converted the cyclobutane into the pyran, thus demonstrating the kinetic preference for the [2 + 2] pathway in this series.[26] Clearly, 3 is a mild Lewis acid, as these cyclizations proceeded rapidly at −78 °C with $BF_3 \cdot OEt_2$. Nonetheless, the potential for rationally designed improvements in coordinating ability and catalytic activity have been clearly demonstrated in the superior Lewis acidity of 3 compared to that of 1. Indeed, whereas 1 was shown to coordinate 4-(dimethylamino)benzaldehyde at low temperature,[11c] it displayed no activity as a Lewis acid in these reactions. Recently, however, Martin has reported the use of 1 as a Lewis acid catalyst in the reduction of carbonyl groups with a hydridosilicate.[27]

The synthesis and reactions of chiral, nonracemic organogermanium complexes as well as further applications of strain release Lewis acidity will be the subject of future reports.

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Supplementary Material Available: Preparation details and full characterization data for 3 and **4a–d**, along with listings of crystal data, positional and thermal parameters, bond lengths and angles, torsional angles, and van der Waals contacts and ORTEP diagrams and unit cell packing figures for 3 and **4b** (42 pages); tables of structure factors for 3 and **4b** (20 pages). Ordering information is given on any current masthead page.

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(25) The stereostructure of 9 is tentatively assigned on the basis of NOEDS experiments.

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Nickel-Catalyzed Cross Couplings of Dithioacetals with Me_3SnCH_2MgI. A Possible β-Trimethylstannide Elimination[†]

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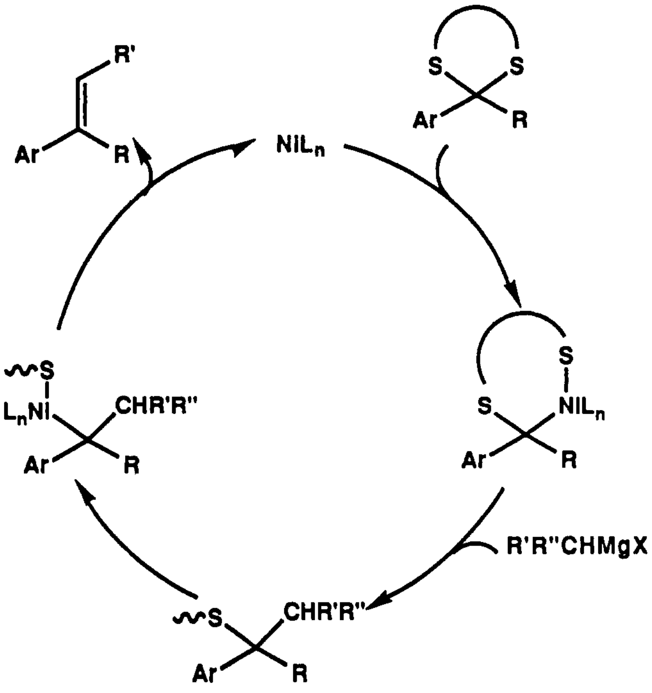
Summary: $NiCl_2(PPh_3)_2$-catalyzed cross coupling reactions of benzylic dithioacetals with Me_3SnCH_2MgI give arylethenes in good yields. The reaction may proceed preferentially via a possible β-trimethylstannide elimination.

β-Elimination of an organometallic species is extremely important in transition-metal-catalyzed reactions.[1] We recently reported several useful nickel-catalyzed cross-coupling reactions of Grignard reagents with dithioacetals.[2,3] Various evidence suggests that the mechanism of this catalytic process may involve the first formation of a carbon–carbon bond followed by an elimination step (Scheme I).[3a,4] When Me_3SiCH_2MgCl is employed, the reaction gives a facile synthesis of allyl-[3b] and vinylsilanes.[3c,d,h] In these cases, β-hydride elimination is apparently more favorable than β-elimination of a Me_3Si group.[5] Since the carbon–tin bond is weaker than the carbon–silicon bond,[6] it seems conceivable that the β-trimethylstannyl group might undergo facile elimination during the course of the catalytic reactions. We have tested this viewpoint and now describe one such elimination reaction in the nickel-catalyzed cross-coupling reac-

Scheme I



(R' = H, Alkyl, or Me_3Si, R" = H or Me_3Sn)

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[†] Dedicated in memory of the late Professor J. K. Stille.

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(1) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA 1987; Chapter 6.

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(3) (a) Ni, Z.-J.; Luh, T.-Y. *J. Chem. Soc., Chem. Commun.* **1987**, 1515. (b) Ni, Z.-J.; Luh, T.-Y. *J. Chem. Soc., Chem. Commun.* **1988**, 1011. (c) Ni, Z.-J.; Luh, T.-Y. *J. Org. Chem.* **1988**, *53*, 2129. (d) Ni, Z.-J.; Luh, T.-Y. *J. Org. Chem.* **1988**, *53*, 5582. (e) Yanf, P.-F.; Ni, Z.-J.; Luh, T.-Y. *J. Org. Chem.* **1989**, *54*, 2261. (f) Ng, D. K. P.; Luh, T.-Y. *J. Am. Chem. Soc.* **1989**, *111*, 9119. (g) Tzeng, Y.-L.; Luh, T.-Y.; Fang, J.-M. *J. Chem. Soc., Chem. Commun.* **1990**, 399. (h) Ni, Z.-J.; Yang, P.-F.; Ng, D. K. P.; Tzeng, Y.-L.; Luh, T.-Y. *J. Am. Chem. Soc.*, in press.

(4) The sulfur moiety has been trapped as bis(benzyl) thioether.

(5) Karabelas, K.; Hallberg, A. *J. Org. Chem.* **1986**, *51*, 5286.

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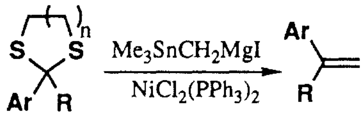
Table I. Reactions of Dithioacetals with Me_3SnCH_2MgI



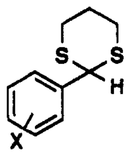
1 2

1	Ar	R	n	% yield of 2
a	2-naphthyl	H	2	84
b	1-naphthyl	H	2	73
c	9-anthracenyl	H	2	77
d	1-naphthyl	Me	1	62
e	2-naphthyl	Me	1	73
f	Ph	Ph	1	63

tions of dithioacetals with Me_3SnCH_2MgI.

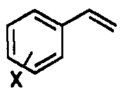
Treatment of benzylic dithioacetals (**1**) with 4 equiv of Me_3SnCH_2MgI (prepared from Me_3SnCH_2I[7] and magnesium) in the presence of 5 mol % $NiCl_2(PPh_3)_2$ in refluxing benzene for 16 h followed by usual workup and chromatographic separation or distillation afforded arylethenes **2** in good yields. No trace amount of vinylstannanes or allylstannanes was detected. The results are compiled in Table I.

As can be seen from Table I, the ring size of the dithioacetals had no effect on the reaction, and substrates derived from ketones or aldehydes showed no apparent difference in reactivity. The halogen atom on the aromatic ring would expectedly react under the reaction conditions,[8] hence, the benzylic trimethylstannyl group being introduced simultaneously. Indeed, when **1g** and **1h** were treated with Me_3SnCH_2MgI under the usual conditions, **3a** and **3b**[9] were obtained in 72% and 61% yields, respectively. This observation indicated that the Me_3SnCH_2 moiety should be responsible for the coupling reactions and the trimethylstannyl group will be lost in the later stage of the reaction.



1g X = 3-Br

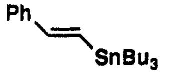
h X = 2-Br



3a X = 3-Me_3SnCH_2

b X = 2-Me_3SnCH_2

It is well-documented that the transmetalation readily happens upon treatment with vinylstannanes with alkyllithium.[6] It is important to investigate if such an exchange reaction also occurs under our reaction conditions. Thus, **1a** was allowed to react with 4 equiv of Me_3SnCH_2MgI under the same conditions followed by quenching the reaction mixture with D_2O and the usual workup. **2a** was obtained in 85% yield without deuterium incorporation. Furthermore, when 0.5 mmol each of **1a** and **4** were treated with 4 mmol of Me_3SnCH_2MgI in the presence of 0.05 mmol of $NiCl_2(PPh_3)_2$ under the same conditions for 16 h, a mixture of **2a** (85%) and **4** (85%) was obtained. These results suggested that, if a vinylstannane were formed from the reaction, it would not undergo transmetallation to give **5** or the like under the reaction conditions.



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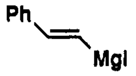

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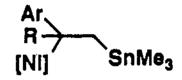

6

Our results indicated that the active species for the cross-coupling reactions of dithioacetals will be the Me_3SnCH_2 moiety and the reaction may follow the general pattern shown in Scheme I. Intermediate **6** may proceed preferentially by β-elimination of Me_3Sn group, giving **2**. The actual mode of such elimination step, however, is not clear at this stage. Either the concerted elimination mechanism or the stepwise radical process via the homolytic cleavage of the carbon–nickel bond in **6** followed by the elimination of a Me_3Sn radical[10,11] would yield the same product.[12]

In summary, we have demonstrated a possible β-elimination of Me_3Sn group in the nickel-catalyzed cross-coupling reaction of dithioacetals with Me_3SnCH_2MgI. The generality of such an elimination reaction in the transition-metal-mediated catalytic process is under investigation.

Acknowledgment. We thank the National Science Council of the Republic of China for support.

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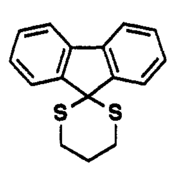
[7] Seyferth, D.; Andrews, S. B. *J. Organomet. Chem.* **1971**, *30*, 151.

[8] Kumada, M. *Pure Appl. Chem.* **1980**, *52*, 669.

[9] **3a.** ^1H NMR: δ 0.05 (s with satellites, $J_{\text{Sn-CH}} = 52.3$ Hz, 9 H), 2.30 (s with satellites, $J_{\text{Sn-CH}} = 61.3$ Hz, 2 H), 5.19 (d, $J = 10.9$ Hz, 1 H), 5.70 (d, $J = 17.6$ Hz, 1 H), 6.66 (dd, $J = 10.9, 17.6$ Hz, 1 H), 6.88 (d, $J = 7.3$ Hz, 1 H), 7.01–7.17 (m, 3 H). ^{13}C NMR: δ −10.6, 20.2, 113.2, 121.3, 124.8, 126.5, 128.5, 137.4, 137.7, 143.4. **3b.** ^1H NMR: δ 0.02 (s with satellites, $J_{\text{Sn-CH}} = 52.3$ Hz, 9 H), 2.36 (s with satellites, $J_{\text{Sn-CH}} = 63.4$ Hz, 2 H), 5.20 (d, $J = 10.9$ Hz, 1 H), 5.55 (d, $J = 17.3$ Hz, 1 H), 6.84 (dd, $J = 10.9, 17.3$ Hz, 1 H), 6.91–7.10 (m, 3 H), 7.39 (d, $J = 7.7$ Hz, 1 H). ^{13}C NMR: δ −9.4, 18.3, 114.6, 123.7, 125.8, 127.7, 127.9, 134.4, 135.4, 141.0.

[10] (a) Keck, G. E.; Enholm, E. J.; Yates, J. B.; Wiley, M. R. *Tetrahedron* **1985**, *41*, 4079. (b) Baldwin, J. E.; Adlington, R. M.; Birch, D. J.; Crawford, J. A.; Sweeney, J. B. *J. Chem. Soc., Chem. Commun.* **1987**, 153. (c) Russell, G. A.; Ngoviwatchai, P.; Tashtoush, H. I. *Organometallics* **1988**, *7*, 696. (d) Curran, D. P.; van Elburg, P. A.; Giese, B.; Gilges, S. *Tetrahedron Lett.* **1990**, *31*, 2861.

[11] Our experience (cf. refs 2 and 3) has shown that only in very rare cases in the nickel-catalyzed cross coupling of dithioacetals with Grignard reagents can we obtain the corresponding dimeric products that may arise from the homolytic cleavage of the carbon–nickel bond in the intermediate like **6**. For example, the reaction of **7** with MeLi in the presence of a catalytic amount of $NiCl_2(PPh_3)_2$ gave **8** and **9** in significant amount. It is noteworthy that such a homolytic process is well-documented in the nickel-catalyzed reactions (cf. Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic: New York, 1978; Chapter 13).



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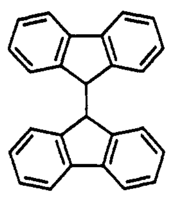

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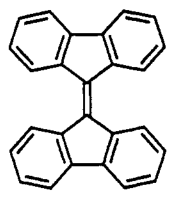

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[12] The referees have suggested an alternative possibility that may occur via elimination of a Me_3SnS∿ group from a β-sulfurated organotin species.