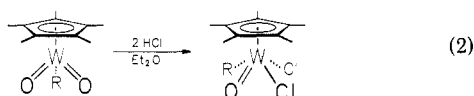
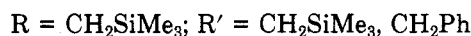
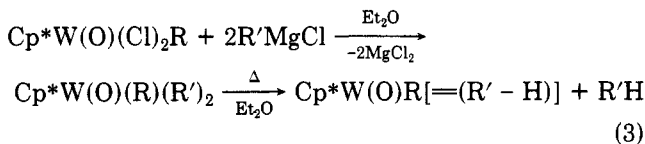


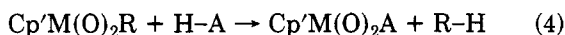
(O)₂R complexes are treated with 2 equiv of HCl in Et₂O (eq 2).¹⁰ The Cp*W(O)(Cl)₂(CH₂SiMe₃) and Cp*W(O)-



(Cl)₂Me products isolated to date from reactions 2 exhibit IR and ¹H and ¹³C{¹H} NMR spectra which are consistent with their possessing the molecular structures shown.⁶ These product complexes are also very useful synthetic precursors, e.g. reactions 3 affording the final oxo alkylidene complexes in much higher yields than other routes.^{5,6}



In essence, the chemical transformations of the M=O links shown in reactions 1 and 2 are those classically found for these functional groups.^{9,11,12} The unusual feature is that the M-C σ bonds remain intact,¹³ there being no evidence for the occurrence of the conversions



where H-A = a protonic acid such as H₂O₂ or HCl. Our preliminary investigations also indicate that the applicability of reactions 1 and 2 is only limited by the availability of the requisite dioxo alkyl complexes of which we now have an extended series.¹⁵ Consequently, we are currently extending this work to include a wide range of protonic acids and are endeavoring to ascertain the effects of the M-C σ bonds on the reactivities of the alkyl peroxy and the oxo alkylidene complexes.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work in the form of grants to P.L. and J.T. We also thank Professors Jack Fallner and Bob Bergman for stimulating conversations and for informing us of their related work prior to publication.

Registry No. CpMo(NO)Me₂, 94620-70-9; CpMo(NO)-(CH₂SiMe₃)₂, 94620-69-6; CpW(NO)Me₂, 109959-57-1; CpW(NO)(CH₂SiMe₃)₂, 94620-67-4; Cp*Mo(NO)Me₂, 115364-23-3; Cp*Mo(NO)(CH₂SiMe₃)₂, 115364-24-4; Cp*W(NO)Me₂, 115364-25-5; Cp*W(NO)(CH₂SiMe₃)₂, 109467-45-0; CpMo(O)₂Me, 115364-26-6; CpMo(O)₂(CH₂SiMe₃), 115364-27-7; CpW(O)₂Me, 115364-28-8; CpW(O)₂(CH₂SiMe₃), 96760-75-7; Cp*Mo(O)₂Me, 115364-29-9; Cp*Mo(O)₂(CH₂SiMe₃), 115364-30-2; Cp*W(O)₂Me, 112247-12-8; Cp*W(O)₂(CH₂SiMe₃), 112247-16-2; CpMo(O)(η²-O₂)Me, 115364-31-3; CpMo(O)(η²-O₂)(CH₂SiMe₃), 115364-32-4; CpW(O)(η²-O₂)Me, 115364-33-5; CpW(O)(η²-O₂)(CH₂SiMe₃), 115364-34-6; Cp*Mo(O)(η²-O₂)Me, 115364-35-7; Cp*Mo(O)(η²-O₂)(CH₂SiMe₃), 115364-36-8; Cp*W(O)(η²-O₂)Me, 112247-13-9;

Cp*W(O)(η²-O₂)(CH₂SiMe₃), 112247-14-0; [Cp*Mo(NO)I₂], 115364-37-9; [Cp*Mo(NO)I₂]₂, 115364-38-0; [Cp*W(NO)I₂], 115364-39-1; [Cp*W(NO)I₂]₂, 115364-40-4; Cp*W(O)(Cl)₂Me, 115364-41-5; Cp*W(O)(Cl)₂(CH₂SiMe₃), 115364-42-6; Cp*W(O)(CH₂SiMe₃)(CHSiMe₃), 115364-43-7; Cp*W(O)(CH₂SiMe₃)(CHPh), 115364-44-8; Me₃SiCH₂MgCl, 13170-43-9; PhCH₂MgCl, 6921-34-2.

Supplementary Material Available: Elemental analysis and spectroscopic (IR, ¹H and ¹³C{¹H} NMR) data for the nine new complexes and tables of fractional coordinates and isotropic and anisotropic thermal parameters for CpW(O)(η²-O₂)(CH₂SiMe₃) (6 pages); a listing of structure factors (5 pages). Ordering information is given on any current masthead page.

1,4-Dilithio-1,3-butadienes

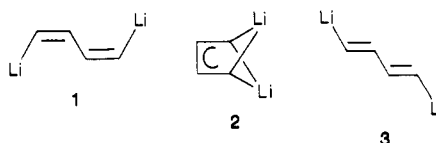
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Received April 13, 1988

Summary: On treatment with (trimethylstannyl)lithium in THF at -78 °C, 1,4-dichlorobutadienes (4) gave the stereoisomeric 1,4-bis(trimethylstannyl)-1,3-butadienes (5-7). Compounds 5 and 7 may be converted to the corresponding 1,4-dilithio-1,3-butadienes (1 and 3) by treatment with excess methyllithium, while 6 and 7 may be converted to 1 by reaction with <1 equiv of methyllithium.

Organopolyolithium compounds have attracted considerable attention due to the interest in their unusual structures.¹ Thus, it has been argued that (1Z,3Z)-1,4-dilithio-1,3-butadiene (1) possesses a symmetrically bridged structure 2,² which is stabilized by favorable electrostatic and orbital interactions. Since MO calculations (4-31G//STO-3G) indicate that 1 is 44 kcal/mol more stable than its *E,E*-isomer 3,³ it should be possible to effect conversion of 3 to the more synthetically useful 1.⁵ We report here a facile preparation of 1, which provides indirect but convincing evidence for the greater thermodynamic stability of 1 over 3.



The reaction of an isomeric mixture of 1,4-dichloro-1,3-butadienes (4)⁶ with an excess of (trimethylstannyl)-lithium in THF at -78 °C gave a 60% yield of the 1,4-bis(trimethylstannyl)-1,3-butadienes (5-7) in the ratio of

(1) Schleyer, P. v. R. *Pure Appl. Chem.* 1983, 55, 355; 1984, 56, 151. Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* 1985, 24, 354. Maercher, A.; Theis, M. *Top. Curr. Chem.* 1987, 138, 1.

(2) An X-ray structure of the tetraphenyl derivative of 1 shows this bridged structure. Schleyer, P. v. R., private communication.

(3) Kos, A. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1980, 102, 7928.

(4) However, see: Streitwieser, A., Jr. *Acc. Chem. Res.* 1984, 17, 353.

(5) (a) Low-yield preparations of 1 have been reported: Ashe, A. J., III; Drone, F. J. *Organometallics* 1985, 4, 1478. Ferede, R.; Noble, M.; Cordes, A. W.; Allison, N. T.; Lay, J., Jr. *J. Organomet. Chem.* 1988, 339, 1. (b) For substituted 1,4-dilithio-1,3-butadienes: Reich, H. J.; Reich, I. L. *J. Org. Chem.* 1976, 40, 2248. Atwell, W. H.; Weyenberg, D. R.; Gilman, H. J. *Org. Chem.* 1967, 32, 885. Smith, L. I.; Hoehn, H. H. *J. Am. Chem. Soc.* 1961, 83, 4406. Ashe, A. J., III; Drone, F. J. *Organometallics* 1984, 3, 495.

(6) Criegee, R.; Hörauf, W.; Schellenberg, W. D. *Chem. Ber.* 1953, 86, 126. Bartlett, P. D.; Wallbillich, G. E. H. *J. Am. Chem. Soc.* 1969, 91, 409.

(10) Typically, stirred colorless solutions of Cp*M(O)₂R were treated with a slight excess of the requisite reagent (either 30% H₂O₂(aq) or HCl in Et₂O), and the mixtures were stirred for 3-12 h whereupon they remained colorless or became yellow. Removal of volatiles from the final solutions in vacuo and recrystallization of the remaining residues from Et₂O afforded the desired products in 70-95% yields as crystalline, air-stable solids.

(11) See, for example: MacLaughlin, S. A.; Murray, R. C.; Dewan, J. C.; Schrock, R. R. *Organometallics* 1985, 4, 796.

(12) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic: New York, 1978.

(13) Such inertness of W-C bonds to HCl is quite rare, another example being provided by W₂O₃(CH₂CMe₃)₆.¹⁴

(14) Feinstein-Jaffe, I.; Gibson, D.; Lippard, S. J.; Schrock, R. R.; Spool, A. J. *Am. Chem. Soc.* 1984, 106, 6305.

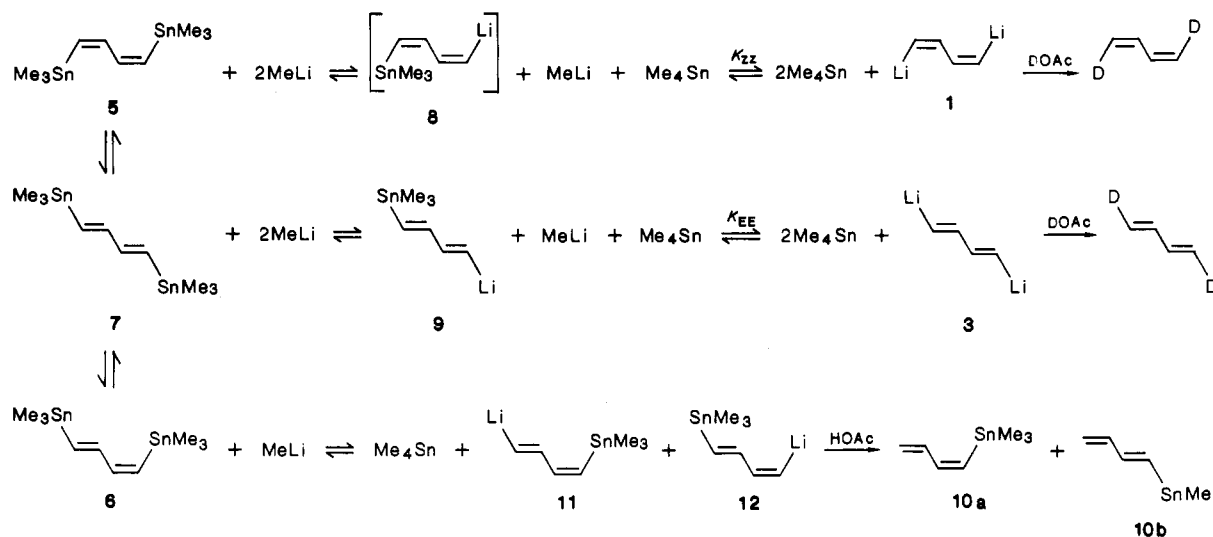
(15) Legzdins, P.; Phillips, E. C.; Sánchez, L., manuscript in preparation.

Table I. ^1H NMR Spectra of Selected 1,4-Disubstituted-1,3-butadienes ($\text{XCH}=\text{CHCH}=\text{CHY}$)^a

compd	X	Y	$\delta(\text{H}_1)$	$\delta(\text{H}_2)$	$\delta(\text{H}_3)$	$\delta(\text{H}_4)$	$\delta(\text{Me}_3\text{Sn})$	J, Hz
1 ^{b,c}	(Z)-Li	(Z)-Li	6.63 ^d	8.00 ^d				$(J_{12} + J_{13}) = 19.2$
3 ^{b,e}	(E)-Li	(E)-Li	6.38 ^d	6.70 ^d				$(J_{12} + J_{13}) = 20.8$
5 ^f	(Z)-SnMe ₃	(Z)-SnMe ₃	6.22 ^d	6.95 ^d			0.15	$J_{12} = 12.9, J_{13} = -0.9, J_{14} = 1.3, J_{23} = 9.5$
6 ^f	(E)-SnMe ₃	(Z)-SnMe ₃	6.34	6.54	6.97	6.08	0.22, 0.17	$J_{12} = 18.4, J_{13} = 0.9, J_{23} = 9.5, J_{34} = 12.4$
7 ^f	(E)-SnMe ₃	(E)-SnMe ₃	6.24 ^d	6.52 ^d			0.14	$J_{12} = 18.8, J_{13} = -0.8, J_{14} = 0.7, J_{23} = 9.5$
9 ^b	(E)-Li	(E)-SnMe ₃	7.17	6.86	6.28	5.54	0.05	$J_{12} = 19.9, J_{23} = 8.7, J_{34} = 17.4$

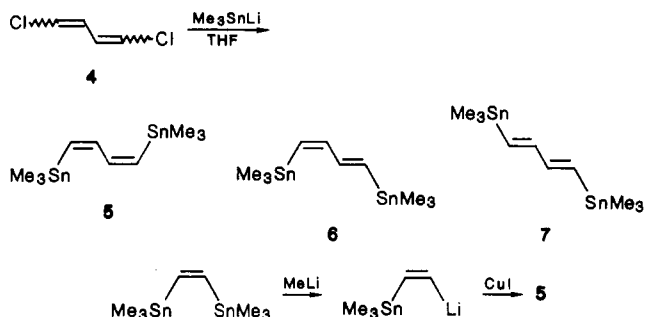
^aSpectra were recorded at 300 MHz. All spectra were computer-simulated by using the RACCOON program. ^bTHF-*d*₆. ^c¹³C NMR (THF-*d*₆): δ 175 (C₁), 151 (C₂). ^dRelative assignment of $\delta(\text{H}_1)$ and $\delta(\text{H}_2)$ is uncertain for A₂B₂ spectra. ^eCDCl₃. ^f¹³C NMR (THF-*d*₆): δ 162 (C₁), 156 (C₂).

Scheme I



6:34:60.^{7,8} Pure samples of the major isomers 6 and 7 may be obtained easily by fractional distillation (bp 55 °C (0.01 Torr)) or by GLPC on an Apiezon L column. The *Z,Z*-isomer 5 may be obtained more conveniently in 15% yield from (*Z*)-1,2-bis(trimethylstannyl)ethene via the reaction with methyllithium followed by CuI coupling of the monolithio intermediate.^{9,10} Treatment of 5 with excess (10 equiv) of methyllithium in THF-*d*₆ at -78 °C followed by warming to 25 °C led to complete Li/Sn exchange to form (1*Z*,3*Z*)-1,4-dilithio-1,3-butadiene (1).¹¹ The ^1H NMR spectrum (Table I) showed the characteristic A₂B₂ pattern assigned to 1, while quenching with acetic acid-*d*₁ produced (1*Z*,3*Z*)-1,4-dideuterio-1,3-butadiene (MS, *m/z* 56 (*M*⁺ for C₄H₄D₂); ^2H NMR (THF) δ 4.6 (d, *J* = 2.4 Hz)). Similar treatment of 7 afforded the (1*E*,3*E*)-1,4-dilithio-1,3-butadiene (3).¹⁰ Quenching 3 with acetic acid-*d*₁ gave (1*E*,3*E*)-1,4-dideuterio-1,3-butadiene (MS, *m/z* 56 (*M*⁺ for C₄H₄D₂); ^2H NMR (THF) δ 4.45 (d, *J* = 1.6 Hz)). Solutions

of 1 and 3 are stable indefinitely at room temperature, indicating that 1 and 3 are configurationally stable.¹²



Although the formation of 1 from 5 must take place by stepwise Sn/Li displacement, we have been unable to detect directly the monolithio intermediate 8. Addition of 5 to a solution of 1 serves to remove the excess methyllithium without producing new ^1H NMR signals that might be assigned to 8. Presumably the equilibrium constant K_{ZZ} for the formation of 1 from 8 is very large ($>10^6$).^{13,14}

The corresponding equilibrium is much less favorable in the case of *E,E*-isomers.¹³ Thus, addition of (1*E*,3*E*)-1,4-bis(trimethylstannyl)-1,3-butadiene (7) to the

(7) All new compounds gave satisfactory analytical and/or spectral data.

(8) **Preparation of 1,4-Bis(trimethylstannyl)-1,3-butadienes (5-7).** A solution of (trimethylstannyl)lithium, prepared from 6.1 g (3.0 mmol) of trimethylstannyl chloride and 0.43 g of lithium metal in 50 mL of tetrahydrofuran, was added dropwise at 0 °C to 1.40 g (11.5 mmol) of isomeric 1,4-dichloro-1,3-butadienes in 30 mL of tetrahydrofuran. After being warmed to 25 °C, the mixture was allowed to stir for 12 h. On removal of solvent, the residue was extracted with pentane. Distillation gave 2.6 g (60%) of 1,4-bis(trimethylstannyl)-1,3-butadiene as a light yellow oil, bp 55 °C (0.01 Torr).

(9) McCullough, R. D.; Kok, G. B.; Lerstrup, K. A.; Cowan, D. O. *J. Am. Chem. Soc.* 1987, 109, 4115. Mitchell, T. N.; Amamria, A.; Killing, H.; Rutschow, D. *J. Organomet. Chem.* 1983, 241, C45; 1986, 304, 257.

(10) For a similar CuI coupling see: Whitesides, G. M.; Casey, C. P.; Krieger, J. K. *J. Am. Chem. Soc.* 1971, 93, 1379.

(11) **Procedure for Preparation of 1 and 3.** 1,4-Bis(trimethylstannyl)-1,3-butadiene (50 mg, 0.13 mmol) was added slowly to 1.0 mL of a 1.4 M solution of methyllithium in tetrahydrofuran-*d*₆ at -78 °C. After being left standing at -78 °C for 10 min, the solution was allowed to warm to 25 °C. The dark blue solution gave satisfactory ^1H NMR spectrum.

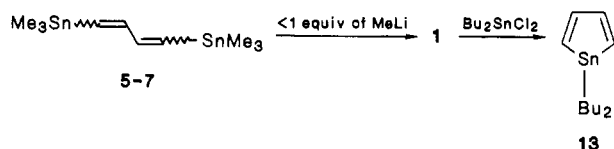
(12) For a discussion of the configurational stability of vinyl lithium compounds see: Wardell, J. L. In Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.: *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, 1982; Vol. 1, pp 94-97.

(13) Based upon estimated minimum observable concentrations of 8 and MeLi using the equation $K_{ZZ} = [1][\text{Me}_3\text{Sn}]/[8][\text{MeLi}]$. However, a complete expression for the equilibrium constant would require knowledge of different aggregation states of various organolithium species. These data are not available.

(14) Similar behavior has been found for the methyllithium exchange of 2,3-bis(trimethylstannyl)-1,3-butadiene for which the related dilithio compound is more stable than the monolithio species. See: Reich, H. J.; Yelm, K. E.; Reich, I. L. *J. Org. Chem.* 1984, 49, 3438.

(*1E,3E*)-1,4-dilithio-1,3-butadiene (**3**) gives (*1E,3E*)-1-lithio-4-(trimethylstannyl)-1,3-butadiene (**9**) as indicated by the ^1H NMR spectrum and by acetic acid quenching to the expected (*E*)-1-(trimethylstannyl)-1,3-butadiene (**10b**).¹⁵ However, if sufficient **7** is added to remove all the methylolithium, the ^1H NMR spectrum of **9** is replaced by that of **1**. Apparently the excess (*E,E*)-bis(trimethylstannyl)butadiene **7** is partially isomerized to the *Z,Z*-isomer **5** which then undergoes the very favorable Li/Sn exchange to the (*Z,Z*)-dilithiobutadiene **1** (see Scheme I). The excess bis(trimethylstannyl)butadiene is lost to polymerization. This overall conversion of **1** to **3** must be driven by the greater thermodynamic stability of **1**.

(*1E,3Z*)-Bis(trimethylstannyl)-1,3-butadiene (**6**) can be similarly covered to **1**. Thus, addition of excess methylolithium to **6** affords a mixture of **11** and **12**¹⁶ as shown by acetic acid quenching to (*E*)- and (*Z*)-1-(trimethylstannyl)-1,3-butadiene (**10a,b**).¹⁵ Addition of sufficient **6** to remove all the methylolithium from this mixture produces **1** and polymer. Synthetically it is most convenient to convert the mixed isomer of 1,4-bis(trimethylstannyl)-1,3-butadiene to **1**, which may be converted to 1,4-disubstituted-(*1Z,3Z*)-butadienes. In this manner, the reaction of **1** with dibutyltin dichloride gave 1,1-dibutylstannole (**13**) as a pale yellow oil (bp 80 °C (0.01 Torr)) in 28% yield.¹⁷ We have been unable to obtain the stannole by the direct hydrostannation of 1,3-butadiene.¹⁸ Since stannoles undergo facile exchange reactions, this preparation offers an efficient method for introduction of a (*1Z,3Z*)-butadienyl functionality.¹⁹



Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Registry No. **1**, 75920-66-0; **3**, 75920-67-1; (*1E,3E*)-**4**, 3588-12-3; (*1E,3Z*)-**4**, 3588-13-4; (*1Z,3Z*)-**4**, 3588-11-2; **5**, 112008-08-9; **6**, 112008-09-0; **7**, 112008-10-3; **9**, 115290-35-2; **10a**, 115290-38-5; **10b**, 93469-37-5; **11**, 115290-36-3; **12**, 115290-37-4; **13**, 115290-39-6; (*1Z,3Z*)-1,4-dideuterio-1,3-butadiene, 39768-32-6; (*1E,3E*)-1,4-dideuterio-1,3-butadiene, 39768-65-5; trimethylstannyl chloride, 1066-45-1; dibutyltin dichloride, 683-18-1.

(15) Alvanipour, A.; Eaborn, C.; Walton, D. R. M. *J. Organomet. Chem.* **1980**, *201*, 233.

(16) (*1E,3Z*)-1,4-Dilithio-1,3-butadiene could not be detected spectroscopically under the same condition for which the *E,E*- and *Z,Z*-isomers were formed. Qualitatively $K_{ZZ} > K_{EE} > K_{EZ}$.

(17) **1,1-Dibutylstannole.** The mixed isomers of 1,4-bis(trimethylstannyl)-1,3-butadiene (0.96 g, 2.5 mmol) were added in 50- μL portions over 15 min to a solution containing 1.8 mL of 1.4 M methylolithium (2.5 mol) in ether and 10 mL of tetrahydrofuran at -78 °C. On warming to 25 °C, the solution became dark blue. Stirring continued for 3 h during which time the presence of **1** can be monitored by following the increase of intensity of the ^1H NMR spectral doublet at δ 8.0. The solution of **1** was then added to 1.0 g (3.3 mmol) of dibutyltin dichloride in 8 mL of tetrahydrofuran at 0 °C. After the solution was stirred for 30 min at 25 °C, the solvent was removed under reduced pressure and the residue extracted with pentane which was then washed with dilute NaOH and water. After drying, vacuum distillation gave 100 mg (28%) of 1,1-dibutylstannole (bp 80 °C (0.01 Torr)). ^1H NMR (CDCl_3): δ 7.16 (A_2B_2 pattern, $J_{\text{HSnH}} = 147.2$ Hz, 2 H), 6.50 (A_2B_2 pattern, $J_{\text{HSnH}} = 156.8$ Hz, 2 H), 1.55 (p, 4 H), 1.31 (sex, 4 H), 1.18 (t, 6 H), 0.87 (t, 4 H). ^{13}C NMR (CDCl_3): δ 145.6, 131.6, 29.6, 26.9, 13.5, 11.4. MS: m/z 229 ($\text{M}^+ - \text{C}_4\text{H}_9$).

(18) Mahmoud, S. Ph.D. Thesis, The University of Michigan, 1988.

(19) Substituted stannoles have been used extensively for the synthesis of heterocycles: Leavitt, F. C.; Manuel, T. A.; Johnson, F.; Matternas, L. U.; Lehman, D. S. *J. Am. Chem. Soc.* **1960**, *82*, 5099. Atwell, W. H.; Weyenberg, D. R.; Gilman, H. *J. Org. Chem.* **1967**, *32*, 885. Killian, L.; Wrackmeyer, B. *J. Organomet. Chem.* **1977**, *132*, 213. Ashe, A. J. III; Diephouse, T. R. *J. Organomet. Chem.* **1980**, *202*, C95.

Supplementary Material Available: A table C, H combustion analyses for 1,4-bis(trimethylstannyl)-1,3-butadienes (1 page). Ordering information is given on any current masthead page.

Spectroscopic Characterization of Diarylgermylene Complexes with Heteroatom-Containing Substrates

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Summary: Characteristic UV absorption bands of diarylgermylene complexes were observed in the reaction of diarylgermylenes with heteroatom-containing substrates in 3-MP/IP matrix at 77 K.

Characterizations of germylenes have been the subject of considerable interest in recent years, and a few stable diarylgermylene complexes were reported on dehydrochlorination of diarylchlorogermanes in triethylamine at room temperature by Satgé et al. in 1982.¹ Recently, however, Masamune et al.² claimed that diarylgermylenes did not form stable adducts with triethylamine at room temperature.

Here, we report the recent spectroscopic observation of diorganogermynes in matrices with heteroatom-containing substrates. In our experiments diarylbis(trimethylsilyl)germanes **1a** and **1b** were photolyzed with a low-pressure mercury lamp in 3-methylpentane/isopentane (3-MP/IP = 3:7) at 77 K to give the corresponding germylene.²⁻⁴ Dimesitylgermylene (**2a**) and bis(2,4,6-triisopropylphenyl)germylene (**2b**) showed the absorption bands with λ_{max} at 550 and 558 nm, respectively. When the matrices were annealed, the germylenes dimerized to give the digermenes **3a** and **3b** with new absorption bands at $\lambda_{\text{max}} = 406$ and 416 nm, respectively (Scheme I).

When a similar photolysis of **1a** was carried out in matrices containing triethylamine, a new band at 414 nm first appeared together with the band due to dimesitylgermylene (Figure 1).

After being allowed to stand at 77 K, the band of germylene decreased and the new band grew and was stable at 77 K. When the matrix was annealed, the new band diminished and a 406-nm band grew. Similar results were obtained for **1b** in the matrix containing triethylamine, and a new band was formed with $\lambda_{\text{max}} = 445$ nm. These new bands are very likely the diarylgermylene-triethylamine complexes **4a** and **4b**.

The new stable complexes of dimethyl- and diarylgermylenes with heteroatom-containing substrates were observed in matrices at 77 K (Table I) and are analogous to the reaction between heteroatom compounds and diarylsilylenes.⁵

Bands due to the complex of germylenes with P, N, S, and O atoms were observed widely from 306 to 376 nm in

(1) Rivière, P.; Castel, A.; Satgé, J. *J. Organomet. Chem.* **1982**, *232*, 123.

(2) Collins, S.; Murakami, S.; Snow, J. T.; Masamune, S. *Tetrahedron Lett.* **1985**, *26*, 1281.

(3) Ando, W.; Tsumuraya, T.; Sekiguchi, A. *Chem. Lett.* **1987**, 317.

(4) Konieczny, S.; Jacobs, S. J.; Wilking, J. K. B.; Gaspar, P. P. *J. Organomet. Chem.* **1988**, *224*, C17.

(5) Ando, W.; Sekiguchi, A.; Hagiwara, K.; Sakakibara, A.; Yoshida, H. *Organometallics* **1988**, *7*, 558.