electrophiles with retention of configuration. While evidence for the equilibration of other heteroatom-substituted carbanions has been reported previously,[4,5,12,13,23d,25] this study is unique in that a simple alkyl-substituted, acyclic, nitrogen-substituted carbanion shows an observable barrier to inversion. When the transmetalation of **1b** was carried out with TMEDA present, no evidence for configurational stability was observed, and only **1a** was produced after quenching with $Bu_3SnCl$ (entry 7). The ligating ability of TMEDA may disrupt the chelate **16**, allowing a more rapid equilibration to **15**.

The use of carbonyl compounds as electrophiles led to the efficient and stereoselective formation of $\beta$-amino alcohol derivatives (entries 10–12) and an $\alpha$-amino ester derivative (entry 13). The stereochemistry of compounds **6c–9d** was based on the assumption that carbonyl addition occurred with retention of configuration. When aldehydes were used, two of the four possible stereoisomers were formed, presumably via high stereoselectivity with respect to the carbanion coupled with modest facial selectivity with respect to the aldehyde.[26]

Oxazolidinones were also useful in achieving high levels of stereoselection (entries 14–21). However, no evidence for the configurational stability of the anion derived from **3a** was obtained (entry 16). Quenching with $Bu_3SnCl$ after 5 min produced only **3b**. Evidently, the equilibration of **16** to **15** is faster in the oxazolidinone series (Figure 2, visualize enantiomers of all structures), perhaps due to the poorer lithium-ligating ability of a carbamate carbonyl oxygen versus a urea carbonyl oxygen. A higher energy chelate would be expected to allow easier inversion since the chelate is probably temporarily disrupted by inversion. The stereochemical outcome of these reactions is also consistent with recent work by Gawley, who studied acyclic benzylic anions derived from the deprotonation of chiral *N*-benzyloxazolidinones.[4a]

In summary, chiral, nonracemic $\alpha$-amino stannane derivatives were prepared, and these stannanes were effective precursors to chiral nitrogen-substituted carbanions, which underwent stereoselective reactions with electrophiles. Evidence for configurational stability was found for these nonconjugated, acyclic anions, with the barrier to inversion being a function of the substrate and reaction conditions. Studies on the use of these chiral, nonracemic anions for the synthesis of optically pure nitrogen-containing molecules are underway and will be reported in due course.

**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the University of Michigan (Gomberg, Riggs, Sokol, and Dow-Britton fellowships to A.C.L.) for support of this work. We thank Dr. Jeff Kampf for determining the X-ray crystal structure of **1c**.

**Supplementary Material Available:** Representative experimental procedures and spectral data for all new compounds and a procedure for making the chiral stannanes by displacement of sulfones with $Bu_3SnLi$ (7 pages). Ordering information is given on any current masthead page.

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[24] Semiempirical MNDO calculations[24a] were carried out with MOPAC[24b] on ether-solvated diastereomeric anions **15** and **16** derived from **1a** and **1b**, respectively, and showed that **15** was more stable by 1.44 kcal/mol. Details will be presented in the full account of this work. (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899–4907. (b) Stewart, J. J. P. Quantum Chemistry Program Exchange, No. 455, Version 6.0. For other studies on the theoretical and experimental structures of similar anions, see refs 4a,b and the following: (c) Rondan, N. G.; Houk, K. N.; Beak, P.; Zajdel, W. J.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Org. Chem.* **1981**, *46*, 4108–4110. (d) Bach, R. D.; Braden, M. L.; Wolber, G. J. *J. Org. Chem.* **1983**, *48*, 1509–1514. (e) Bartolotti, L. J.; Gawley, R. E. *J. Org. Chem.* **1989**, *54*, 2980–2982. (f) Seebach, D.; Hansen, J.; Seiler, P.; Gromek, J. M. *J. Organomet. Chem.* **1985**, *285*, 1–13.

[25] (a) Rychnovsky, S. D. *J. Org. Chem.* **1989**, *54*, 4982–4984 and references therein. (b) Molander, G. A.; Mautner, K. *J. Org. Chem.* **1989**, *54*, 4042–4050 and references therein. (c) Denmark, S. E.; Dorow, R. L. *J. Org. Chem.* **1990**, *55*, 5926–5928. (d) Reich, H. J.; Bowe, M. D. *J. Am. Chem. Soc.* **1990**, *112*, 8994–8995.

[26] Previous observations on the addition of nitrogen-substituted carbanions to aldehydes show that the erythro/threo selectivities vary widely.[1,2,4–6,9–11,14]

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# Tractable Silicon-Containing Poly(diphenylacetylenes): Their Synthesis and High Gas Permeability

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Silicon-containing polyacetylenes tend to exhibit high gas permeability, and poly[1-(trimethylsilyl)-1-propyne] [poly(**1**)], one of those polymers, shows extremely high oxygen permeability.[1] Though poly(diphenylacetylene)[3] [poly(**2**)] is, to our knowledge, thermally the most stable polyacetylene,[4] it is insoluble in any solvent.[5] We anticipated that introduction of the trimethylsilyl group into poly(**2**) might provide soluble, highly gas permeable polymers. This communication reports on the polymerization of 1-phenyl-2-[*p*-(trimethylsilyl)phenyl]acetylene (*p*-**3**) and 1-phenyl-2-[*m*-(trimethylsilyl)phenyl]acetylene (*m*-**3**) by $TaCl_5$-based catalysts and polymer properties.[6] The product polymers, poly(*p*-**3**) and poly(*m*-**3**), possess high molecular weights over $1 \times 10^6$, dissolve in various organic solvents, are thermally appreciably stable, and show very high gas permeability.

Polymerizations[8] of *p*-**3** and *m*-**3** were carried out using $TaCl_5$–cocatalyst systems, which are effective in the polymerization of **2**, under dry nitrogen by the method described before.[3] The monomers were consumed virtually quantitatively in the presence of $TaCl_5$–*n*-$Bu_4Sn$ (1:2) and $TaCl_5$–$Et_3SiH$ (1:2) catalysts to give methanol-insoluble polymers in over 70% yields (Table I). As was expected, the produced polymers totally dissolved in various organic solvents such as toluene and $CHCl_3$. The weight-average molecular weights ($\bar{M}_w$) based on gel permeation chromatography (GPC)[10] were as high as $\sim 2 \times 10^6$ with poly(*p*-**3**) and $\geq 1 \times 10^6$ with poly(*m*-**3**). The methanol-soluble byproducts were linear oligomers according to GPC and NMR. The polymerizations of *p*-**3** and *m*-**3** by $TaCl_5$–*n*-$Bu_4Sn$ proceeded without induction phases and were completed in 15 and 90 min, respectively, under the conditions of Table I. In contrast, no polymers were formed with $TaCl_5$ alone.

From elemental analyses and NMR and IR spectra, it is concluded that the polymers obtained possess alternating double bonds along the main chain.[11] The present polymers showed UV

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[1] (a) Masuda, T.; Isobe, E.; Higashimura, T.; Takada, K. *J. Am. Chem. Soc.* **1983**, *105*, 7473–7474. (b) Takada, K.; Matsuya, H.; Masuda, T.; Higashimura, T. *J. Appl. Polym. Sci.* **1985**, *30*, 1605–1616. (c) Ichiraku, Y.; Stern, Y. A.; Nakagawa, T. *J. Membr. Sci.* **1987**, *34*, 5–18. (d) Masuda, T.; Iguchi, Y.; Tang, B.-Z.; Higashimura, T. *Polymer* **1988**, *29*, 2041–2049. (e) Langsam, M.; Robeson, L. M. *Polym. Eng. Sci.* **1988**, *29*, 44–54. Poly(**1**) possesses some disadvantages such as low permselectivity and time dependence of gas permeability; improvements have been attempted.[2]

[2] (a) Langsam, M.; Anand, M.; Karawacki, E. J. *Gas Sep. Purif.* **1988**, *2*, 162–170. (b) Nakagawa, T.; Saito, T.; Asakawa, S.; Saito, Y. *Gas Sep. Purif.* **1988**, *2*, 3–8. (c) Nagase, Y.; Ueda, T.; Matsui, K.; Uchikura, M. *J. Polym. Sci., Part B: Polym. Phys.* **1991**, *29*, 171–179.

[3] Niki, A.; Masuda, T.; Higashimura, T. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 1553–1562.

[4] According to thermogravimetric analysis (TGA; heating rate 10 °C/min), the temperature at which the weight loss of poly(**2**) starts in air is ~500 °C.[3]

[5] In general, high molecular weight polymers from symmetrically disubstituted acetylenes [e.g., poly(4-octyne)] are insoluble in any solvent.[9c]

[6] The monomers were prepared with reference to the method of T.-L. Chang et al.;[7] i.e., phenylacetylene was reacted with bromoiodobenzenes in the presence of $(PPh_3)_2PdCl_2$, and the products were lithiated with *n*-BuLi followed by reaction with $ClSiMe_3$.

[7] Chang, T.-L.; Holzknecht, L. J.; Mark, H. B., Jr.; Ridgway, T. H.; Zimmer, H. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 989–997.

[8] The polymerization of substituted acetylenes by group 5 and 6 transition-metal catalysts is considered to proceed via metal carbenes like the ring-opening polymerization of cycloolefins,[9a,b] because identical catalysts are effective and many common features are observed in both polymerizations.[9c]

[9] (a) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 165–172. (b) Grubbs, R. H.; Tumas, W. *Science* **1989**, *243*, 907–915. (c) Masuda, T.; Higashimura, T. *Adv. Polym. Sci.* **1986**, *81*, 121–165.

[10] GPC curves were observed on a Shimadzu LC-9A liquid chromatograph (eluent $CHCl_3$, Shodex A805, A806, and A807 polystyrene gel columns). A polystyrene calibration was used to calculate $\bar{M}_w$ and $\bar{M}_n$.

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**Table I.** Polymerization of *p*-3 and *m*-3 by $TaCl_5$–Cocatalyst Systems[a]

| cocatalyst | monomer conversn, % | polymer[b] yield, % | $\bar{M}_w$,[c] $10^5$ | $\bar{M}_n$,[c] $10^5$ |
|---|---|---|---|---|
| | | *p*-3 | | |
| *n*-$Bu_4Sn$ | 95 | 85 | 22 | 7.5 |
| $Et_3SiH$ | 100 | 71 | 21 | 5.7 |
| | | *m*-3 | | |
| *n*-$Bu_4Sn$ | 100 | 87 | 14 | 2.5 |
| $Et_3SiH$ | 100 | 93 | 10 | 2.1 |

[a] Polymerized in toluene at 80 °C for 2 h; $[M]_0$ = 0.50 M, $[TaCl_5]$ = 20 mM, concentration of cocatalyst = 40 mM. [b] Methanol-insoluble product. [c] Determined by GPC.[10]

**Table II.** Gas Permeability of Silicon-Containing Polymers

| polymer | $P^a$ He | $H_2$ | $O_2$ | $N_2$ | $CO_2$ | $CH_4$ | $P_{O_2}/P_{N_2}$ |
|---|---|---|---|---|---|---|---|
| poly(*p*-3) | 1000 | 2100 | 1100 | 520 | 4700 | 1500 | 2.1 |
| poly(*m*-3) | 1000 | 2100 | 1200 | 610 | 4000 | 1500 | 2.0 |
| poly(**1**) | 3300 | 7800 | 4500 | 2700 | 29000 | 6500 | 1.7 |
| PDMS[b] | 230 | 460 | 490 | 230 | 3200 | | 2.1 |

[a] Gas permeability coefficients at 25 °C in the units of $1 \times 10^{-10}$ $cm^3(STP) \cdot cm/(cm^2 \cdot s \cdot cmHg)$ (=barrer). [b] At 0 °C; from ref 17c.

absorptions only below 500 nm,[12] indicating that conjugation of the main chain is relatively short. Free-standing films could be obtained by casting the polymers from toluene solution. The temperatures at which weight loss starts in TGA (in air, heating rate 10 °C/min) were 420 and 400 °C for poly(*p*-3) and poly(*m*-3), respectively; these values are somewhat lower than that for poly(**2**), but fairly higher than those for any other substituted polyacetylenes.[9c] No decrease in molecular weight was observed even though the present polymers were heated in air at 120 °C for 20 h. Thus, it can be said that these polymers have excellent thermal stability. The polymers were hard and brittle with respect to mechanical properties.[13] Their glass transition temperatures measured by dynamic viscoelasticity were above 200 °C.[14]

The oxygen permeability coefficients,[15] $P_{O_2}$, of poly(*p*-3) and poly(*m*-3), were about twice the value of poly(dimethylsiloxane) (PDMS), which is well-known as a highly gas-permeable rubber, and about a quarter the value of poly(**1**), which is the most permeable to oxygen (Table II).[16,18] The permeability coefficients of the present polymers to other gases are also $^1/_3$–$^1/_7$ those of poly(**1**); thus the permeation behaviors of these three polymers are similar. The $P_{O_2}/P_{N_2}$ values of the present polymers are larger than that of poly(**1**) and similar to that of PDMS, corresponding to a general tendency that the lower the permeability of a polymer, the higher the permselectivity of the polymer. It is noteworthy that the present polymers show high gas permeability, although aromatic polymers are generally the least gas permeable among substituted polyacetylenes [e.g., poly(1-phenyl-1-propyne); $P_{O_2}$ = 6.3 barrer[1d]].

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**Registry No. 1** (homopolymer), 87842-32-8; *p*-**3** (homopolymer), 136459-73-9; *m*-**3** (homopolymer), 136459-75-1; He, 7440-59-7; $H_2$, 1333-74-0; $O_2$, 7782-44-7; $N_2$, 7727-37-9; $CO_2$, 124-38-9; $CH_4$, 74-82-8; $TaCl_5$, 7721-01-9; *n*-$Bu_4Sn$, 1461-25-2; $Et_3SiH$, 617-86-7.

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(11) Poly(*p*-3): $^1H$ NMR ($CDCl_3$, 270 MHz) $\delta$ 7.5–5.5 (br s, 9, Ph), –0.5 (br s, 9, $SiMe_3$); IR (KBr) 2990 (s), 1650 (w), 1600 (m), 1500 (m), 1440 (m), 1250 (s), 1120 (s), 840 (s), 810 (w), 750 (m), 700 (m), 630 (m), 550 (s) $cm^{-1}$. Anal. Calcd for $(C_{17}H_{18}Si)_n$: C, 81.5; H, 7.2; Si, 11.2. Found: C, 81.9; H, 7.0. Poly(*m*-3): $^1H$ NMR ($CDCl_3$, 270 MHz) $\delta$ 7.5–5.5 (br s, 9, Ph), –0.5 (br s, 9, $SiMe_3$); IR (KBr) 2990 (s), 1600 (m), 1500 (m), 1440 (m), 1250 (s), 1120 (s), 840 (s), 780 (m), 750 (m), 700 (m), 630 (m), 570 (m) $cm^{-1}$. Anal. Found: C, 81.1; H, 7.7.

(12) $UV_{max}$ (THF): poly(*p*-3), 430 nm ($\epsilon$ 5000); poly(*m*-3), 425 nm ($\epsilon$ 4800).

(13) The tensile properties at 25 °C were as follows. Poly(*p*-3): Young's modulus (*E*), 1460 MPa; elongation at break ($\gamma_B$), 1.5%; tensile strength ($\sigma_B$), 19 MPa. Poly(*m*-3): *E*, 800 MPa; $\gamma_B$, 2.1%; $\sigma_B$, 14 MPa.

(14) Dynamic mechanical measurements were performed with a Rheovibron Model DDV-II-C instrument (Toyo Baldwin Co.).

(15) Gas permeability coefficients were measured with a K-315-N gas permeability apparatus (Rikaseiki Co.).

(16) The absolute $P_{O_2}$ values of highly gas permeable, glassy polymers vary widely. Their relative values are as follows (25 °C): poly(TMSP), 1.0; poly($MeC\equiv CGeMe_3$), 0.40;[17a] poly($MeC\equiv CSiEt_3$), 0.20;[17b] poly($MeC\equiv CSiMe_2Et$), 0.11;[1b] cf. PDMS 0.10.[17c]

(17) (a) Langsam, M. U.S. Patent 4759776, 1988. (b) Masuda, T.; Isobe, E.; Hamano, T.; Higashimura, T. *J. Polym. Sci., Part A*: *Polym. Chem.* **1987**, *25*, 1353–1362. (c) Pauly, S. In *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1989; pp VI/435–449.

(18) According to a preliminary experiment, the $P_{O_2}$ values after the aging of polymers at 80 °C for 26 h in vacuum were as follows: poly(*p*-3), 600 barrer ($P_{O_2}/P_{N_2}$ = 2.0); poly(*m*-3), 67 barrer ($P_{O_2}/P_{N_2}$ = 2.9); poly(**1**), 330 barrer ($P_{O_2}/P_{N_2}$ = 2.6). Thus, quite interestingly, the $P_{O_2}$ value of poly(*p*-3) was much less affected by time, temperature, and pressure.

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# Observation of an Unusual Surface Reaction: Direct Abstraction of CO from Furan Adsorbed on Molybdenum Surfaces

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The catalyzed removal of heteroatoms from heterocycles is an important part of the processing of petroleum and coal to liquid fuels. The surface chemistry of thiophene adsorbed on single-crystal model catalysts has received some considerable attention.[1-3] No corresponding studies involving the O analogue, furan, have been reported; there have been experiments conducted at high pressures.[4] During preliminary experiments on this system we have noted an unusual mode of surface reaction that distinguishes furan from thiophene. Thiophene decomposes to atomic fragments on such surfaces, and the only gas-phase product is dihydrogen. The S heteroatom remains firmly bonded to the Mo surface. In the case of furan we observe the *low-temperature direct abstraction of the heteroatom from the furan molecule to form a stable gas-phase reaction product*: *carbon monoxide*. The reaction occurs on both the (100) and (110) surfaces of molybdenum, both clean and when sulfur overlayers are present.

The experiments have been performed in a standard vacuum system containing facilities for low-energy electron diffraction and Auger electron spectroscopy. Sulfur overlayers were deposited from a solid-state electrochemical source, and furan was admitted from a doser with the crystal at 225 K. Temperature-programmed reaction spectroscopy (TPRS) was then used to monitor the fate of adsorbed furan.

The TPRS spectrum from a saturation furan dose (about 0.5 L) on a Mo(100) surface with approximately 0.2 ML of adsorbed sulfur (Figure 1) reveals significant signals at *m*/*e* values of 68, 39, 28, and 2. The 39 and 68 amu desorption signals apparent near 275 K are the dominant cracking fraction and parent peaks from molecularly adsorbed furan. The 2 amu signal is similar to reports[3,5] of the $H_2$ TPRS spectrum from thiophene/Mo(100) and can be reasonably assigned to stepwise dehydrogenation of chemisorbed hydrocarbon intermediates after dissociative adsorption of furan. The 28 amu spectrum shows a low-temperature peak at about 330 K followed by two small peaks and a further peak that commences below 1000 K and continues to above 1100 K. A fragment of *m*/*e* 28 is not a significant cracking feature of the mass spectrum of furan, and furthermore, the low-tem-

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(1) Bussell, M. E.; Somorjai, G. A. *J. Catal.* **1987**, *106*, 93–104.

(2) Gellman, A. J.; Bussell, M. E.; Somorjai, G. A. *J. Catal.* **1987**, *107*, 103–113.

(3) Roberts, G. T.; Friend, C. M. *Surf. Sci.* **1987**, *186*, 201–218.

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