Model 5890 chromatograph equipped with a flame-ionization detector and a 25 m × 0.20 mm cross-linked methyl silicone (0.33-μm film thickness) fused-silica capillary column or a Hewlett-Packard 5870B GC/MSD system with Chemstation software operating at 70 eV and fitted with a 12.5 m × 0.20 mm cross-linked dimethyl silicone fused-silica capillary column.

All reactions involving alkyllithiums were performed in glassware that had been flame-dried under an atmosphere of dry argon, and all manipulations of organolithiums were conducted by using standard syringe/cannula techniques[32] under an atmosphere of dry, oxygen-free argon that had been passed through a 5 cm × 50 cm glass column containing an activated BASF R3-11 copper catalyst. Diethyl ether was freshly distilled from dark-purple solutions of sodium/benzophenone. Dry, olefin-free *n*-pentane was obtained by repeated washings of commercial *n*-pentane with concentrated sulfuric acid until the acid layer remained clear, followed by washing successively with several portions of water, saturated aqueous sodium bicarbonate, and water, drying ($MgSO_4$), and distillation of the purified pentane under nitrogen from lithium aluminum hydride. Acetone (Baker, analytical grade) was dried over calcium sulfate and distilled. Sodium iodide was dried at 100 °C (ca. 5 mm) for 8–10 h in a vacuum oven. The concentration of commercial solutions of *t*-BuLi in *n*-pentane (Aldrich) was determined immediately prior to use by titration with *sec*-butyl alcohol in xylene using 1,10-phenanthroline as indicator.[33] Thin-layer chromatography (TLC) was performed on E. Merck precoated (0.2-mm) silica gel 60 F_{254} plates: visualization was accomplished by spraying with 10% ethanolic phosphomolybdic acid and heating. Reaction products were purified by flash chromatography, conducted as described by Still,[34] using Universal Scientific 32–60 μm silica gel.

Neopentyl iodide and *n*-butyl iodide were purchased from Aldrich and the remaining iodides were prepared by iodine exchange (NaI in acetone) from commercially available bromides or, via the mesylate, from alcohols. The physical and spectroscopic properties of the iodides were fully in accord with those reported for 1-iodooctane,[35] 1-iodooctadecane,[36] (iodomethyl)cyclopentane,[37] phenethyl iodide,[38] 1-(iodomethyl)adamantane,[39] and 2-(2-iodoethyl)-1,3-dioxane.[40] Prior to use, the alkyl iodides were purified by passage through a short column of silica gel, using *n*-pentane as eluent.

General Procedure for the Preparation of Primary Alkyllithiums. An appropriately sized round-bottomed flask, fitted with Teflon-coated magnetic stirring bar and rubber septa, was flushed with a steady stream of dry, oxygen-free argon (introduced through the septa using 22-gauge stainless steel needles) and the entire assembly was flame-dried using a Bunsen burner and then allowed to cool to room temperature while being swept with argon. The cool, dry flask was charged with the primary alkyl iodide and enough dry *n*-pentane–diethyl ether (3:2 by volume) to give an approximately 0.1 M solution of the iodide. All additions were performed by using argon-flushed syringes and a positive pressure of argon was maintained within the flask during all subsequent operations. The solution was cooled to −78 °C by lowering the flask into a dry ice–acetone bath, the stirrer was started, and 2.1 to 2.2 molar equiv of a solution of *t*-BuLi in *n*-pentane was then added dropwise via an argon-flushed syringe. Stirring was continued at −78 °C for an additional 5 min following the addition, the cooling bath was then removed, and the mixture was allowed to warm and stand at room temperature for 1 h to consume unreacted *t*-BuLi. Argon flow was adjusted to a minimum to avoid loss of solvent by evaporation at room temperature. The mixture was then re-cooled to −78 °C, an excess of the electrophile (typically 2.0–2.2 molar equiv) was then added (in the case of 1,2-dibromoethane and carbon dioxide, the alkyllithium solution was added to the electrophile in diethyl ether), the cooling bath was removed, and the reaction mixture was worked up in the usual manner.[9]

The products listed in Table I are known compounds whose physical and spectroscopic properties were fully in accord with those reported for 5-nonanol,[41] 2-methyl-2-decanol,[42] *n*-octadecane,[43] 2,2-dimethyl-4-heptanol,[44] cyclopentylacetic acid,[45] 1,3-diphenyl-1-propanol,[46] and 2-(2-bromoethyl)-1,3-dioxane.[47]

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Clean and Convenient Procedure for Converting Primary Alkyl Iodides and α,ω-Diiodoalkanes into the Corresponding Alkyllithium Derivatives by Treatment with *tert*-Butyllithium

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Whereas lithium–halogen exchange[2] has been widely used for generating alkenyl- and aryllithiums,[3] its application to the preparation of alkyllithiums has not been widely reported. We have recently noted that the reaction of alkyl iodides with 2 equiv of *t*-BuLi can provide a clean, high-yielding, and convenient method for preparing the corresponding alkyllithiums as discrete products.[4] This method has also been used to generate alkene- and alkyne-containing alkyllithiums for both mechanistic[5] and synthetic[6] purposes. These results suggested to us that the method might provide a general route to primary alkyllithiums, which in some cases is superior to the previously developed alternatives.[7] We now report that this

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Table I. Preparation of Primary Alkyllithiums by Treatment of Alkyl Iodides with *tert*-Butyllithium[a]

	yield (%) of RLi[b]			
RI	by ^{1}H NMR	GLC yield, of $RSiMe_3$	GLC yield of RI	^{1}H NMR signal of α-CH_2
EtI	95	*c*	*c*	−0.90 (t, *J* = 8 Hz)
n-OctI	95	*c*	80	−0.90 (t, *J* = 8 Hz)
i-BuI	95	*c*	*c*	−1.10 (d, *J* = 7 Hz)
neo-PentI	95	95[d]	*c*	−0.68 (s)
$Ph(CH_2)_2I$	90	90	85	−0.60 (t, *J* = 9 Hz)
$H_2C{=}CH(CH_2)_2I$	90	88[e]	85	−0.95 (t, *J* = 9 Hz)
n-$BuC{\equiv}C(CH_2)_2I$	80	*c*	*c*	−0.80 (t, *J* = 8.5 Hz)
Me_3SiCH_2I	90	*c*	*c*	−2.20 (s)
$I(CH_2)_4I$	95	85	90	−0.8 to −1.1 (m)
$I(CH_2)_5I$	90	80	*c*	−0.81 (t, *J* = 9 Hz)
$I(CH_2)_6I$	*c*	90	60	*c*
$Cl(CH_2)_4I$	*c*	60	*c*	*c*

[a] The reaction conditions are as detailed in the text. [b] No significant amounts (<2–3%) of the possible β-elimination or coupling products were present. The amounts of the deiodinated products, i.e., RH, were ≤5%. [c] Not performed. [d] GLC yield of *neo*-$PentSnMe_3$. [e] GLC yield of 3-butenyltrimethylstannane.

is indeed the case.

The procedure for converting primary alkyl iodides into the corresponding alkyllithiums simply involves treatment of an alkyl iodide in ether with 2.0–2.1 equiv of *t*-BuLi[8] in pentane or hexane at −78 °C for 0.5–1 h, followed by warming the mixture to 23 °C over 0.5–1 h. An appropriate *n*-alkane was added to the reaction mixture to analyze the reaction mixture by GLC. An aliquot was quenched with 3 N HCl and analyzed by GLC (SE-30). The complete absence of the starting alkyl iodide was taken as an indication that the amount of *t*-BuLi was sufficient. If more than a few percent of the starting alkyl iodide remained unreacted, an additional and appropriate amount of *t*-BuLi was added to the reaction mixture. A second aliquot was treated with either freshly purified Me_3SiCl or iodine, and the amount of the silylated or back-iodinated product was taken as an indication of the GLC yield of the alkyllithium product. The amounts of the deiodinated alkane product as well as the possible elimination and homocoupling products were also determined in cases where these compounds were readily detectable by GLC. The silylated product was isolated and fully characterized. To another reaction mixutre prepared in the same way was added an NMR standard, e.g., benzene or naphthalene. The mixture was then directly analyzed by ^{1}H NMR spectroscopy. The α-methylene signals of alkyllithiums appeared in the −0.6 to −2.2 ppm range, allowing a convenient quantitative determination of their yields.[9] Finally, the alkyllithium products were further converted to organic or organometallic derivatives to confirm their synthetic utilities.

The experimental results summarized in Table I indicate the following. The reaction of primary alkyl iodides with 2.0–2.1 equiv of *t*-BuLi is remarkably free from side reactions. Thus, no significant amounts (<2–3%) of the possible β-elimination or coupling products (RR) were present in cases where these products were readily detectable by GLC and/or NMR spectroscopy. Even homobenzyl, homoallyl, and homopropargyl iodides did not give β-elimination products. Thus, for example, no more than a trace, if any, of styrene was detected in the conversion of $Ph(CH_2)_2I$ to $Ph(CH_2)_2Li$. This must mean that the β-elimination reaction of *t*-BuI with *t*-BuLi or $Ph(CH_2)_2Li$ is far faster than the corresponding β-elimination reaction of $Ph(CH_2)_2I$. Although no accurate determination was attempted, isobutylene was detected in each case to the extent of 80–100% of the theoretical amount by ^{1}H NMR. Essentially the only detectable byproducts were the deiodinated parent alkanes and alkane derivatives (≤5%) arising, most probably via the reaction of the desired alkyllithiums with *t*-BuI.

The present method is applicable to the preparation of not only *n*-alkyllithiums but also β-monoalkyl- and β,β-dialkyl-substituted alkyllithiums, such as *i*-BuLi and neopentyllithium. Although some of these compounds are more economically prepared by lithiation of alkyl halides with Li metal, the Li–I exchange method provides a convenient laboratory procedure for their small-scale preparation. Another notable feature is the exceedingly high rate of formation of alkyllithiums relative to lithiation with Li metal. For example, the preparation of neopentyllithium in 80% yield by treatment of neopentyl chloride with Li containing 1% Na reportedly requires refluxing a mixture in hexane for 1 week,[10] while conversion of neopentyl iodide into neopentyllithium by the present method is complete well within 1 h at −78 °C.

The Li–I exchange method is particularly useful for preparing homobenzyl-, homoallyl-, and homopropargyllithiums. We had previously encountered a considerable difficulty in generating $Ph(CH_2)_2Li$ in a high yield by treatment of (β-haloethyl)benzenes containing Cl, Br, or I with Li metal.[11] The current method reproducibly permits its preparation in 90% yield, and it appears to be superior to yet another reported procedure involving treatment of $Ph(CH_2)_2SPh$ with either Li metal or lithium naphthalenide.[12] The preparation of homoallyllithium and 3-octynyllithium was achieved by the same method in 90 and 80% yields, respectively. Although our investigation of the preparation of α-hetero-substituted alkyllithiums has been limited only to Me_3SiCH_2Li, its clean formation in 90% yield suggests that the method might be applicable to the preparation of other α-hetero-substituted alkyllithiums as well. The reported syntheses of Me_3SiCH_2Li include treatment of Me_4Si with *n*-BuLi TMEDA to give a 36% yield of $(Me_3Si)_2CH_2$ after silylation[13a] and treatment of Me_3SiCH_2Cl with LiSn(Bu-*n*)$_3$ followed by treatment with *n*-BuLi.[13b]

It was earlier reported that treatment of α,ω-diiodoalkanes with 2.0–2.2 molar equiv of *t*-BuLi resulted in nearly quantitative yields of 3- through 5-numbered cycloalkanes.[14] In the present study, treatment of α,ω-diiodoalkanes containing 4–6 carbon chains with 4.0–4.2 molar equiv of *t*-BuLi provided the corresponding dilithioalkanes in 80–90% yields. One commonly used alternative for generating α,ω-dilithioalkanes involves

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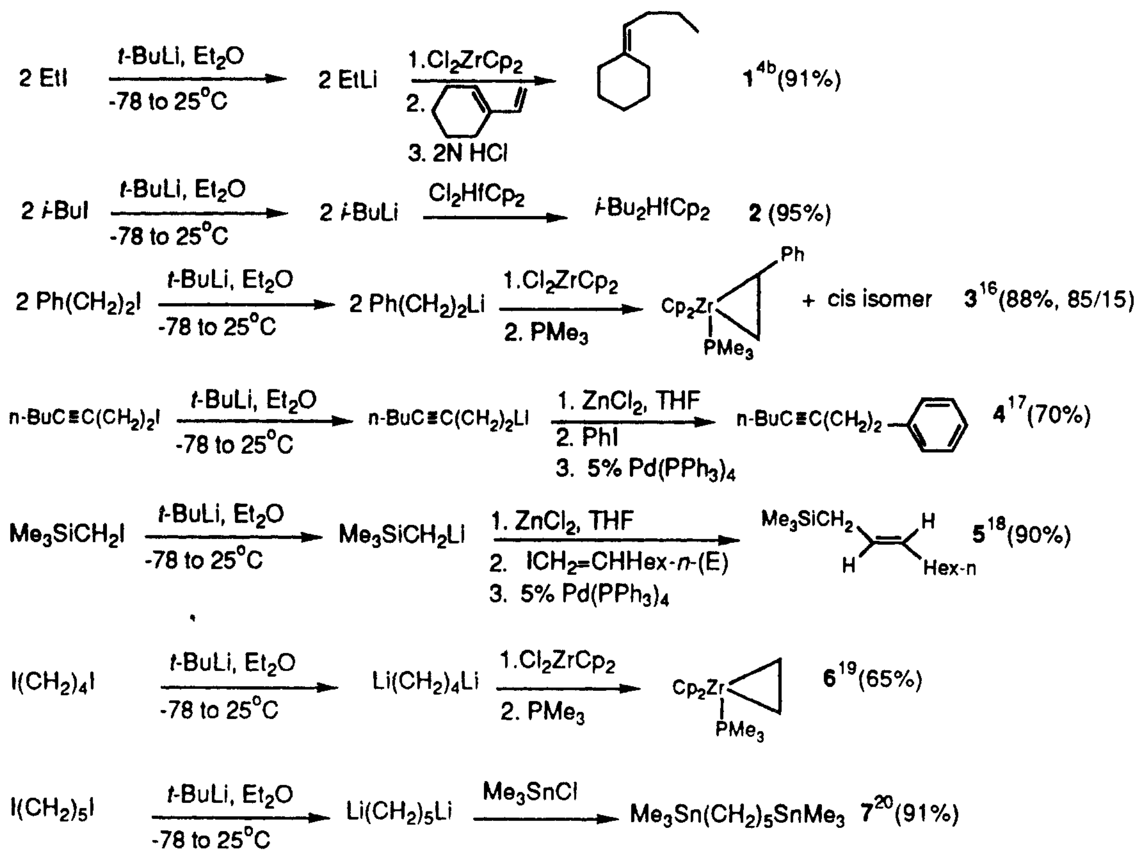
Scheme I



treatment of α,ω-dichloroalkanes with Li metal.[15] 4-Chloro-1-iodobutane was also converted to 4-chloro-1-lithiobutane, which was then treated with Me_3SiCl to give a 60% yield of (4-chlorobutyl)trimethylsilane.

As anticipated, our brief attempts to use primary alkyl bromides and secondary alkyl iodides, e.g., *i*-PrI, did not lead to satisfactory generation of alkyllithiums. In view of the known rapid reaction of *t*-BuLi with THF, its use as a solvent was avoided. Diethyl ether not only is compatible with *t*-BuLi but also appears to serve as its scavenger. Thus, the general absence of the *t*-Bu-containing products suggest that small excesses of *t*-BuLi, if any, must have been destroyed by ether upon warming the organolithium mixtures to 25 °C.

In addition to conversions of alkyllithiums to the corresponding alkanes, iodides, and silanes, the transformations in Scheme I confirm the synthetic utilities of the current method.

Experimental Section

General Procedure. Manipulations involving organometallics were carried out under an atmosphere of N_2 or Ar. *tert*-Butyllithium was titrated with 2-butanol and 1,10-phenanthroline.[21] As needed, THF and diethyl ether were distilled from sodium benzophenone ketyl. (2-Iodoethyl)benzene and 1-chloro-4-iodobutane were prepared by the reaction of the corresponding bromides with NaI in acetone. 4-Iodo-1-butene and 3-octynyl iodide were prepared by treating the corresponding alcohols with I_2, PPh_3, and pyridine in CH_2Cl_2.[22] All other starting materials were purchased from commercial sources and used as received, except for Me_3SiCl, which was kept on cross-linked poly(4-vinylpyridine).[23] Zirconocene dichloride and hafnocene dichloride were purchased from Boulder Chemical Co.

Preparation of Primary Alkyllithiums. (a) (2-Phenylethyl)lithium: Representative Procedure. An oven-dried, 50-mL round-bottomed flask equipped with a magnetic stirring bar, a septum inlet, and an outlet connected to a mercury bubbler was flushed with nitrogen and cooled to −78 °C. To this were sequentially introduced (2-iodoethyl)benzene (464 mg, 2.0 mmol), 4 mL of Et_2O, and 1.7 M *t*-BuLi in pentane (2.47 mL, 4.2 mmol). The reaction mixture was stirred for 0.5–1 h at −78 °C and warmed to 25 °C. Each of the following experiments was performed with a reaction mixture separately prepared as described above.

(i) To the reaction mixture prepared above were added at 0 °C *n*-decane (282 mg, 2.0 mmol) and Me_3SiCl (428 mg, 4.0 mmol) in 2 mL of Et_2O. After the reaction mixture had been stirred for 1 h at 25 °C, it was hydrolyzed, and the organic layer was dried over $MgSO_4$. Analysis by GLC (SE-30) indicated the formation of $Ph(CH_2)_2SiMe_3$[24] (90% yield) and ethylbenzene (5%). Neither styrene nor 1,4-diphenylbutane was detectable. The NMR spectra of $Ph(CH_2)_2SiMe_3$ display the following signals: ^1H NMR ($CDCl_3$, Me_4Si) δ 0.00 (s, 9 H), 0.85 (t, $J = 9$ Hz, 2 H), 2.61 (t, $J = 9$ Hz, 2 H), 7.1–7.3 (m, 5 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.77, 18.69, 30.05, 125.44, 127.77, 128.25, 145.27.

In another run, *n*-decane (282 mg, 2.0 mmol) was added to the reaction mixture. An aliquot was treated with 3 N HCl, worked up, and analyzed by GLC, which revealed the presence of ethylbenzene produced in 95–98% yield. Another aliquot was

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treated with iodine dissolved in THF. A small excess of iodine was destroyed with aqueous $Na_2S_2O_3$, and the mixture was worked up and analyzed by GLC, which indicated an 85% regeneration of $Ph(CH_2)_2I$.

(ii) Another mixture prepared in the same manner was examined by ^1H NMR spectroscopy using naphthalene as a standard. Comparison of the peak area of a triplet at δ –0.60 (J = 9 Hz) assignable to the Li-bound CH_2 with that of naphthalene indicated that $Ph(CH_2)_2Li$ was formed in 90% yield.

(iii) In the fourth run, the volatiles were evaporated, and the residue was dissolved in Et_2O (2 mL). The resultant mixture yielded the following NMR data: ^1H NMR (Et_2O, Me_4Si) δ –0.56 (t, J = 9 Hz, 2 H), 2.80 (t, J = 9 Hz, 2 H), 6.9–7.3 (m, 5 H); ^{13}C NMR (Et_2O, Me_4Si) δ 13.83, 36.64, 124.89, 128.05, 128.68, 152.93.

(b) Isobutyllithium. This compound was prepared from *i*-BuI (386 mg, 2.0 mmol) and *t*-BuLi in pentane (1.7 M, 2.47 mL, 4.2 mmol) using 4 mL of Et_2O. Quantitative analysis of the ^1H NMR signal for the α-CH_2 doublet at δ –1.1 (J = 7 Hz) using naphthalene as an internal standard indicated a 90% yield of *i*-BuLi.[25]

(c) Neopentyllithium. This compound was prepared from neopentyl iodide (0.132 mL, 0.198 g, 1 mmol) and *t*-BuLi in pentane (1.7 M, 1.23 mL, 2.1 mmol), using 1 mL of Et_2O. Quantitative analysis of the ^1H NMR signal for the α-CH_2 singlet at δ –0.68 using benzene as an internal standard indicated a 95% yield of neopentyllithium.[10]

(d) 3-Butenyllithium. This compound was prepared from 4-iodo-1-butene (364 mg, 2.0 mmol) and *t*-BuLi in pentane (1.7 M, 2.47 mL, 4.2 mmol) using 3 mL of ether. Analysis of the ^1H NMR spectrum for the α CH_2 triplet at α –0.95 (J = 9 Hz) indicated a 90% yield of the title compound,[26] using naphthalene as an internal standard. Its treatment with Me_3SnCl (418 mg, 2.0 mmol) gave an 88% yield of **3-butenyltrimethylstannane**: ^1H NMR ($CDCl_3$, Me_4Si) δ 0.06 (s, 9 H), 0.90 (t, J = 8 Hz, 2 H), 2.27 (q, J = 8 Hz, 2 H), 4.85–5.05 (m, 2 H), 5.75–6.0 (m, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ –10.26, 9.90, 30.66, 113.30, 142.07.

(e) 3-Octynyllithium. This compound was prepared from 1-iodo-3-octyne (472 mg, 2.0 mmol) and *t*-BuLi in pentane (1.7 M, 2.47 mL, 4.2 mmol), using 4 mL of Et_2O. Analysis of the ^1H NMR signal for the α-CH_2 protons at δ –0.8 (J = 8 Hz) indicated a yield of 80%. Silylation with Me_3SiCl (856 mg, 8 mmol) gave an 86% yield of **1-(trimethylsilyl)-3-octyne**: ^1H NMR ($CDCl_3$, Me_4Si) δ 0.02 (s, 9 H), 0.77 (t, J = 8 Hz, 2 H), 0.90 (t, J = 7 Hz, 3 H), 1.35–1.5 (m, 4 H), 2.1–2.25 (m, 4 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ –1.65, 13.38, 13.69, 16.60, 18.54, 22.06, 31.35, 79.80, 82.45.

(f) [(Trimethylsilyl)methyl]lithium. This compound was prepared by the reaction of Me_3SiCH_2I (428 mg, 2.0 mmol) with *t*-BuLi (1.7 M, 2.47 mL, 4.2 mmol) in Et_2O. Analysis of the ^1H NMR signal for the α-CH_2 group at δ–2.20 (s) indicated a yield of 90% for the title compound.[13]

(g) (4-Chlorobutyl)trimethylsilane. To 1 mL of Et_2O at –78 °C were successively added *t*-BuLi in pentane (1.7 M, 1.23 mL, 2.1 mmol) and a solution of 1-chloro-4-iodo-butane[28] (0.218 g, 1 mmol) in Et_2O (1 mL). The reaction mixture was stirred for 1 h at –78 °C, and neat Me_3SiCl, (0.218 g, 0.25 mL, 2 mmol) was added dropwise. The reaction mixture was allowed to warm up to 25 °C, quenched with 3 N HCl, extracted with pentane, washed with $NaHCO_3$, and dried over $MgSO_4$. Concentration followed by distillation provided 91 mg (55%) of the title compound:[27] bp 65 °C (10 mmHg, Kugelrohr); ^1H NMR ($CDCl_3$, Me_4Si) δ –0.03 (s, 9 H), 0.4–0.5 (m, 2 H), 1.35–1.5 (m, 2 H), 1.76 (quin, J = 7.0 Hz, 2 H), 3.51 (t, J = 6.7 Hz, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ –1.74, 15.86, 21.23, 36.20, 44.69; IR (neat) 1245 (s), 860 (s), 835 (s) cm^{-1}.

Preparation of α,ω-Dilithioalkanes. (a) 1,4-Dilithiobutane. Representative Procedure. To 2 mL of Et_2O were successively added at –78 °C 1.7 M *t*-BuLi in pentane (2.47 mL, 4.2 mmol) and 1,4-diiodobutane (0.310 g, 0.13 mL, 1 mmol). The reaction mixture was stirred for 0.5 h at –78 °C and warmed to 25 °C. Analysis of the ^1H NMR α-CH_2 signals at δ –0.8 to –1.1 using benzene as an internal standard indicated a 95% yield of the title compound.[15] **1,4-Bis(trimethylsilyl)butane.** To the reaction mixture prepared above was added at –78 °C Me_3SiCl (0.325 g, 0.38 mL, 3.0 mmol). The reaction mixture was warmed to 25 °C, quenched with 3 N HCl, extracted with pentane, washed with $NaHCO_3$, and dried over $MgSO_4$. Concentration and distillation provided 0.14 g (70%) of the title compound:[15] bp 75 °C (10 mmHg, Kugelrohr); ^1H NMR ($CDCl_3$, Me_4Si) δ –0.05 (s, 18 H), 0.4–0.55 (m, 4 H), 1.2–1.4 (m, 4 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ –1.61, 16.46, 27.88; IR (neat) 1235 (s), 860 (s), 835 (s) cm^{-1}.

(b) 1,5-Dilithiopentane. This compound[15] was prepared in 90% yield from 1,5-diiodopentane (0.324 g, 0.15 mL, 1 mmol) and 1.7 M *t*-BuLi in pentane (2.47 mL, 4.2 mmol): ^1H NMR ($CDCl_3$, Me_3Si) δ –0.81 (t, J = 9 Hz). **1,5-Bis(trimethylsilyl)pentane:**[15] 70% yield; bp 95 °C (10 mmHg, Kugelrohr); ^1H NMR ($CDCl_3$, Me_4Si) δ –0.04 (s, 18 H), 0.4–0.5 (m, 4 H), 1.25–1.35 (m, 6 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ –1.58, 16.68, 23.68, 37.68; IR (neat) 1235 (s), 860 (s), 835 (s) cm^{-1}.

(c) 1,6-Bis(trimethylsilyl)hexane. This compound[15] was prepared in 75% yield from 1,6-diiodohexane (0.338 g, 0.165 mL, 1 mmol), 1.7 M *t*-BuLi in pentane (2.47, mL, 4.2 mmol), and Me_3SiCl (0.325 g, 0.38 mL, 3.0 mmol): bp 115 °C (10 mmHg, Kugelrohr); ^1H NMR ($CDCl_3$, Me_4Si) δ –0.03 (s, 18 H), 0.45–0.55 (m, 4 H), 1.25–1.35 (m, 8 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ –1.56, 16.80, 23.93, 33.44; IR (neat) 1235 (s), 860 (s), 835 (s) cm^{-1}.

Diisobutylbis(η^5-cyclopentadienyl)hafnium. To *i*-BuLi in Et_3O–pentane prepared from 2.0 mmol of *i*-BuI was added at –78 °C Cl_2HfCp_2 (379 mg, 1.0 mmol), and the reaction mixture was warmed to 25 °C. Analysis of the ^1H NMR Cp signal at δ 6.24 (s) using benzene as an internal standard indicated a 95% yield of the title compound: ^1H NMR (C_6H_6, Me_4Si) δ 0.16 (d, J = 7 Hz, 4 H), 0.93, (d, J = 7 Hz, 12 H), 2.11 (n, J = 7 Hz, 2 H), 5.69 (s, 10 H); ^{13}C NMR (C_6H_6, Me_4Si) δ 29.35, 33.23, 71.49, 110.16; IR (Nujol) 1610 (m), 1029 (m), 805 (s) cm^{-1}.

Neopentyl(trimethyl)stannane.[29] To neopentyllithium in Et_2O–pentane prepared from 1 mmol of neopentyl iodide was added at –78 °C Me_3SnCl (0.30 g, 1.5 mmol) in 2 mL of THF, and the mixture was warmed to 25 °C, quenched with 3 N HCl, extracted with pentane, washed with aqueous $NaHCO_3$, and dried over $MgSO_4$. Concentration and distillation provided 0.17 g (74% yield) of the title compound: bp 95 °C (60 mmHg, Kugelrohr); ^1H NMR ($CDCl_3$, Me_4Si) δ 0.06 (s, 9 H), 0.97 (s, 9 H), 0.99 (s, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ –8.34, 31.06, 31.92, 33.26; IR (neat) 1185 (m), 765 (s) cm^{-1}.

1-Phenyl-3-octyne. To 3-octynyllithium in Et_2O–pentane prepared from 2 mmol of 1-iodo-3-octyne was added at –78 °C dry $ZnCl_2$ (136 mg, 1 mmol) in 2 mL of THF, and the mixture was warmed to 25 °C and transferred to a flask containing iodobenzene (326 mg, 1.6 mmol), $Pd(PPh_3)_4$ (70 mg, 0.06 mmol), and *n*-decane (142 mg, 1.0 mol).[17] After 1 h at 25 °C, examination of a quenched aliquot by GLC indicated a 70% yield of 1-phenyl-3-octyne[29] identified by GLC coinjection with an authentic sample.

1,5-Bis(trimethylstannyl)pentane. This compound was prepared from 1,5-diiodopentane (0.324 g, 0.15 mL, 1 mmol), 1.7 M *t*-BuLi in pentane (2.47 mL, 4.2 mmol), and Me_3SnCl (0.597 g, 3 mmol) in THF (2 mL). Concentration provided 0.317 g (80%) of the title compound:[20] ^1H NMR ($CDCl_3$, Me_4Si) δ 0.03 (s, 18 H), 0.75–0.9 (m, 4 H), 1.2–1.35 (m, 2 H), 1.45–1.6 (m, 4 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ –10.26, 11.07, 26.31, 38.45; IR (neat) 1185 (m), 765 (s) cm^{-1}.

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