J|A|C|S
COMMUNICATIONS

Published on Web 03/06/2004

Catalytic Enantioselective Hydrostannation of Cyclopropenes

Marina Rubina, Michael Rubin, and Vladimir Gevorgyan*

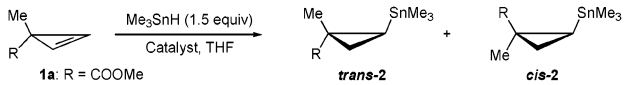
Department of Chemistry, University of Illinois at Chicago, 845 West Taylor Street, Chicago, Illinois 60607-7061

Received January 16, 2004; E-mail: vlad@uic.edu

Hydrostannation of the carbon−carbon double bond is an important process,[1] which allows for the straightforward preparation of various types of useful building blocks for organic synthesis.[2] While enantioselective versions of related hydrometalation processes, such as hydrosilylation[3] and hydroboration,[4] are well-known, no precedents on enantioselective hydrostannation have been reported to date. Although diastereoselective radical hydrostannation employing chiral auxiliaries on either the substrate[5] or tin hydride moiety[6] have been reported, the obtained de's were below 40%. Herein we report the first example of catalytic highly enantioselective hydrostannation of the double bond of cyclopropenes, which allows for easy access to valuable optically active cyclopropylstannanes.[7]

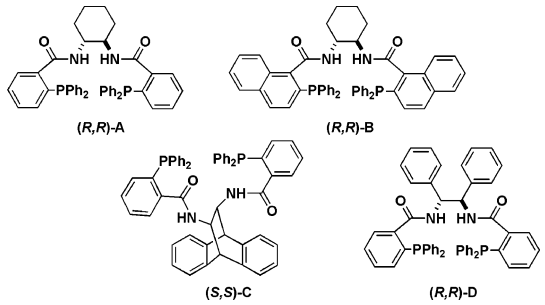
We have recently reported the highly diastereoselective transition metal-catalyzed hydrostannation of cyclopropenes.[8] This method allowed for efficient introduction of up to five different substituents in the cyclopropyl ring. Obviously, we were interested in achieving asymmetric hydrostannation of cyclopropenes en route to nonracemic cyclopropylstannanes. Encouraged by the remarkable efficiency of the [Pd(π-allyl)Cl]$_2$/(±)-MOP catalyst system in the hydrostannation of a series of multisubstituted cyclopropenes,[8] we naturally attempted enantioselective hydrostannation of **1a** in the presence of optically active (+)-*R*-MOP ligand. This catalyst system was previously shown by Hayashi to be very effective in the enantioselective hydrosilylation of olefins.[3] However, this combination provided disappointingly low enantiomeric induction (12% ee) in the hydrostannation of **1a** (Table 1, entry 1). Screening a number of commercially available ligands revealed that the Trost ligand (**A**) in combination with the Pd catalyst smoothly effected the reaction, exhibiting a moderate ee (47%, entry 2), while all other chiral ligands tested provided either no reaction or decomposition of the starting material. Further improvement of enantioselectivity (62% ee, entry 3) was achieved when Rh catalyst[9] was employed instead of Pd in combination with ligand **A**. Moreover, switching to Rh allowed for complete suppression of the undesired formation of ditin,[10] significant quantities of which were observed in all the Pd-catalyzed reactions. The hydrostannation of **1b** under these conditions provided comparable degrees of enantiomeric induction (entry 4). Inspired by the promising results obtained with ligand **A**, we decided to screen a series of different diphenylphosphinobenzoic acid-derived ligands, analogues of **A**, which were previously demonstrated by Trost to efficiently catalyze asymmetric allylic alkylation reactions.[11] Employment of naphthyl-based ligand **B**, however, significantly impeded the reaction and afforded lower enantioselectivity (42% ee, entry 6). Furthermore, anthracene-based ligand **C** provided completely racemic product (entry 7). Gratifyingly, hydrostannation of **1b** in the presence of stilbene-derived ligand **D** proceeded smoothly, affording cyclopropylstannane **2a** with respectable enantioselectivity (80% ee, entry 8). With this result in hand, we performed further optimization of the reaction condition. Expectedly, the enantiomeric induction was significantly improved at lower reaction temperatures. Thus, a slightly higher ee was obtained at 0 °C (entry 9), whereas a dramatic improvement to up to 94% ee was achieved at temperatures as low as −30 °C (entry 10). Hydrostannation of cyclopropene **1b** under these conditions also displayed a very high enantiomeric induction (90%, entry 11). Notably, the replacement of trimethyltin hydride with Bu_3SnH, in this reaction, resulted in the totally racemic product (entry 5).

Table 1. Optimization of Enantioselective Hydrostannation of **1a**,**b**



entry	R	catalyst	*T*, °C	time	trans/cis	ee,%[a]
1	CO_2Me	[Pd][b]/(*R*)-MOP	−85	5 min	95/5	12
2	CO_2Me	[Pd]/ligand **A**	r.t.	10 min	98/2	47
3	CO_2Me	[Rh][c]/ligand **A**	r.t.	20 min	>99/1	62
4	Ph	[Rh]/ligand **A**	r.t.	20 min	>99/1	65
5	CO_2Me	[Rh]/ligand **A**	r.t.	5 h	>99/1	0[d]
6	CO_2Me	[Rh]/ligand **B**	r.t.	1 day	>99/1	42
7	CO_2Me	[Rh]/ligand **C**	r.t.	20 min	>99/1	0
8	CO_2Me	[Rh]/ligand **D**	r.t.	20 min	>99/1	80
9	CO_2Me	[Rh]/ligand **D**	0	30 min	>99/1	84
10	CO_2Me	[Rh]/ligand **D**	−30	45 min	>99/1	94
11	Ph	[Rh]/ligand **D**	−30	45 min	>99/1	90

[a] Enantiomeric excess was determined by chiral GC analysis. [b] [Pd(π-allyl)Cl]$_2$. [c] [Rh(COD)Cl]$_2$. [d] Bu_3SnH was employed.

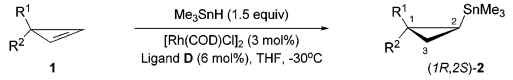


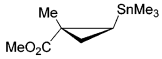
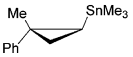
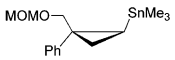
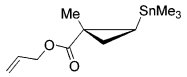
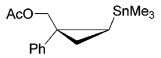
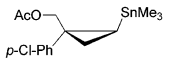
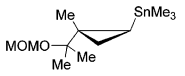
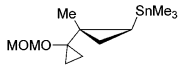
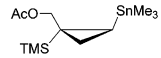
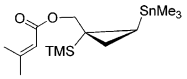
Next, the optimized conditions were applied to the hydrostannation of a series of 3,3-disubstituted cyclopropenes (Table 2). We were pleased to find that preparative hydrostannation of **1a**,**b** reproduced the high ee's and allowed for the synthesis of cyclopropylstannanes **2a**,**b** in high isolated yields (entries 1, 2). Likewise, hydrostannation of MOM-protected cyclopropenyl carbinol **1c** proceeded smoothly to give **2c** with high yield and enantioselectivity (entry 3). Hydrostannation of allyl ester **1d** similarly to its methyl analogue **1a**, proceeded uneventfully to give **2d** with very high enantiomeric excess (97% ee, entry 4). Esters **1e**,**f**,**i**,**j** and MOM-ethers **1g**,**h** of differently substituted cyclopropenyl carbinols were also smoothly hydrostannated under these reaction conditions to afford optically active cyclopropylstannanes **2e**−**j** with high yields and ee's (entries 5−10).

Remarkably, facial selectivity of the Rh-catalyzed hydrostannation was perfectly controlled by steric effects of substituents at C-3 of cyclopropenes, affording cyclopropylstannanes (*1R*,*2S*)-**2**[12] as

10.1021/ja0496928 CCC: $27.50

Table 2. Rh-Catalyzed Enantioselective Hydrostannation of Cyclopropenes[a]



	cyclopropene **1**		cyclopropane **2**		yield, %[b]	ee, %[c]	$[\alpha]_D$[d]
	R^1	R^2					
1	Me	CO_2Me **(1a)**		**2a**	90	94	+56.5
2	Me	Ph **(1b)**		**2b**	87	90	+69.8
3	CH_2OMOM	Ph **(1c)**		**2c**	86	93	+70.6
4	Me	CO_2All **(1d)**		**2d**	79	97	+59.7
5	CH_2OAc	Ph **(1e)**		**2e**	88	95	+80.9
6	CH_2OAc	Ph-*p*-Cl **(1f)**		**2f**	83	96	+84.1
7	Me	$C(Me)_2OMOM$ **(1g)**		**2g**	77	92	+24.8
8	Me	$(c\text{-}C_3H_4)$-1-OMOM **(1h)**		**2h**	76	88	+37.8
9	CH_2OAc	TMS **(1i)**		**2i**	73	96	+43.2
10	$CH_2OC(O)CH=CMe_2$	TMS **(1j)**		**2j**	87	94	+39.7

[a] All reactions were performed in 1 mmol scale. [b] Isolated yield. [c] Enantiomeric excess was determined by chiral GC. [d] (c 1.00, CH_2Cl_2).

single diastereoisomers. This observation is in a striking contrast with the previously reported Rh-catalyzed enantioselective hydroboration of cyclopropenes,[9] which was governed by a requisite directing effect of ester or alkoxymethyl substituents. As can be seen from Table 2, the reaction is very general with respect to substituents at C-3 and displays good functional group compatibility.

Thus, we feel that synthesis of optically active cyclopropylmetal synthons via enantioselective hydrostannation of cyclopropenes has a more general scope compared to enantioselective hydroboration,[9] as it does not require directing groups for achieving high degrees of enantioselectivity. Furthermore, this method allows for easy access to optically active *trans*-stannyl derivatives of cyclopropylcarboxylates, complimentary to the earlier reported *cis*-boronyl derivatives. It should be mentioned that tri- and tetrasubstituted cyclopropenes did not undergo the hydrostannation reaction at all under these reaction conditions.

In conclusion, we believe that the chemistry described herein is not only fundamentally important as the first example of catalytic enantioselective hydrostannation of a C=C double bond, but it also has high potential in synthesis as it allows for the very efficient and straightforward approach to optically active cyclopropylstannanes, invaluable building blocks for organic synthesis.

Acknowledgment. The support of the National Science Foundation (CHE-0354613) is gratefully acknowledged.

Supporting Information Available: Experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) See for example: (a) Nakamura, E.; Machii, D.; Inubushi, T. *J. Am. Chem. Soc.* **1989**, *111*, 6849. (b) Lambert, M.-P.; Ratier, M.; Duboudin, J.-G.; Petraud, M. *J. Organomet. Chem.* **1994**, *467*, 181. (c) Nakamura, E.; Imanishi, Y.; Machii, D. *J. Org. Chem.* **1994**, *59*, 8178. (d) Voskoboynikov, A. Z.; Beletskaya, I. P. *New J. Chem.* **1995**, *19*, 723. (e) Lautens, M.; Klute, W. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 442. (f) Lautens, M.; Kumanovic, S.; Meyer, C. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1329. (g) Gevorgyan, V.; Liu, J.-X.; Yamamoto, Y. *Chem. Commun.* **1998**, 37.

(2) For reviews, see: (a) Fugami, K.; Kosugi, M. *Top. Curr. Chem.* **2002**, *219*, 87. (b) Boudier, A.; Brom, L. O.; Lotz, M.; Knochel, P. *Angew. Chem., Int. Ed.* **2000**, *39*, 4414.

(3) For reviews, see: (a) Hayashi, T. *Acc. Chem. Res.* **2000**, *33*, 354−362. (b) Hayashi, T. *Catal. Today* **2000**, *62*, 3.

(4) See for example: (a) Burgess, K.; Ohlmeyer, M. J. *J. Org. Chem.* **1988**, *53*, 5178. (b) Hayashi, T.; Matsumoto, Y.; Ito, Y. *J. Am. Chem. Soc.* **1989**, *111*, 3426. (c) Evans, D. A.; Fu, G. C.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1992**, *114*, 6671. (d) Togni, A.; Breutel, C.; Schnyder, A.; Spindler, F.; Landert, H.; Tijani, A. *J. Am. Chem. Soc.* **1994**, *116*, 4062. (e) Fernandez, E.; Maeda, K.; Hooper, M. W.; Brown, J. M. *Chem. Eur. J.* **2000**, *6*, 1840. (f) Demay, S.; Volant, F.; Knochel, P. *Angew.* Chem., Int. Ed. **2001**, *40*, 1235. (g) Perez Luna, A.; Ceschi, M. A.; Bonin, M.; Micouin, L.; Husson, H.-P. *J. Org. Chem.* **2002**, *67*, 3522.

(5) (a) Rahm, A.; Pereyre, M.; Valade J.; Calas, R. *C. R Acad. Sci., Ser. C* **1971**, *273*, 518. (b) Rahm, A.; Pereyre, M. *J. Organomet. Chem.* **1975**, *88*, 79. (c) Rahm, A.; Degueil-Castaing, M.; Pereyre, M. *Tetrahedron Lett.* **1980**, *21*, 4649. (d) Podestá, J. C.; Chopa, A. B.; Koll, L. C.; Mandolesi, S. D. *J. Organomet. Chem.* **1992**, *434*, 269. (e) Ayala, A. D.; Chopa, A. B.; Giagante, N. N.; Koll, L. C.; Mandolesi, S. D.; Podestá, J. C. *Anal. Asoc. Quim. Argentina* **1998**, *86*, 139. (f) Mandolesi, S. D.; Koll, L. C.; Chopa, A. B.; Podestá, J. C. *J. Organomet. Chem.* **1998**, *555*, 151.

(6) Mandolesi, S. D.; Koll, L. C.; Podestá, J. C. *J. Organomet. Chem.* **1999**, *587*, 74.

(7) See, for example: (a) Itoh, T.; Inoue, H.; Emoto, S. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 409. (b) Hoffmann, R. W.; Koberstein, R. *Chem. Commun.* **1999**, 33. (c) Falk, J. R.; Mekonnen, B.; Yu, J.; Lai, J.-Y. *J. Am. Chem. Soc.* **1996**, *118*, 6096. (d) Liebeskind, L. S.; Riesenger, S. W. *Tetrahedron Lett.* **1991**, *32*, 5681. (e) Charette, A. B.; Juteau, H.; Lebel, H.; Molinaro, C. *J. Am. Chem. Soc.* **1998**, *120*, 11943. (f) Doyle, M. P.; Pieters, R. J.; Martin, S. F.; Austin, R. E.; Oalmann, C. J.; Muller, P. *J. Am. Chem. Soc.* **1991**, *113*, 1423. (g) Corey, E. J.; De, B. *J. Am. Chem. Soc.* **1984**, *106*, 2735. (h) Wakamatsu, H.; Isono, N.; Mori, M. *J. Org. Chem.* **1997**, *62*, 8917.

(8) Rubina, M.; Rubin, M.; Gevorgyan, V. *J. Am. Chem. Soc.* **2002**, *124*, 11566.

(9) For Rh-catalyzed asymmetric hydroboration of cyclopropenes, see: Rubina, M.; Rubin, M.; Gevorgyan, V. *J. Am. Chem. Soc.* **2003**, *125*, 7198.

(10) For formation of ditin species from tin hydrides in the presence of Pd catalyst, see for example: (a) Bumagin, N. A.; Gulevich, Y. N.; Beletskaya, I. P. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1982**, 2639. (b) Bumagin, N. A.; Gulevich, Y. N.; Beletskaya, I. P. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1984**, 1137.

(11) (a) Trost, B. M.; Oslob, J. D. *J. Am. Chem. Soc.* **2001**, *121*, 3057. (b) Trost, B. M.; Lee, C. B. *J. Am. Chem. Soc.* **2001**, *123*, 3671. (c) Trost, B. M.; Schroeder, G. M.; Kristensen, J. *Angew. Chem., Int. Ed.* **2002**, *41*, 3492.

(12) For determination of absolute configuration of **2**, see Supporting Information.

JA0496928