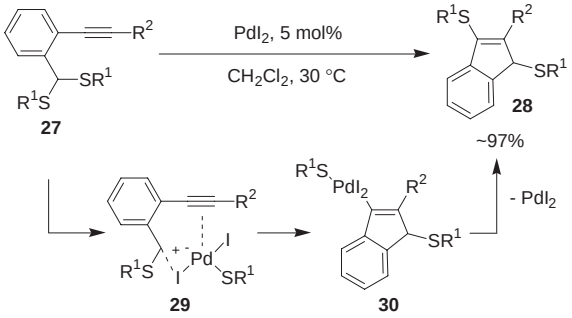
A similar σ-bond metathesis utilizing the unique polarity of $N^{\delta-}$–$S^{\delta+}$ of sulfenamide was also proposed in the palladium-catalyzed azathiolation of carbon monoxide.[15] Furthermore, intramolecular carbamoylselenation and carbamoylthiolation of alkynes to yield exomethylene lactams **25** took place successfully



Scheme 13.



Scheme 14.

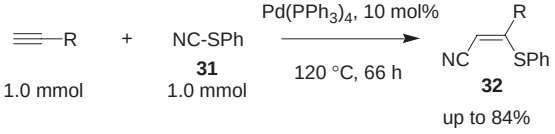


Scheme 15.

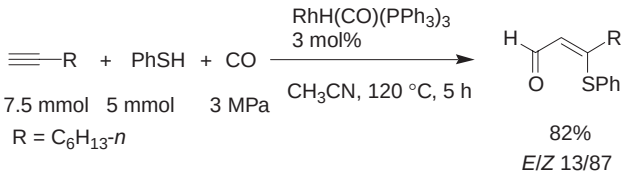
with $Pd(PPh_3)_4$ as a catalyst (Scheme 14).[21] Internal alkynes (R = Et), which are generally not very active as a substrate for transition metal-catalyzed X–S bond addition to alkynes,[9] and selenoester (**Z** = CMe_2) also underwent the reaction. Palladacycle **26** was proposed as a probable intermediate.

Yamamoto and co-workers reported that PdI_2 catalyzed the intermolecular carbothiolation of thioacetals **27** to furnish **28** (Scheme 15).[22] The formation of cationic species **29** was proposed based on NMR and computational studies. The formation of a C–S bond via reductive elimination from Pd^{IV} complex **30** gives **28** with the regeneration of PdI_2. It must be noted that carbon and sulfur functional groups are introduced across the triple bond in a trans fashion with each other.

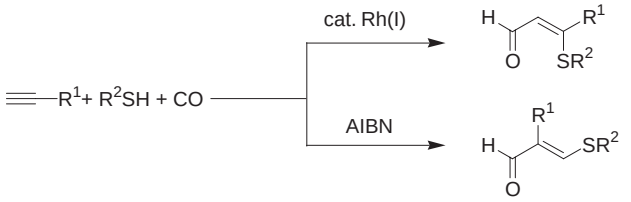
It was also disclosed that Pd^0 complex catalyzed the cyanothiolation of terminal alkynes using NCSPh (**31**) as a reagent to form **32** (Scheme 16).[23] A probable intermediate *trans*-$Pd(SPh)(CN)(PPh_3)_2$ formed by the oxidative addition of **31** to $Pd(PPh_3)_4$ was isolated and the structure was determined by X-ray crystallographic analysis.



Scheme 16.



Scheme 17.



Scheme 18.

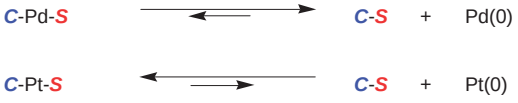
♦ *Rh-catalyzed Carbothiolation*

Ogawa and co-workers also reported that formylthiolation of terminal alkynes, which is the simultaneous introduction of C(O)H and ArS and considered to be the counterpart of silylformylation,[1h–1m] was catalyzed by a Rh-complex (Scheme 17).[24] The regio- and stereochemistry are both complementary to radical formylthiolation (Scheme 18).[25]

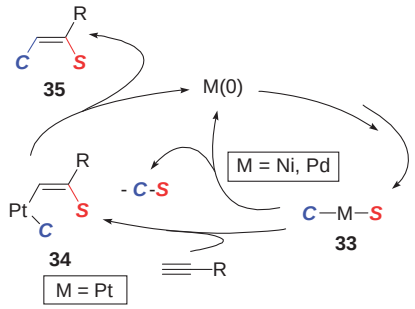
♦ *Pt-catalyzed Carbochalcogenation*

Based on catalytic and stoichiometric investigations concerning the reactivities of thiolato ligands of Pd^{II} and Pt^{II} complexes,[11,14,26] it was demonstrated that the direction of *C*–*S* bond-forming reductive elimination and its reverse oxidative addition can be controlled by simply changing the metal from Pd to Pt (Scheme 19).[27] That is, the *C*–*S* bond formation tends to be thermodynamically prevented even if the same combination of ligands is employed.

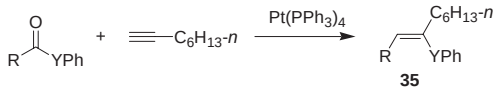
This contrastive reactivity led us to find a simple reaction strategy for the Pt-catalyzed carbothiolation of alkynes (Scheme 20). When the reagents used for *C*–*S* bond-forming cross-coupling reaction were subjected to a Pt-catalyst in the presence of a terminal alkyne, intermediate **33** with a *C*–Pt–*S* fragment resisted *C*–*S* bond-forming reductive elimination and underwent cis-insertion of an alkyne into the *S*–Pt bond to afford vinyl platinum **34**. Eventual vinyl-*C* bond-forming reductive elimination of **35** reproduces the Pt^0-complex. For example, when the Pd-catalyzed decarbonylation of PhC(O)SPh[28] was performed employing $Pt(PPh_3)_4$ as a catalyst precursor in the presence of 1-octyne, the arylthiolation product **35a** was selectively produced in 77% yield (Scheme 21).[29a] It must be noted that thioether PhSPh **36a** was not produced from this reaction. According to the present strategy, the Pt-catalyzed regio- and stereoselective 2- and 3-thienylthiolation,[29b] 2- and 3-furylthio-



Scheme 19.

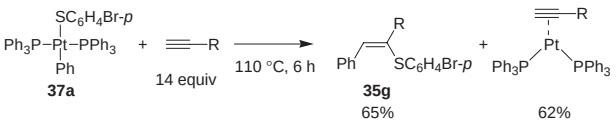


Scheme 20.



R	Y	yield of **35**	R	Y	yield of **35**
Ph	S	**35a** 77%	2-furyl	S	**35d** 78%
2-thienyl	S	**35b** 88%	3-furyl	S	**35e** 75%
3-thienyl	S	**35c** 84%	Ph	Se	**35f** 89%

Scheme 21.

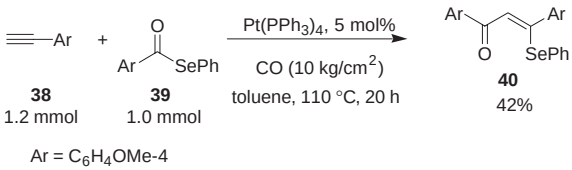


Scheme 22.

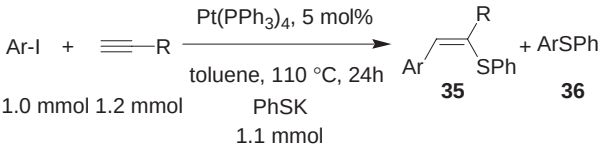
lation,[29c] and even arylselenation[29d] of terminal alkyne can be realized using the corresponding thioesters and selenoesters as the reaction substrates (Scheme 21). From the NMR spectrum of the reaction of $Pt(SC_6H_4Br\text{-}p)(Ph)(PPh_3)_2$ (**37a**) with 1-octyne, the formations of **35g** and alkyne-coordinated $Pt(RCCH)(PPh_3)_2$ were confirmed in 65 and 62% yields, respectively (Scheme 22). The vinyl platinum complex was not detected during the course of the reaction, again suggesting that reductive elimination took place faster than the insertion of the alkyne into the S–Pt bond. It should be noted that the Pt-catalyzed reaction of $HCCC_6H_4OMe\text{-}4$ (**38**) with $4\text{-}MeOC_6H_4C(O)SePh$ (**39**) under CO (10 kg/cm^2) yielded the aroylselenation product **40** in 42% yield (Scheme 23).

The Pt^{II}-intermediate with a *C*–Pt–*S* fragment can be generated through alternative routes, such as the oxidative addition of ArI to Pt^0 and following transmetalation with Ar′SK.

In contrast to the reactions using arylthioesters as the coupling partner (Scheme 21), direct cross-coupling also occurs between PhI and PhSK to afford thioether **36** (Scheme 24). The formation of **36** was strongly dependent on the species of alkynes; the reaction of 1-octyne with PhI and PhSK produced

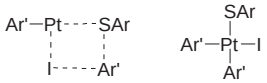


Scheme 23.



Ar	R		35		36	
Ph	C_6H_{13}-*n*	**35a**	83%	**36a**	3%
Ph	Ph	**35h**	30%	**36a**	66%
3-pyridyl	C_6H_{13}-*n*	**35i**	78%	**36b**	14%
2-thienyl	C_6H_{13}-*n*	**35b**	98%	**36c**	0%

Scheme 24.

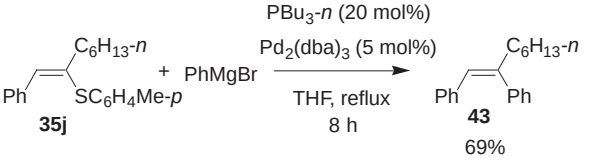


41 **42**

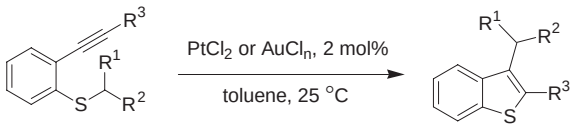
Scheme 25.

the arylthiolation products **35a** and **36a** in 83 and 3% yields, respectively, while the reaction using phenylacetylene afforded **35h** and **36a** in 30 and 66% yields, respectively.[29f] From a similar pyridylthiolation, **36b** was produced in 14% yield together with 78% yield of **35i**, while 2-thienylthiolation selectively produced **35b** in high yield.[29e,29f] Mechanistic investigations suggested that direct C–S bond-forming reductive elimination from $Pt(SAr)(Ar')(PPh_3)_2$ (**37**) was not involved, and ArS–Ar′ (**36**) was formed from the ArS ligand in complex **37** and free Ar′I. These facts may demonstrate that σ-bond metathesis between the S–Pt bond of **37** and the Ar′–I bond through an intermediate like **41**, where alkyne assists in some way, is participated (Scheme 25). However, considering the fact that C–S bond formation of MeSMe took place from the Pt^{IV} complex, generated by the oxidative addition of MeI to $[Pt(SMe)(PMe_2Ph)(\mu\text{-SMe})]_2$,[30] reductive elimination from a Pt^{IV} complex, such as **42** formed by the oxidative addition of Ar′–I to **37**, cannot be fully precluded. That is, the trans C–Pt–S geometry of the complex **37** can be retained during the oxidative addition of Ar′–I and reductive elimination of ArSAr′ sequence. The product of arylthiolation of terminal alkyne **35j** reacts with Grignard reagent in the presence of a Pd-catalyst to give **43** (Scheme 26), enabling the introduction of two Ar groups into an alkyne by Pt-catalyzed carbothiolation and subsequent Pd-catalyzed cross-coupling reaction.

Nakamura, Yamamoto, and co-worker reported that $PtCl_2$ or $AuCl_n$ ($n = 1$ or 2) catalyzed intramolecular carbothiolation of alkyne **44** took place smoothly in toluene at 25 °C to give the compound **45** in good yields (Scheme 27).[31] The authors proposed the nucleophilic attack of the sulfur atom of **44** to the C–C triple bond activated by the catalyst. It should be noted



Scheme 26.



44 **45**

R^1 = H, R^2 = CH=CH_2, R^3 = Ph	93%
R^1 = H, R^2 = C_6H_4OMe-*p*, R^3 = Ph	98%
R^1 = H, R^2 = OMe, R^3 = *n*-Pr	93%
R^1 = Me, R^2 = OEt, R^3 = *n*-Pr	92%

Scheme 27.

that the carbon and sulfur functional groups were added to the intramolecular C–C triple bond in a trans-fashion.

In summary, the studies described herein demonstrate the utility of transition metal-catalyzed carbochalcogenation of alkynes, which can be performed by using readily available catalysts, such as $M(PPh_3)_4$ and MX_n (M = Pd and Pt). Organochalcogen compounds were once regarded as catalytic poisons; however, these reactions clearly showed that chalcogenides are actually quite active in a variety of transition metal-catalyzed reactions.

References and Notes

1 For representative papers, see: a) N. Chatani, N. Amishiro, S. Murai, *J. Am. Chem. Soc.* **1991**, *113*, 7778. b) N. Chatani, N. Amishiro, T. Morii, T. Yamashita, S. Murai, *J. Org. Chem.* **1995**, *60*, 1834. c) Y. Obora, Y. Tsuji, T. Kawamura, *J. Am. Chem. Soc.* **1993**, *115*, 10414. d) Y. Obora, Y. Tsuji, T. Kawamura, *J. Am. Chem. Soc.* **1995**, *117*, 9814. e) M. Wu, F. Yang, C. Cheng, *J. Org. Chem.* **1999**, *64*, 2471. f) N. Asao, T. Shimada, Y. Yamamoto, *J. Am. Chem. Soc.* **2001**, *123*, 10899. g) J. Terao, A. Oda, A. Ikumi, A. Nakamura, H. Kuniyasu, N. Kambe, *Angew. Chem., Int. Ed.* **2003**, *42*, 3412. h) I. Matsuda, A. Ogiso, S. Sato, Y. Izumi, *J. Am. Chem. Soc.* **1989**, *111*, 2332. i) I. Ojima, R. J. Donovan, W. R. Shay, *J. Am. Chem. Soc.* **1992**, *114*, 6580. j) I. Ojima, E. Vidal, M. Tzamarioudaki, I. Matsuda, *J. Am. Chem. Soc.* **1995**, *117*, 6797. k) M. J. Zacuto, S. J. O'Malley, J. L. Leighton, *J. Am. Chem. Soc.* **2002**, *124*, 7890. l) J. L. Leighton, E. Chapman, *J. Am. Chem. Soc.* **1997**, *119*, 12416. m) M. J. Zacuto, J. L. Leighton, *J. Am. Chem. Soc.* **2000**, *122*, 8587.

2 a) E. Shirakawa, H. Yoshida, T. Kurahashi, Y. Nakao, T. Hiyama, *J. Am. Chem. Soc.* **1998**, *120*, 2975. b) Y. Nakao, J. Satoh, E. Shirakawa, T. Hiyama, *Angew. Chem., Int. Ed.* **2006**, *45*, 2271, and references therein.

3 For the synthetic utility of vinyl sulfide, see: a) R. J. Cremlyn, *An Introduction to Organo-sulfur Chemistry*, John Wiley & Sons, Inc., New York, **1996**. b) B. M. Trost, A. C. Lavoie, *J. Am. Chem. Soc.* **1983**, *105*, 5075. c) P. Magnus, D. Quagliato, *J. Org. Chem.* **1985**, *50*, 1621.

4 For the synthetic utility of vinyl selenide, see: a) J. V. Comasseto, L. W. Ling, N. Petragnani, H. A. Stefani, *Synthesis* **1997**, 373. b) C. Paulmier *Selenium Reagents and Intermediates in Organic Synthesis*, Pergamon Press, Oxford, **1986**. c) J. V. Comasseto, *J. Organomet. Chem.* **1983**, *253*, 131. d) J. V. Comasseto, N. Petragnani, *J. Organomet. Chem.* **1978**, *152*, 295. e) L. Hevesi, B. Hermans, C. Allard, *Tetra-*

hedron Lett. **1994**, *35*, 6729. f) S. Yamazaki, *Rev. Heteroat. Chem.* **1999**, *21*, 43.
5 a) D. H. R. Barton, M. Ramesh, *J. Am. Chem. Soc.* **1990**, *112*, 891. b) T. Otsu, *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 2121. c) J. Boivin, J. Camara, S. Z. Zard, *J. Am. Chem. Soc.* **1992**, *114*, 7909, and references therein.
6 a) K. Tsuchii, M. Doi, T. Hirao, A. Ogawa, *Angew. Chem., Int. Ed.* **2003**, *42*, 3490. b) D. P. Curran, E. Eichenberger, M. Collos, M. G. Roepel, G. Thoma, *J. Am. Chem. Soc.* **1994**, *116*, 4279. c) J. H. Byers, C. C. Whitehead, M. E. Duff, *Tetrahedron Lett.* **1996**, *37*, 2743, and references therein.
7 a) C. Chen, D. Crich, A. Papadatos, *J. Am. Chem. Soc.* **1992**, *114*, 8313. b) J. H. Byers, B. C. Harper, *Tetrahedron Lett.* **1992**, *46*, 6953. c) L. B. Han, K. Ishihara, N. Kambe, A. Ogawa, I. Ryu, N. Sonoda, *J. Am. Chem. Soc.* **1992**, *114*, 7591. d) L. Engman, V. Gupta, *J. Org. Chem.* **1997**, *62*, 157. e) S. Fujiwara, Y. Shimizu, T. Shin-ike, N. Kambe, *Org. Lett.* **2001**, *3*, 2085. f) D. Crich, C. Chen, J. T. Hwang, H. Yuan, A. Papadatos, R. I. Walter, *J. Am. Chem. Soc.* **1994**, *116*, 8937. g) A. Goto, Y. Kwak, T. Fukuda, S. Yamago, K. Iida, M. Nakajima, J. Yoshida, *J. Am. Chem. Soc.* **2003**, *125*, 8720, and references therein.
8 a) C. Zhao, X. Huang, J. Meng, *Tetrahedron Lett.* **1998**, *39*, 1933. b) C. Zhao, J. Li, J. Meng, Y. Wang, *J. Org. Chem.* **1998**, *63*, 4170.
9 a) H. Kuniyasu, in *Catalytic Heterofunctionalization*, ed. by A. Togni, H. Grützmacher, Wiley-VCH, Weinheim, **2001**, Chap. 7, pp. 217–252. b) L. B. Han, M. Tanaka, *Chem. Commun.* **1999**, 395. c) I. Beletskaya, C. Moberg, *Chem. Rev.* **1999**, *99*, 3435. d) A. Ogawa, in *Main Group Metals in Organic Synthesis*, ed. by H. Yamamoto, K. Oshima, Wiley-VCH, Weinheim, **2004**, pp. 813–866. e) T. Kondo, T. Mitsudo, *Chem. Rev.* **2000**, *100*, 3205. f) B. El Ali, H. Alper, in *Handbook of Organopalladium Chemistry for Organic Synthesis*, ed. by E. Negishi, Wiley-Interscience, New York, **2002**, Chap. VI. 2.1.1.2. g) A. Ogawa, in *Handbook of Organopalladium Chemistry for Organic Synthesis*, ed. by E. Negishi, Wiley-Interscience, New York, **2002**, Chap. VII. 6. h) A. Ogawa, *J. Organomet. Chem.* **2000**, *611*, 463.
10 N. Choi, Y. Kabe, W. Ando, *Tetrahedron Lett.* **1991**, *32*, 4573.
11 H. Kuniyasu, A. Ogawa, S. Miyazaki, I. Ryu, N. Kambe, N. Sonoda, *J. Am. Chem. Soc.* **1991**, *113*, 9796.
12 T. Kato, H. Kuniyasu, T. Kajiura, Y. Minami, A. Ohtaka, M. Kinomoto, J. Terao, H. Kurosawa, N. Kambe, *Chem. Commun.* **2006**, 868.
13 Y. Minami, T. Kato, H. Kuniyasu, J. Terao, N. Kambe, *Organometallics* **2006**, *25*, 2949.
14 a) H. Kuniyasu, K. Sugoh, S. Moon, H. Kurosawa, *J. Am. Chem. Soc.* **1997**, *119*, 4669. b) H. Kuniyasu, A. Maruyama, H. Kurosawa, *Organometallics* **1998**, *17*, 908.
15 H. Kuniyasu, H. Hiraike, M. Morita, A. Tanaka, K. Sugoh, H. Kurosawa, *J. Org. Chem.* **1999**, *64*, 7305.
16 A. Ogawa, H. Kuniyasu, N. Sonoda, T. Hirao, *J. Org. Chem.* **1997**, *62*, 8361.
17 a) R. Hua, H. Takeda, S. Onozawa, Y. Abe, M. Tanaka, *J. Am. Chem. Soc.* **2001**, *123*, 2899. b) M. Tanaka, R. Hua, *Pure Appl. Chem.* **2002**, *74*, 181.
18 K. Sugoh, H. Kuniyasu, H. Kurosawa, *Chem. Lett.* **2002**, 106.
19 a) D. J. Knapton, T. Y. Meyer, *Org. Lett.* **2004**, *6*, 687. b) D. J. Knapton, T. Y. Meyer, *J. Org. Chem.* **2005**, *70*, 785.
20 H. Kuniyasu, T. Kato, S. Asano, J. H. Ye, T. Ohmori, M. Morita, H. Hiraike, S. Fujiwara, J. Terao, H. Kurosawa, N. Kambe, *Tetrahedron Lett.* **2006**, *47*, 1141.
21 M. Toyofuku, S. Fujiwara, T. Shin-ike, H. Kuniyasu, N. Kambe, *J. Am. Chem. Soc.* **2005**, *127*, 9706.
22 a) I. Nakamura, G. B. Bajracharya, Y. Mizushima, Y. Yamamoto, *Angew. Chem., Int. Ed.* **2002**, *41*, 4328. b) I. Nakamura, G. B. Bajracharya, H. Wu, K. Oishi, Y. Mizushima, I. D. Dridnev, Y. Yamamoto, *J. Am. Chem. Soc.* **2004**, *126*, 15423.
23 I. Kamiya, J. Kawakami, S. Yano, A. Nomoto, A. Ogawa, *Organometallics* **2006**, *25*, 3562.
24 a) A. Ogawa, M. Takeba, J. Kawakami, I. Ryu, N. Kambe, N. Sonoda, *J. Am. Chem. Soc.* **1995**, *117*, 7564. b) J. Kawakami, M. Takeba, I. Kamiya, N. Sonoda, A. Ogawa, *Tetrahedron* **2003**, *59*, 6559.
25 S. Nakatani, J. Yoshida, S. Isobe, *J. Chem. Soc., Chem. Commun.* **1992**, 880.
26 a) H. Kuniyasu, A. Ohtaka, T. Nakazono, M. Kinomoto, H. Kurosawa, *J. Am. Chem. Soc.* **2000**, *122*, 2375. b) H. Kuniyasu, T. Kato, M. Inoue, J. Terao, N. Kambe, *J. Organomet. Chem.* **2006**, *691*, 1873.
27 H. Kuniyasu, H. Kurosawa, *Chem.—Eur. J.* **2002**, *8*, 2660.
28 K. Osakada, T. Yamamoto, A. Yamamoto, *Tetrahedron Lett.* **1987**, *28*, 6321.
29 a) K. Sugoh, H. Kuniyasu, T. Sugae, A. Ohtaka, Y. Takai, A. Tanaka, C. Machino, N. Kambe, H. Kurosawa, *J. Am. Chem. Soc.* **2001**, *123*, 5108. b) T. Hirai, H. Kuniyasu, N. Kambe, *Chem. Lett.* **2004**, *33*, 1148. c) T. Hirai, H. Kuniyasu, S. Asano, J. Terao, N. Kambe, *Synlett* **2005**, 1161. d) T. Hirai, H. Kuniyasu, T. Kato, Y. Kurata, N. Kambe, *Org. Lett.* **2003**, *5*, 3871. e) T. Hirai, H. Kuniyasu, N. Kambe, *Tetrahedron Lett.* **2005**, *46*, 117. f) H. Kuniyasu, F. Yamashita, T. Hirai, J. H. Ye, S. Fujiwara, N. Kambe, *Organometallics* **2006**, *25*, 566.
30 R. J. Puddephatt, C. E. E. Upton, *J. Organomet. Chem.* **1975**, *91*, C17.
31 I. Nakamura, T. Sato, Y. Yamamoto, *Angew. Chem., Int. Ed.* **2006**, *45*, 4473.