Notes

Effects of a Bidentate Phosphine Ligand on Palladium-Catalyzed Nucleophilic Substitution Reactions of Propargyl and Allyl Halides with Thiol

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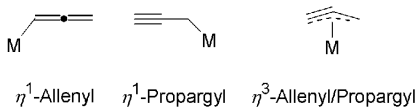
Received February 20, 2003

Summary: Palladium-catalyzed nucleophilic substitution reactions of propargyl halides ***1*** *with n-PrSH proceed smoothly with excellent yield by using dppe (dppe > P(t-Bu)$_3$ > PPh$_3$ > P(biphenyl)(t-Bu)$_2$) in polar solvent (DMF-d$_7$ > chloroform-d > benzene-d$_6$). A suitable catalytic intermediate in this reaction is discussed. In addition, dppe was found to be an efficient ligand in the reaction of allyl chloride with thiol.*

Introduction

Several useful reactions using propargyl or allenyl compounds that are catalyzed by transition metals have been reported in the last few decades,[1] and much attention has been given to transition-metal complexes that contain propargylic or allenylic ligands as key intermediates during the catalytic reactions.[2] Typical structural modes of allenyl and propargyl transition-metal complexes are presented in Chart 1. In particular, the preparation and reactivities of the palladium complexes have been elucidated, because palladium is one of the most useful catalysts. Initially, the neutral (η^1-allenyl)- and (η^1-propargyl)palladium complexes have been prepared,[3] and they are assumed to play a crucial role in catalytic cycles. On the other hand, Kurosawa and Wojcicki reported on the synthesis of η^3-bonding (propargyl)- and (allenyl)palladium complexes, as neutral or cationic types, as well as their reactivities.[4,5]

Chart 1



η^1-Allenyl η^1-Propargyl η^3-Allenyl/Propargyl

However, to the best of our knowledge, very few catalytic reactions actually proceed with the η^3-type complexes as the key intermediates.[6,7] The preparation of these complexes is easy to control in catalytic reactions by adjusting reaction conditions as follows. The neutral η^1-type complexes are obtained by the reaction of propargyl halide with Pd(0) and 2 equiv or more of monophosphine ligands,[3,4] and the neutral η^3-type complexes are prepared in the case of using 1 equiv of PPh$_3$.[4] We previously reported that the cationic η^3-type complexes can be generated in solution as an equilibrium isomer of the neutral η^1-type complexes.[5a,c] Furthermore, by using a bidentate ligand (dppe > PPh$_3$) (dppe = 1,2-bis(diphenylphosphino)ethane) in more polar solvents, the equilibrium lies in favor of the cationic species.[5c] Because of its electronic nature, cationic-type complexes may show higher reactivities toward nucleophiles as compared to neutral types.

This paper discusses a suitable catalytic intermediate in the palladium-catalyzed nucleophilic substitution of propargylic halides with thiol. Despite the typical poisoning effects of sulfur-containing compounds on

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(2) Reviews and recent report for the chemistry of allenyl/propargyl transition-metal complexes: (a) Doherty, S.; Corrigan, J. F.; Carty, A. J.; Sappa, E. *Adv. Organomet. Chem.* **1995**, *37*, 39. (b) Wojcicki, A. *New J. Chem.* **1994**, *18*, 61. (c) Kurosawa, H.; Ogoshi, S. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 973. (d) Wojcicki, A.; Shuchart, C. E. *Coord. Chem. Rev.* **1990**, 35. (e) Chen, J.-T. *Coord. Chem. Rev.* **1999**, 1143. (f) Blosser, P. W.; Calligaris, M.; Schimpff, D. G.; Wojcicki, A. *Inorg. Chim. Acta* **2001**, *320*, 110. (g) Wojcicki, A. *Inorg. Chem. Commun.* **2002**, *5*, 82. (h) Casey, C. P.; Boller, T. M.; Kraft, S.; Guzei, I. A. *J. Am. Chem. Soc.* **2002**, *124*, 13215.

(3) (a) Elsevier, C. J.; Kleijin, H.; Ruitenberg, K.; Vermeer, P. *J. Chem. Soc., Chem. Commun.* **1983**, 1529. (b) Elsevier, C. J.; Kleijn, H.; Boersma, J.; Vermeer, P. *Organometallics* **1986**, *5*, 716.

(4) Neutral type: Tsutsumi, K.; Ogoshi, S.; Nishiguchi, S.; Kurosawa, H. *J. Am. Chem. Soc.* **1998**, *120*, 1938.

(5) Cationic type: (a) Ogoshi, S.; Tsutsumi, K.; Kurosawa, H. *J. Organomet. Chem.* **1995**, *493*, C19. (b) Baize, M. W.; Blosser, P. W.; Plantevin, V.; Schimpff, D. G.; Gallucci, J. C.; Wojcicki, A. *Organometallics* **1996**, *15*, 164. (c) Tsutsumi, K.; Kawase, T.; Kakiuchi, K.; Ogoshi, S.; Okada, Y.; Kurosawa, H. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 2687.

(6) We reported that the neutral (η^3-allenyl/η^3-propargyl)palladium complex was an efficient intermediate in the Migita−Stille coupling reactions of propargylic halides; see: Tsutsumi, K.; Ogoshi, S.; Kakiuchi, K.; Nishiguchi, S.; Kurosawa, H. *Inorg. Chim. Acta* **1999**, *296*, 37.

(7) We and other groups commented that the key intermediate of the palladium-catalyzed reactions of propargylic carbonates with soft carbon nucleophiles might be a cationic (η^3-allenyl/η^3-propargyl)-palladium complex; see: (a) Reference 5c. (b) Casey, C. P.; Nash, J. R.; Yi, C. S.; Selmeczy, A. D.; Chung, S.; Powell, D. R.; Hayashi, R. K. *J. Am. Chem. Soc.* **1998**, *120*, 722. (c) Radinov, R.; Hutchings, S. D. *Tetrahedron Lett.* **1999**, *40*, 8955.

10.1021/om030120q CCC: $25.00
Publication on Web 06/11/2003

catalysts,[8] useful transition-metal-catalyzed reactions involving organosulfur compounds have been developed.[9] Recently, excellent Ru-catalyzed C−S bond formation reactions of propargyl alcohols or carbonates have been reported,[10] but the mechanistic aspects were not clarified.[10b,c] We have found that dppe is the most efficient ligand among those examined, and the catalyst system also can be applied to allyl chloride.

Experimental Section

NMR spectra were recorded on a JNM-ECP-500 (^{1}H at 500 MHz, ^{13}C at 126 MHz) spectrometer. ^{1}H NMR spectra are reported as chemical shifts in parts per million (ppm) relative to the $SiMe_4$ signal (0.00 ppm). The following abbreviations are used to describe spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and b = broad. Coupling constants (J) are reported in hertz (Hz). ^{13}C NMR spectra are reported as chemical shifts in ppm based on the middle peak of chloroform-*d* (77.0 ppm). High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-700 mass spectrometer. Analytical GLC was carried out on a Hitachi G-3500 gas chromatograph with a TC-1 capillary column (0.25 mm × 10 m) (helium as carrier gas). Flash column chromatography was performed with Merck silica gel 60N. Oxygen- and moisture-sensitive reactions were conducted using glassware that had been dried under nitrogen. Commercially available reagents were used without further purification. All anhydrous solvents were purified by standard procedures. *t*-BuC≡CCH(Me)OH,[11] *t*-BuC≡CCH$_2$OH,[11] *t*-BuC≡CCH(*t*-Bu)OH,[11] $Pd_2(dba)_3$·$CHCl_3$ (dba = 1,5-diphenyl-1,4-pentadien-3-one),[12] and *trans*-(η^1-PhC≡CCH$_2$)Pt(PPh_3)$_2$Cl[13] were prepared according to the published methods. Bromination or chlorination of RC≡CCH(R′)OH (R = *t*-Bu, R′ = Me; R = *t*-Bu, R′ = H; R = R′ = *t*-Bu) and PhCH=CHCH$_2$OH was conducted according to the literature procedure.[14]

Pd(dppe)-Catalyzed Reaction of 1a with *n*-PrSH. To a DMF-d_7 solution (0.5 mL) of **1a** (18.9 mg, 0.10 mmol) and 1,3,5-trioxane (4.5 mg, 0.050 mmol) as an internal standard in an NMR tube were added [$Pd_2(dba)_3$·$CHCl_3$] (2.6 mg, 0.0025 mmol) and dppe (2.0 mg, 0.0050 mmol) under a nitrogen atmosphere. After 5 min, *n*-PrSH (9.1 mg, 0.12 mmol) and NEt_3 (12.1 mg, 0.12 mmol) were added to the NMR tube and the mixture was heated to 60 °C. The reaction was monitored by ^{1}H NMR. Other NMR experiments were carried out similarly.

Isolation of *t*-BuC≡CCH(Me)SPr (2). [$Pd_2(dba)_3$·$CHCl_3$] (25.9 mg, 0.025 mmol) and dppe (19.9 mg, 0.050 mmol) were added to a solution of **1a** (189.1 mg, 1.00 mmol) in dry DMF (5.0 mL) under a nitrogen atmosphere. After 5 min, *n*-PrSH (91.4 mg, 1.20 mmol) and NEt_3 (121.4 mg, 1.20 mmol) were added and the mixture was heated to 60 °C. After 3 h, the reaction mixture was purified by column (silica gel 60N, pentane), and the solvent was removed in vacuo carefully to provide **2** (174.7 mg, 0.948 mmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.00 (t, $^3J_{H,H}$ = 7.5 Hz, 3H, Pr), 1.21 (s, 9H, *t*-Bu), 1.44 (d, $^3J_{H,H}$ = 7.0 Hz, 3H, Me), 1.65 (m, 2H, Pr), 2.59 (m, 1H, Pr), 2.72 (m, 1H, Pr), 3.63 (q, $^3J_{H,H}$ = 7.0 Hz, 1H, CH). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 13.63, 22.27, 22.96, 27.42, 29.27, 31.21, 33.32, 79.08, 91.85. HRMS: *m*/*z* calcd for $C_{11}H_{20}S$ 184.1286, found 184.1282.

***t*-BuC≡CCH$_2$SPr (3).** The isolation of **1b** (130.1 mg, 1.00 mmol) was carried out similarly to that of **1a** to give **3** (126.4 mg, 0.742 mmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.00 (t, $^3J_{H,H}$ = 7.5 Hz, 3H, Pr), 1.22 (s, 9H, *t*-Bu), 1.65 (tq, $^3J_{H,H}$ = 7.5, 7.5 Hz, 2H, Pr), 2.63 (t, $^3J_{H,H}$ = 7.5 Hz, 2H, Pr), 3.24 (s, 2H, CH_2). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 13.46, 19.65, 22.48, 27.49, 31.10, 33.44, 74.15, 91.90. HRMS: *m*/*z* calcd for $C_{10}H_{18}S$ 170.1129, found 170.1127.

HC≡CCH$_2$SPr (4). The isolation of **1c** (74.5 mg, 1.00 mmol) was carried out similarly to that of **1a** to give **4** (67.8 mg, 0.594 mmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.98 (t, $^3J_{H,H}$ = 7.3 Hz, 3H, Pr), 1.62 (tq, $^3J_{H,H}$ = 7.3, 7.3 Hz, 2H, Pr), 2.21 (t, $^3J_{H,H}$ = 2.4 Hz, 1H, CH), 2.63 (t, $^3J_{H,H}$ = 7.3 Hz, 2H, Pr), 3.21 (d, $^3J_{H,H}$ = 2.4 Hz, 2H, CH_2). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 13.46, 19.10, 22.33, 33.65, 70.79, 80.22. HRMS: *m*/*z* calcd for $C_6H_{10}S$ 114.0503, found 114.0504.

(*t*-Bu)HC=C=CH(*t*-Bu)SPr (5). The reaction of **1d** (6.9 mg, 0.030 mmol) was carried out similarly to that of **1a** in an NMR tube, but the product **5** was not purified completely. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.97 (t, $^3J_{H,H}$ = 7.3 Hz, 3H, Pr), 1.04 (s, 9H, *t*-Bu), 1.14 (s, 9H, *t*-Bu), 1.63 (tq, $^3J_{H,H}$ = 7.3, 7.3 Hz, 2H, Pr), 2.51 (t, $^3J_{H,H}$ = 7.3 Hz, 2H, Pr), 5.37 (s, 1H, CH_2). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 13.65, 22.59, 29.88, 30.14, 32.74, 34.86, 35.35, 109.40, 115.49, 192.31.

PhC=CCH$_2$SPr (6). The isolation of **1e** (152.6 mg, 1.00 mmol) was carried out similarly to that of **1a** to give **6** (106.9 mg, 0.556 mmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.98 (t, $^3J_{H,H}$ = 7.5 Hz, 3H, Pr), 1.61 (tq, $^3J_{H,H}$ = 7.5, 7.0 Hz, 2H, Pr), 2.47 (t, $^3J_{H,H}$ = 7.0 Hz, 2H, Pr), 3.29 (d, $^3J_{H,H}$ = 7.0 Hz, 2H, CH_2), 6.18 (dt, $^3J_{H,H}$ = 11.0, 7.0 Hz, 1H, CH), 6.41 (d, $^3J_{H,H}$ = 11.0 Hz, 1H, CH), 7.22 (t, $^3J_{H,H}$ = 7.5 Hz, 1H, Ph), 7.30 (t, $^3J_{H,H}$ = 7.5 Hz, 2H, Ph), 7.37 (d, $^3J_{H,H}$ = 7.0 Hz, 2H, Ph). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 13.44, 22.65, 32.78, 34.21, 126.22 (2C), 127.41, 128.50, 131.81, 136.77. HRMS: *m*/*z* calcd for $C_{12}H_{16}S$: 192.0973, found 192.0971.

Results and Discussion

As was mentioned above, some kinds of palladium complexes containing propargyl or allenyl ligands were prepared selectively under the appropriate conditions.[3,4,5c] Initially, we investigated the suitable catalytic intermediate in the palladium-catalyzed thiolation using propargylic bromide **1a** and *n*-PrSH (Table 1). The reaction was carried out in the presence of $Pd_2(dba)_3$·$CHCl_3$ and dppe in DMF-d_7 at 60 °C to provide the corresponding propargyl sulfide **2** in 99% yield (Table 1, entry 1). In the absence of the palladium catalyst, the reaction resulted in a low yield of **2** (Table 1, entry 2). The structure of **2** was unambiguously assigned using the ^{13}C NMR spectrum, which exhibited two sp carbon signals (δ 91.9 and 79.1). Other Pd(0) complexes generated in situ from $Pd_2(dba)_3$·$CHCl_3$ and L (L = PPh_3, P(*t*-Bu)$_3$, P(biphenyl)(*t*-Bu)$_2$) were much less effective than Pd(dppe) (Table 1, entries 3−6). When less polar solvents (chloroform-*d* and benzene-d_6) were employed, longer reaction times were required (Table 1, entries 7 and 8). These results suggested the participation of a polar species, such as a cationic (η^3-allenyl/η^3-propargyl)palladium complex, at the rate-determining step.

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(10) (a) Nishibayashi, Y.; Wakiji, I.; Hidai, M. *J. Am. Chem. Soc.* **2000**, *122*, 11019. (b) Inada, Y.; Nishibayashi, Y.; Hidai, M.; Uemura, S. *J. Am. Chem. Soc.* **2002**, *124*, 15172. (c) Kondo, T.; Kanda, Y.; Baba, A.; Fukuda, K.; Nakamura, A.; Wada, K.; Morisaki, Y.; Mitsudo, T. *J. Am. Chem. Soc.* **2002**, *124*, 12960.

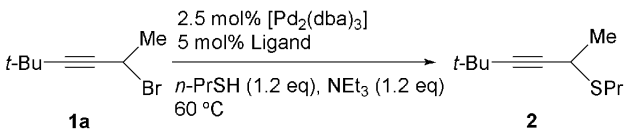
(11) Maclnnes, I.; Walton, J. C. *J. Chem. Soc., Perkin Trans.* **1987**, *2*, 1077.

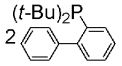
(12) Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnett, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253.

(13) Ogoshi, S.; Fukunishi, Y.; Tsutsumi, K.; Kurosawa, H. *Inorg. Chim. Acta* **1997**, *265*, 9.

(14) Calzada, J. G.; Hooz, J. *Organic Syntheses*; Wiley: New York, 1988; Collect Vol. VI, p 634.

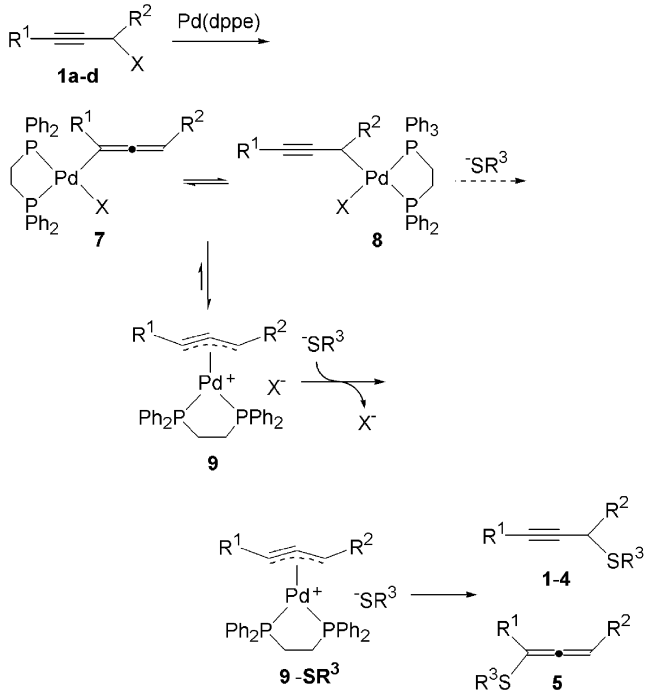
Table 1. Ligand and Solvent Effects in the C−S Bond Formation[a]



entry	ligand	solvent	time (h)	yield (%)[b]
1	dppe	DMF-d_7	2	99 (95)
2[c]	——	DMF-d_7	10	20
3[d]	$2PPh_3$	DMF-d_7	12	55
4[d]	$2P(t\text{-Bu})_3$	DMF-d_7	13	61
5[d]		DMF-d_7	13	51
6	PPh_3	DMF-d_7	12	59
7	dppe	chloroform-*d*	5	89
8	dppe	benzene-d_6	12	84

[a] Reactions were carried out under a nitrogen atmosphere. [b] Determined by ^{1}H NMR spectroscopy (isolated yields are shown in parentheses). [c] In the absence of $Pd_2(dba)_3$ and ligand. [d] $Pd_2(dba)_3$ (2.5 mol %) and PR_3 (10 mol %) were used.

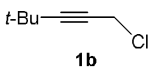
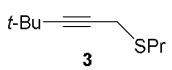
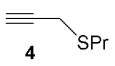
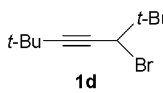
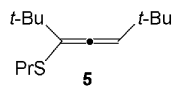
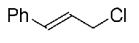
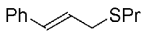
Scheme 1



Subsequently, we extended our studies to help define the scope of these palladium-catalyzed C−S bond formations of other substrates (Table 2). Primary chlorides **1b**,**c** were facially converted to the corresponding propargyl sulfides **3** and **4** in high yields (Table 2, entries 1 and 2). Although the addition of thiols to terminal alkynes in the presence of palladium catalysts is well-known,[15] vinyl sulfides were not produced (Table 2, entry 2). In the case of bulky substituents (*t*-Bu group) at the propargylic position in **1**, the yield of coupling product **5** was low (Table 2, entry 3). However, structural analysis of product **5** using the ^{13}C NMR spectrum exhibited an allenylic sp carbon signal at 192.3 ppm, which suggested the well-known propargylic and allenylic rearrangement for the palladium-catalyzed reaction.[1] This was a different example of producing the allenyl sulfide from the propargyl compound from Ru-catalyzed reactions.[10] The allyl chloride also reacted with *n*-PrSH to give **6** in good yields, and dppe was also more effective than $P(t\text{-Bu})_3$ in these reactions (Table 2, entries 4−5). Trost and Sinou reported palladium-catalyzed nucleophilic substitution of allyl carbonate with thiol, and they used the bidentate ligands dppp (1,3-bis(diphenylphosphino)propane) and dppb (1,4-bis(diphenylphosphino)butane).[16] The Pd(dppe) catalyst, which we presented, may be the most efficient in the C−S bond formation of chlorides.

Considering the relationship between the catalytic reactivity and the stability of the cationic η^3-allenyl/η^3-propargyl species, we propose a catalytic mechanism that involves cationic-type complexes (Scheme 1). Oxidative addition of propargylic compounds **1a**−**d** using Pd−dppe can yield an equilibrium mixture of neutral η^1-type complexes **7** and **8** and the cationic η^3-type complex **9**. The subsequent exchange of the anion (X^-) with the thiolate anion ($^-SR^3$) can yield the thiolate complex **9-SR^3**. This exchange reaction may be feasible for **9** compared with **7** or **8**, since the X^- ligand is already liberated from the metal in the cationic η^3-type complex. We observed that (η^1-PhC≡CCH$_2$)Pt(PPh$_3$)$_2$-Cl, which hardly isomerized to the cationic η^3-allenyl/

Table 2. Palladium-Catalyzed Carbon−Sulfur Bond Formation of 1b−e with *n*-PrSH[a]

entry	substrates	product	ligand	solvent	time (h)	yield (%)[b]
1	 **1b**	 **3**	dppe	DMF-d_7	2	90 (74)
2	 **1c**	 **4**	dppe	DMF-d_7	2	97 (59)
3	 **1d**	 **5**	dppe	DMF-d_7	24	7
4	 **1e**	 **6**	dppe	chloroform-*d*	3	99 (76)
5[c]			$2P(t\text{-Bu})_3$	chloroform-*d*	96	44

[a] Reaction was carried out under a nitrogen atmosphere at 60 °C. [b] Determined by ^{1}H NMR spectroscopy (isolated yields are shown in parentheses). [c] $Pd_2(dba)_3$ (2.5 mol %) and $P(t\text{-Bu})_3$ (10 mol %) were used.

η^3-propargyl complex,[5a,c] did not react with *n*-PrSH and NEt_3 in DMF-d_7 at 60 °C for 1 h. This fact does not contradict the present result. Similar anion-exchange processes have been reported for the palladium-catalyzed reaction of allyl compounds with nucleophiles.[17] Therefore, it is important to generate cationic type complexes by using dppe in polar solvent in the nucleophilic substitution reaction. Although the precise mechanism for the nucleophilic attack of the $^-SR^3$ anion is not clear, one possibility is that the thiolate anion might directly attack the terminal carbon of the η^3-allenyl/η^3-propargyl or η^3-allyl ligand, leading to **2**−**5** or **6**. We should note that, although cationic η^3-allenyl/η^3-propargyl transition-metal complexes tend to undergo regioselective additions of soft nucleophiles at the central carbon,[2e,5b,18] we did not observe the corresponding adduct in our catalytic reactions. Another possibility involves reductive elimination of the carbon and sulfur ligands after coordination of the thiolate anion to palladium to form the (η^1-allenyl)- and (η^1-propargyl)-palladium thiolate complexes. In the reaction of the allyl compound, the liberation of a Cl^- ligand might easily generate the cationic palladium complex by use of dppe rather than PR_3.

Conclusion

We have investigated palladium-catalyzed nucleophilic substitution reactions of propargyl halides with thiol to produce the propargyl and allenyl sulfides. The yields of the coupling products were shown to be dependent on the phosphorus ligand (bidentate > monodentate) and on the nature of the solvent (DMF-d_7 > chloroform-*d* > benzene-d_6), thus indicating that the cationic (η^3-allenyl/η^3-propargyl)palladium complex may be an important intermediate in this reaction. In addition, a similar effect was observed in the reaction of the allyl halide. The present systematic and fundamental data might be useful in gaining insight into various metals bearing unsaturated hydrocarbon ligands and serve as guides for the application of related organometallic compounds in synthetic chemistry.

Acknowledgment. We thank Associate Professor S. Ogoshi and Professor Dr. H. Kurosawa, Faculty of Engineering, Osaka University, for their valuable discussions and suggestions. Thanks are due to Ms. Y. Nishikawa for her assistance in obtaining HRMS measurements. This research was financially supported in part by the Sasagawa Scientific Research Grant from The Japan Science Society and by the Grant-in-Aid for Encouragement of Young Scientists from the Ministry of Education, Science, Sports and Culture, Japan.

OM030120Q

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