group of **2** by a (*Z*)-enolate **4** opposite to the bulky sulfonamide group[3] and (2) coordination of Zn^{II} with the oxygen atom of the nitroso group trans to the N—C(2) bond.[11]

An analogous transition state $B^{\ddagger}$ involving (*E*)-enolates suffers repulsion between the C(3) of the bornane skeleton and the enolate C(α) substituent. Indeed, (E)-zinc enolates derived from cyclic ketones such as α-tetralone, β-tetralone, or cyclohexanone or from the propionate ester of 2,6-dimethylphenol[10] reacted sluggishly with **2a**. Only partial conversion to complex mixtures was observed.

In conclusion, reagents **2a** and **2b**, which are readily accessible in both antipodal forms,[2] represent the first chiral [NH_2^+] equivalents and thus open a new route to diastereo- and enantiomerically pure β-aminols. The synthetic potential of electrophilic nitroso compounds is being further explored in our laboratory.

Acknowledgment. Financial support of this work by the Swiss National Science Foundation, Sandoz Ltd., Basel, and Givaudan SA, Vernier, is gratefully acknowledged. We thank Professor M. T. Reetz for kindly providing reference spectra.

Supplementary Material Available: Preparations and analysis data, including mp, IR, ^{1}H NMR, ^{13}C NMR, MS, and [α] values (11 pages). Ordering information is given on any current masthead page.

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(11) An X-ray structure analysis of dichlorobis(4-nitroso-*N*,*N*-dimethylaniline)zinc(II) exhibits torsional angles Zn–O–N–C = −171.5° and 176.7°; Hu, S.; Thompson, D. M.; Ikekwere, P. O.; Barton, R. J.; Johnson, K. E.; Robertson, B. E. *Inorg. Chem.* **1989**, *28*, 4552–4554.

The First Example of Transition-Metal-Catalyzed Addition of Aromatic Thiols to Acetylenes

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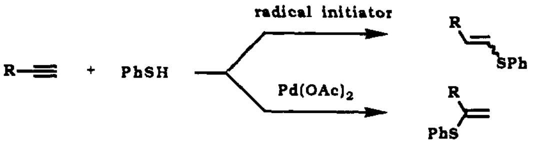
Table I. Effects of Catalysts on the Addition of PhSH to **1a**[a]

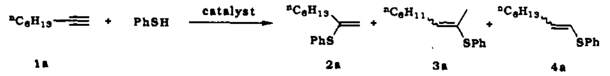
entry	catalyst	condition[b]	yield (%)[c] 2a	3a	4a
1	$Pd(OAc)_2$	A	85[d]	<1	<1
2	$Pd(OAc)_2$	B	62	14	4
3[e]	$Pd(OAc)_2$	C	67	2	<1
4	none	A	0	0	47
5	AcOH	A	0	0	78
6	$Pd(PPh_3)_4$	B	4	10	2
7	$Pd(PPh_3)_4$	C	1	45	4
8	$Pd(PhCN)_2Cl_2$	C	2	73	0
9	$Pt(PPh_3)_4$	C	2	80	18
10	$Ni(PPh_3)_2Cl_2$	C	1	22	2
11	$Rh(PPh_3)_3Cl$	C	14	23	52[f]

[a] **1a** (1.0 mmol), catalyst (0.02 mmol), solvent (0.5 mL), and PhSH (1.0 mmol) for 16 h. [b] A: THF, 40 °C. B: THF, 67 °C. C: PhH, 80 °C. [c] Determined by GLC and ^{1}H NMR spectrometry. [d] Isolated yield. [e] 2,2-Bis(phenylthio)octane (5% based on **1a**) and $(PhS)_2$ (14%) were also produced. [f] *E*/*Z* = 98/2.

Scheme I



While the properties of the complexes resulting from stoichiometric reactions of thiols with transition-metal complexes have been well-studied,[1] there are few reports of transition-metal-catalyzed synthetic reactions with thiols.[2] For instance, for transition-metal-catalyzed addition of thiols to carbon–carbon unsaturated compounds, there is only one example of addition to a 1,3-diene to the best of our knowledge.[2d] Perhaps widespread prejudice that thiols are catalyst poisons has precluded investigation in this area. In this paper we describe the interesting finding that many transition-metal catalysts indeed catalyze the addition of aromatic thiols to acetylenes to provide vinyl sulfides.[3] Table I summarizes the results of the addition of benzenethiol to 1-octyne (**1a**) in the presence of various transition-metal catalysts. Among



(1)

the catalysts examined, $Pd(OAc)_2$ exhibited excellent selectivity to afford the adduct **2a** (eq 1) in good yield (entries 1–3).[4,5] In the absence of catalyst or presence of AcOH, **2a** was not obtained at all, and only **4a** was produced (entries 4 and 5).[6] This may indicate that the palladium complex formed in situ also played an important role in suppression of the formation of **4a**.[7] It has been well-established that the free radical additions of thiols to terminal acetylenes provide anti-Markovnikov adducts,[8] while the present $Pd(OAc)_2$-catalyzed addition afforded the Markovnikov adducts successfully. Thus, these methods presented the regiocomplementary approach to give vinyl sulfides (Scheme I).[9] When $Pt(PPh_3)_4$ was employed as a catalyst, **3a** was produced

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(1) For notable examples, see: (a) Kim, Y. J.; Osakada, K.; Sugita, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1988**, *7*, 2182. (b) Keskinen, A. E.; Senoff, C. V. *J. Organomet. Chem.* **1972**, *37*, 201. (c) Ugo, R.; La Monica, G.; Cenini, S. *J. Chem. Soc. A* **1971**, 522. (d) Nyholm, R. S.; Skinner, J. F.; Stiddard, M. H. B. *J. Chem. Soc. A* **1968**, 38. (e) Chatt, J.; Mann, F. G. *J. Chem. Soc.* **1938**, 1949. (f) Chatt, J.; Hart, F. A. *J. Chem. Soc.* **1960**, 2807. (g) Chatt, J.; Hart, F. A. *J. Chem. Soc.* **1953**, 2363. (h) Fenn, R. H.; Segrott, G. R. *J. Chem. Soc., Dalton Trans.* **1972**, 330. (i) Fenn, R. H.; Segrott, G. R. *J. Chem. Soc. A* **1970**, 3197. (j) Umakoshi, K.; Ichimura, A.; Kinoshita, I.; Ooi, S. *Inorg. Chem.* **1990**, *29*, 4005. (k) Gaylor, J. R.; Senoff, C. V. *Can. J. Chem.* **1972**, *50*, 1868. (l) Osakada, K.; Hayashi, H.; Maeda, M.; Yamamoto, T.; Yamamoto, A. *Chem. Lett.* **1986**, 597. (m) Gaines, T.; Roundhill, D. M. *Inorg. Chem.* **1974**, *13*, 2521. (n) Rakowski DuBois, M. *Chem. Rev.* **1989**, *89*, 1.

(2) (a) Antebi, S.; Alper, H. *Organometallics* **1986**, *5*, 596. (b) Shim, S. C.; Antebi, S.; Alper, H. *J. Org. Chem.* **1985**, *50*, 147. (c) Shim, S. C.; Antebi, S.; Alper, H. *Tetrahedron Lett.* **1985**, *26*, 1935. (d) Dzhemilev, U. M.; Kunakova, R. V.; Gaisin, R. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1981**, *11*, 2655. (e) Talley, J. J.; Colley, A. M. *J. Organomet. Chem.* **1981**, *215*, C38. (f) McKervey, M. A.; Ratananukul, P. *Tetrahedron Lett.* **1982**, *23*, 2509. (g) Holmquist, H. E.; Carnahan, J. E. *J. Org. Chem.* **1960**, *25*, 2240. (h) Iqbal, J.; Pandey, A.; Shukla, A.; Srivastava, R. R.; Tripathi, S. *Tetrahedron* **1990**, *46*, 6423.

(3) For the synthetic utility of vinyl sulfides, see: (a) Trost, B. M.; Lavoie, A. C. *J. Am. Chem. Soc.* **1983**, *105*, 5075. (b) Magnus, P.; Quagliato, D. *J. Org. Chem.* **1985**, *50*, 1621.

(4) Procedure (entry 1): In a reaction vessel were placed $Pd(OAc)_2$ (0.02 mmol), THF (0.5 mL), **1a** (1.0 mmol), and then PhSH (1.0 mmol). After 16 h at 40 °C, the resulting catalyst was removed by filtration through Celite, and then the solvent was evaporated. The crude oil was subjected to MPLC (silica gel) to obtain **2a** (85%). Also isolated in smaller quantities were 2,2-bis(phenylthio)octane (3% based on **1a**) and diphenyl disulfide (6%).

(5) The additions to **1a** of some other thiols such as nBuSH, C_6F_5SH, $MeOCOCH_2SH$, and 2-pyridinethiol were not catalyzed by $Pd(OAc)_2$ under similar reaction conditions.

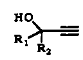
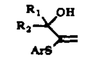
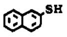
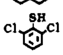
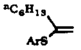
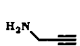
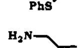
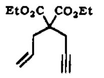
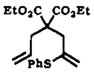
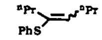
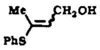
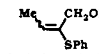
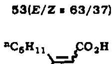
(6) The addition proceeded probably via a free radical mechanism by an adventitious amount of oxygen.

(7) It has been reported that $Fe(CO)_5$ inhibited the radical addition of ArSH to phenylacetylene, see: Kandror, I. I.; Petrova, R. G.; Petrovskii, P. V.; Freidlina, R. Kh. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1969**, *7*, 1621.

(8) (a) Peach, M. E. In *The Chemistry of the Thiol Group*; Patai, S., Ed.; Wiley: London, 1974; Vol. 2. (b) Ichinose, Y.; Wakamatsu, K.; Nozaki, K.; Birbaum, J. L.; Oshima, K.; Utimoto, K. *Chem. Lett.* **1987**, 1647. (c) Griesbaum, K. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 273.

(9) There are few examples of Markovnikov addition of thiols to acetylenes by nucleophilic attack of thiolate anion, but the relatively longer reaction time or more severe conditions are essential; see: (a) Truce, W. E.; Simms, J. A. *J. Am. Chem. Soc.* **1956**, *78*, 2756. (b) Borisova, A. I.; Filippova, A. K.; Voronov, V. K.; Shostakovski, M. F. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1969**, 2498.

Table II. $Pd(OAc)_2$-Catalyzed Addition of ArSH to Acetylenes[a]

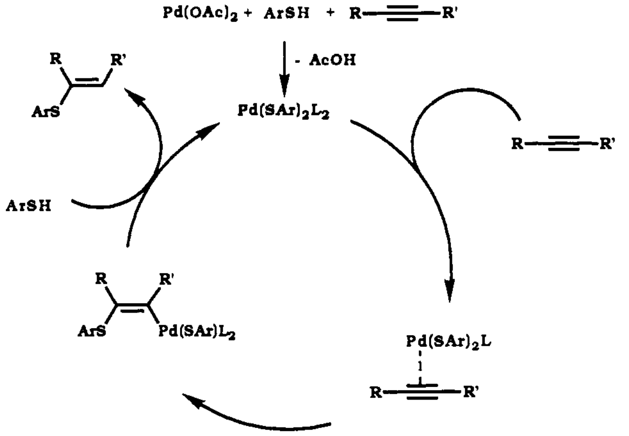
entry	acetylene	ArSH	product and yield (%)[b]	yield of regioisomers (%)[c]
				
1	$R_1 = R_2 = Me$	PhSH	86	0
2	$R_1, R_2 = -(CH_2)_4-$	PhSH	63	0
3	$R_1 = R_2 = Me$		85	0
4	${}^{n}C_6H_{13}$—≡		 55	–[d]
5[e]	Me_3Si—≡	PhSH	 56	5
6[f]		PhSH	 65 (87)[g]	0
7		PhSH	 70	–[d]
8	${}^{n}Pr$—≡—${}^{n}Pr$	PhSH	 72 (E/Z = 34/66)[c] (E/Z = 92/8)[c,h]	
9	Me—≡—CH_2OH	PhSH	 53(*E*/*Z* = 63/37)[c]  29 (*E*/*Z* = 48/52)[c]	
10	${}^{n}C_5H_{11}$—≡—CO_2H	PhSH	 87(E/2 = 98/2)[i]	2

[a] Conditions: acetylene (1.0 mmol), $Pd(OAc)_2$ (0.02 mmol), and ArSH (1.0–1.3 mmol) in THF (0.5 mL) at 67 °C for 12–16 h. [b] Isolated yield. [c] Determined by ^1H NMR and GLC. [d] A complex mixture was produced as byproduct. [e] Without solvent at 70 °C. [f] 24 h. [g] NMR yield. [h] 10 min. [i] See ref 14.

as a major product (entry 9). Considering that PhSH oxidatively adds to $Pt(PPh_3)_4$ to afford $PtH(PPh_3)_2(PhS)$,[1b,c] similar species may be generated in this catalytic reaction system.[10] $Pd(PPh_3)_4$, $Pd(PhCN)_2Cl_2$, and $Ni(PPh_3)_2Cl_2$ also exhibited catalytic activity and similar selectivity of the products (entries 6–8 and 10), while the $Rh(PPh_3)_3Cl$-catalyzed reaction provided (*E*)-**4a** as a major product with high stereoselectivity (entry 11).

To ascertain the stereochemistry of the $Pd(OAc)_2$-catalyzed addition to give Markovnikov adduct **2a**, the reaction of PhSH with 1-octyne-*1*-*d* (containing >93% *d*) in THF-d_8 was followed by ^1H NMR spectroscopy. The *E*/*Z* ratio[11] of monodeuterated adducts **2a** changed from 100/0 (6% conversion) after 15 min to 86/14 (81% conversion) after 8 h. Thus, the *E* isomer can be accepted as the kinetic product, which gradually isomerized to the *Z* isomer.[12] This clearly indicated that cis addition of PhSH to **1a** proceeded at least at the initial stage. The results of the $Pd(OAc)_2$-catalyzed addition of some aromatic thiols to acetylenes are shown in Table II. Hydroxy, trimethylsilyl, and amino groups may be present in the acetylenes (entries 1–3, 5, and 6). Among the aromatic thiols examined, 2,6-dichlorobenzenethiol and 2-naphthalenethiol also added to acetylenes (entries 3 and 4).[13] The acetylene bearing a tethered olefin unit underwent chemoselective addition to the triple bond (entry 7). The addition also proceeded smoothly with internal acetylenes to give a mixture of stereoisomers, although the cis adduct (*E* isomer) was also predominantly formed at the beginning of the reaction (entry 8). The addition to 2-butyn-1-ol gave slight regioselectivity (entry 9). Interestingly, the addition to 2-octynoic acid afforded the adducts with good stereo- and regioselectivity (entry 10).[14]

Scheme II. Proposed Reaction Path for the $Pd(OAc)_2$-Catalyzed Addition of ArSH to Acetylenes



To obtain some insight into the active catalyst of the $Pd(OAc)_2$-catalyzed addition, the reaction of $Pd(OAc)_2$ with 3 equiv of PhSH[15] was carried out in THF-d_8. The mixture immediately deposited dark brown precipitates,[16] and the formation of ca. 2 equiv of AcOH was confirmed by ^1H NMR spectroscopy. Although the actual reaction pathway of $Pd(OAc)_2$-catalyzed addition of ArSH to acetylenes is still unknown, a mechanistic proposal includes the following: (1) ligand exchange of AcO ligand with PhS group in the presence of acetylene[16,17] to give AcOH and an active catalyst; (2) coordination of acetylene to palladium; (3) syn-thiopalladation[18] to acetylene to form *cis*-vinylpalladium (the order of R′ preferred: hydrogen > oxygen-containing group > alkyl group); and (4) trapping of the vinyl group by PhSH[19] or AcOH with retention of stereochemistry to give the Markovnikov adduct with regeneration of the catalyst (Scheme II).

Further study is focusing on details of the mechanisms of this addition catalyzed by $Pd(OAc)_2$ and other catalysts. The present study presages the development of a new class of transition-metal-catalyzed reactions based on thiols.

Acknowledgment. This research was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture, Japan. Thanks are due to Instrumental Analysis Center, Faculty of Engineering, Osaka University, for assistance in obtaining mass spectra with a JEOL JMS-DX303 instrument.

Supplementary Material Available: Listings of experimental procedures and analysis data for the compounds in this communication and ^1H NMR spectra for the reaction of 1-octyne-*1*-*d* with PhSH (7 pages). Ordering information is given on any current masthead page.

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(10) The ratio of a mixture of isolated **2a**/**3a** (82/18) changed to 13/87 in the presence of $Pt(PPh_3)_4$, PhSH, and acetylene, suggesting that **2a** is a precursor of **3a**.

(11) The assignment of the vinyl protons was confirmed by an NOE experiment of **2a**.

(12) The formation of the product containing two deuteriums was not observed judging from the fragmentation of the mass spectrum of the product. This fact may indicate that the isomerization of *E* to *Z* is promoted by addition and elimination of Pd–SPh (and/or PhS•) to the C–C double bond of **2a**.

(13) The substituents on aromatic thiol had drastic effects on the $Pd(OAc)_2$-catalyzed addition. For example, the addition of 4-chloro- or 4-hydroxybenzenethiol to **1a** gave bis-adducts as the main products. On the other hand, the addition of 4-methyl- or 4-methoxybenzenethiol to **1a** was scarcely catalyzed by $Pd(OAc)_2$ under similar reaction conditions. The details are now under investigation.

(14) The assignment of stereochemistry was confirmed by ^1H NMR spectroscopy. The signal of the cis vinyl proton for the PhS group appeared upfield from that of trans vinyl proton by ca. 0.3–0.7 ppm. See the supplementary material.

(15) Nyholm et al. have already described that the reaction of $Pd(OAc)_2$ with PhSH gave a polymeric product; see ref 1d.

(16) This precipitate scarcely exhibited the catalytic activities for the addition of PhSH to **1a**. On the other hand, the precipitates prepared *in the presence of* **1a** had a moderate catalytic activity. Detailed results are provided in the supplementary material.

(17) To obtain good yields of Markovnikov adducts in this $Pd(OAc)_2$-catalyzed addition, acetylenes must be added to $Pd(OAc)_2$ before the addition of PhSH; see ref 4.

(18) We have already reported the $Pd(PPh_3)_4$-catalyzed addition of diphenyl disulfide to acetylenes, indicating the facile insertion of acetylene into the Pd–S bond; see: Kuniyasu, H.; Ogawa, A.; Miyazaki, S.; Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1991**, *113*, 9796.

(19) For the ability of thiol to cleave the alkyl-metal bond, see: Johnson, A.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1975**, 115.