

unit is compressed while the  $WN_3$  unit is elongated; the W atom lies ca. 0.86 Å out of the plane defined by O(1), O(2), and C(1) and ca. 1.54 Å out of the plane defined by the three N atoms. Consistent with previous observations in other oxo polypyrazolylborate complexes, the W-N(11) and W-N(21) bonds which are trans to the oxo ligands are significantly longer than the remaining W-N(31) bond. The pyrazole rings containing N(11) and N(21) are slightly splayed as a result of the occupation of the cleft between them by the R group. The atoms of the R groups lie on or close to the pseudomirror plane of the molecules, thus minimizing steric interactions. The dihedral angles in the C(2)-C(1)-W-N(31) fragments of **3** and **5** are 7.2 and 1°, respectively. The W-C(1) distances for **3** and **5** are 2.21 (1) and 2.271 (6) Å, respectively, the C(1)-C(2) distance in the ethyl ligand is 1.55 (1) Å, and the phenyl group is planar with C-C distances averaging 1.385 Å.

The structures of **3** and **5** can be compared with those established by Schrauzer et al.<sup>6</sup> for members of the series (bpy)WO<sub>2</sub>(R)<sub>2</sub> (R = Me,<sup>6a</sup> *n*-Pr,<sup>6a</sup> and Ph<sup>6b</sup>); a distinct structural similarity is noted. The (bpy)WO<sub>2</sub>(R)<sub>2</sub> complexes exhibit skewed-trapezoidal-bipyramidal geometries in which oxo and N-donor atoms define the trapezoidal plane and the R groups occupy apical positions. The

W=O bond distances range from 1.710 (5) to 1.729 (5) Å while the O-W-O bond angles range from 107.8 (3) to 109.4 (2)°. The C-W-C angles associated with the trans R groups range from 147.8 (3) to 161.0 (4)°. The complex (bpy)MoO<sub>2</sub>(Et)<sub>2</sub> has also been structurally characterized<sup>25</sup> and exhibits a structure and ethyl ligand geometrical parameters consistent with those observed for **3**. Similar geometrical parameters have been observed in other (alkyl)-oxo-W complexes, e.g. ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)WO<sub>2</sub>(CH<sub>2</sub>SiMe<sub>3</sub>).<sup>5a</sup>

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**Registry No.** 1, 138997-64-5; 2, 138997-58-7; 3, 138997-59-8; 3-H<sub>2</sub>O, 138997-65-6; 4, 138997-60-1; 5, 138997-61-2; 5-CH<sub>2</sub>Cl<sub>2</sub>, 141784-01-2; K{HB(Me<sub>2</sub>pz)<sub>3</sub>}, 17567-17-8.

**Supplementary Material Available:** A listing of elemental analyses and tables of anisotropic thermal parameters, hydrogen atom parameters, and bond distances and angles (7 pages). Ordering information on any current masthead page.

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## Practical Synthesis of Tris(trimethylsilyl)methyl Bromide and Its Conversion to the Corresponding Grignard Reagent and (Tris(trimethylsilyl)methyl)lithium

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**Summary:** A practical synthesis of tris(trimethylsilyl)methyl bromide in 75% yield by photobromination of neat tris(trimethylsilyl)methane at 180–190 °C in less than 5 h is reported. The bromide was converted to tris(trimethylsilyl)methyl lithium in over 75% yield by reaction with lithium metal in diethyl ether and THF and via facile halogen-metal interconversion with phenyllithium. The first synthesis of the Grignard reagent (tris(trimethylsilyl)methyl)magnesium bromide in 75–90% yield from the corresponding bromide and magnesium metal in diethyl ether also is described.

In 1970, Eaborn et al. reported the synthesis of (tris(trimethylsilyl)methyl)lithium (hereafter referred to as trisyllithium) in high yield by metalation of tris(trimethylsilyl)methane with methyl lithium in THF,<sup>1</sup> and improvements in this procedure were published in 1984.<sup>2</sup> To date, trisyllithium has proven to be a useful reagent for the preparation of many unique molecules, especially those in which the bulky (Me<sub>3</sub>Si)<sub>3</sub>C group is attached to metals or metalloids. The major impetus for interest in this area is due to findings that organometallic compounds bearing the trisyl moiety possess unique properties and often have novel structures.<sup>3,4</sup>

In routine laboratory practice, organolithium and Grignard reagents are most often prepared from organic halogen compounds and the appropriate metal. However, to date the preferred route to trisyllithium involves the accessible tris(trimethylsilyl)methane because practical routes to the trisyl halides have yet to be reported.<sup>1,5</sup> For example, two methods have been reported for the preparation of tris(trimethylsilyl)methyl bromide (hereafter referred to as trisyl bromide): (1) an indirect procedure involving a halogen-metal exchange between bis(trimethylsilyl)dibromomethane and butyllithium followed by a reaction of the intermediate (bis(trimethylsilyl)bromomethyl)lithium with chlorotrimethylsilane<sup>6</sup> and (2) a direct route in which a mixture of *N*-bromosuccinimide, benzoyl peroxide, and tris(trimethylsilyl)methane was refluxed for 5 days.<sup>7</sup>

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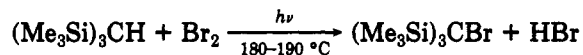
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## Results and Discussion

Seyferth et al. reported that irradiation of a carbon tetrachloride solution of tris(trimethylsilyl)methane and bromine at reflux for 180 h afforded a greater than 70% yield of trisyl bromide on a 0.07-mol scale.<sup>6a</sup> We recently discovered that photobromination of neat tris(trimethylsilyl)methane at higher temperatures under illumination with a 150-W tungsten filament light bulb afforded excellent yields of trisyl bromide in considerably less time:<sup>8</sup>



For example, photobromination of 1 mol of tris(trimethylsilyl)methane was achieved in less than 5 h, affording trisyl bromide 75% yield at temperatures between 180 and 190 °C. Varying the rate of addition of bromine between 1.5 and 10 h within the temperature range of 145–205 °C causes very slight changes in the yields of trisyl bromide, which were 70–78%. It is noteworthy that photobrominations were very slow at temperatures below 120 °C, as evidenced by the rate of decoloration of bromine.

Trisyl bromide is very reactive toward lithium, magnesium, and phenyllithium. Reaction of trisyl bromide with lithium metal in ethyl ether afforded 75% yields of trisyllithium, which upon derivatization with water, chlorotrimethylsilane, and mercuric chloride yielded tris(trimethylsilyl)methane (73%), tetrakis(trimethylsilyl)methane (76%), and bis[tris(trimethylsilyl)methyl]mercury (70%), respectively. Efforts to prepare trisyllithium in THF at room temperature were unsuccessful, the only isolable product being tris(trimethylsilyl)methane (57%) even after attempted derivatization with chlorotrimethylsilane prior to hydrolysis. However, trisyllithium was formed in high yield in THF at –50 °C; upon treatment with chlorotrimethylsilane it afforded the expected tetrakis(trimethylsilyl)methane (77%). Trisyl bromide also undergoes a facile halogen–metal interconversion with phenyllithium to give trisyllithium and bromobenzene (100%). The high yield of trisyllithium was substantiated by derivatization with chlorotrimethylsilane, affording tetrakis(trimethylsilyl)methane in 85% yield.

(Tris(trimethylsilyl)methyl)magnesium bromide (hereafter referred to as trisylmagnesium bromide) was prepared in 75–90% yields from trisyl bromide and magnesium metal in refluxing diethyl ether. The magnesium was first activated by stirring with an ethereal solution of ethylene bromide. Trisyl bromide in ether was then added to the magnesium at reflux over ca. 1 h. The reaction mixture then was refluxed for an additional 2 h. Higher yields (ca. 90%) were obtained when the mixture was refluxed for more than 12 h. The Grignard reagent afforded tris(trimethylsilyl)methyl iodide (65%), 1,1,1-tris(trimethylsilyl)-2-phenylethane (74%), and bis[tris(trimethylsilyl)methyl]mercury (82%) when derivatized with iodine, benzyl chloride, and mercuric chloride, respectively. Formation of trisylmagnesium bromide from trisyl bromide and magnesium represents the first unequivocal synthesis of the Grignard reagent. Bock et al. previously proposed the intermediacy of trisylmagnesium bromide, formed in situ via a halogen–metal interconversion, as being responsible for the formation of 1,1,1-tris(trimethylsilyl)-2-phenylethane from benzylmagnesium bromide and trisyl bromide.<sup>7</sup>

## Experimental Section

**General Procedure.** All glassware was oven-dried and purged while hot with nitrogen before reactants were introduced. Except for photochemical experiments (vide infra), the standard apparatus consisted of a 500-mL three-necked round-bottomed flask with ground glass joints fitted with a Trubore stirrer, a Friedrich condenser, and an addition funnel.

Tris(trimethylsilyl)methane<sup>9</sup> and phenyllithium<sup>10</sup> were synthesized according to published directions. Chlorotrimethylsilane was purchased from Eastman Kodak Co. Lithium metal (~0.01% sodium content) was obtained commercially as wire from Aldrich Chemical Co. and wiped free of its protective coating, and cut into small pieces into the nitrogen-filled reaction flask immediately prior to use. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under nitrogen prior to use. Diethyl ether was dried over sodium wire. All other reagents were used as obtained from commercial sources.

Melting points were determined with an Electrothermal melting point apparatus in capillary tubes and are uncorrected. Boiling points are also uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 710B double-beam grating infrared spectrophotometer. Gas chromatographic (GC) measurements were effected with a Perkin-Elmer Sigma 3B instrument using a 3% OV-101 on 80/100 mesh Chromosorb W packed column (4 ft. × 1/8 in.). <sup>1</sup>H NMR spectra were recorded on a Varian EM 3630L spectrometer using carbon tetrachloride as the solvent. Chemical shifts are reported in δ units (ppm) from internal cyclopentane.

Quantitative analyses of organolithiums and Grignard reagents were carried out by a double-titration procedure using 1,2-dibromoethane.<sup>11</sup> Quantitative analyses of mixtures of tris(trimethylsilyl)methane with tetrakis(trimethylsilyl)methane, and with trisyl bromide (obtained via photochemical reactions), were determined from GC data. These compounds were also routinely characterized by comparison of their physical properties, IR spectral data, and GC retention times with those of authentic samples. Elemental analyses and molecular weights were performed by Galbraith Laboratories, Inc., Knoxville, TN.

**Photochemical Bromination of Tris(trimethylsilyl)methane. (a) General Technique.** Photobromination reactions were carried out in a 500-mL four-necked round-bottomed flask with ground glass joints, fitted with a Trubore stirrer, Friedrich condenser, thermometer, and addition funnel. A 150-W tungsten filament lamp was positioned about 1 in. beneath the round-bottomed flask. Both the flask and the lamp were encased with aluminum foil in a manner that the emitted light was reflected onto the flask. Through proper adjustment of the aluminum foil encasing, the heat generated by the lamp could be regulated to keep the temperature of the reaction mixture within the desired limits. The outlet of the condenser was attached to a gas absorption trap.

**(b) Procedure.** Tris(trimethylsilyl)methane (232 g, 1 mol) was added to the flask, slow stirring was started, and the lamp was turned on. When the temperature of tris(trimethylsilyl)methane reached 150 °C under the heat of illumination, dropwise addition of bromine (192 g, 1.2 mol) was initiated. The temperature was allowed to rise to 180 °C and thereafter maintained between 180 and 190 °C. Upon completed addition (ca. 3 h), irradiation was continued for 30 min before the lamp and stirrer were turned off. The dark brown solid that developed upon cooling to room temperature was dissolved in hot petroleum ether (bp 37–56 °C) and stirred briefly with 10–20 g of alkaline decolorizing charcoal (Norit A). The cooled mixture was filtered, and petroleum ether was evaporated from the filtrate on a steam bath. Other volatiles were removed from the residue via distillation under reduced pressure, leaving a semisolid residue. Sufficient 95% ethanol was stirred with the residue, precipitating crude trisyl bromide, which was collected by vacuum filtration. Recrystallizations from ethyl acetate/95% ethanol afforded 234 g (75%) of pure trisyl bromide: mp 194–195 °C (sealed tube) (lit.<sup>5</sup> mp 194–195 °C). Anal. Calcd

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for  $C_{10}H_{27}BrSi_3$ : C, 38.55; H, 8.57. Found: C, 38.22; H, 8.63. The molecular weight was determined by vapor pressure osmometry in benzene: found 329 (calcd 312). The  $^1H$  NMR spectrum showed a sharp singlet at  $\delta$  0.19, which is consistent with that reported in the literature.<sup>5</sup>

**General Preparation of Trisyllithium from Trisyl Bromide and Lithium Metal.** About 25 mL of a solution of trisyl bromide (31 g, 0.1 mol) dissolved in 250 mL of diethyl ether was added to vigorously stirred lithium metal (3.4 g, 0.5 mol) at room temperature. After ca. 5 min of stirring, an exothermic reaction commenced and the remainder of the trisyl bromide solution was added dropwise over a 1-h period. Upon completed addition, the reaction mixture was cooled to room temperature; unreacted lithium metal was separated by filtration under nitrogen through a glass-wool-plugged ground glass hose adapter fitted to the three-necked flask into a 250-mL graduated addition funnel. Double titration of 3-mL aliquots indicated a 75% yield of trisyllithium.

Essentially the same procedure was used when trisyllithium was prepared in THF, except that the reaction temperature had to be maintained at  $-50^\circ C$ . The trisyllithium yield (by titration) was 70%.

(a) **Reaction with Chlorotrimethylsilane.** Trisyllithium (0.07 mol) was added dropwise over a 30-min period at room temperature with stirring to a solution of  $Me_3SiCl$  (10.9 g, 0.1 mol) in 50 mL of diethyl ether. Upon completed addition, the reaction mixture was refluxed for 1 h prior to addition to 200 mL of ice-cold 10% HCl. The organic layer was separated and the aqueous layer extracted with diethyl ether (100 mL). The combined organic layers were dried over anhydrous  $CaCl_2$  and filtered, and the volatiles were removed from the filtrate by evaporation on a steam bath, leaving a semisolid residue. Recrystallization from 95% ethanol afforded 18.5 g (76% yield) of  $(Me_3Si)_3C$ : mp  $310-312^\circ C$  (sealed tube) (lit.<sup>9</sup> mp  $307-308^\circ C$ , sealed tube).

(b) **Reaction with Hydrochloric Acid.** Trisyllithium (0.15 mol) was hydrolyzed by addition to a mixture of crushed ice and 200 mL of 10% HCl. The organic layer was separated and the aqueous layer extracted with diethyl ether (100 mL). The combined organic layers were dried over anhydrous  $CaCl_2$  and filtered, and the volatiles were removed from the filtrate by evaporation on a steam bath. Distillation of the residue under reduced pressure afforded 29 g (83% yield) of  $(Me_3Si)_3CH$ : bp  $110-116^\circ C$  (16 mmHg).

(c) **Reaction with Mercuric Chloride.** Trisyllithium (0.07 mol) was added dropwise over a 30-min period at room temperature with stirring to a solution of  $HgCl_2$  (10.0 g, 0.04 mol) dissolved in 100 mL of diethyl ether. Upon completed addition, the reaction mixture was refluxed for 2 h prior to addition of the cooled mixture to 200 mL of ice-cold 10% aqueous HCl. The organic layer was separated, and the aqueous layer was extracted with diethyl ether (100 mL). The combined organic layers were dried over anhydrous  $CaCl_2$  and filtered, and the volatiles were removed from the filtrate by evaporation on a steam bath, leaving a solid residue. Recrystallization of the residue from ethyl acetate/95% ethanol afforded 16.3 g (70% yield) of bis[tris(trimethylsilyl)methyl]mercury: mp  $284-287^\circ C$  (lit.<sup>12</sup> mp  $282-285^\circ C$ ). Anal. Calcd for  $C_{20}H_{54}Si_6Hg$ : C, 36.18; H, 8.22. Found: C, 36.37; H, 8.41. The  $^1H$  NMR spectrum showed a singlet at  $\delta$  0.25, which is consistent with that reported in the literature.<sup>12</sup>

**Preparation of Trisyllithium from Trisyl Bromide and Phenyllithium.** To trisyl bromide (15.6 g, 0.05 mol) dissolved in diethyl ether (100 mL) and cooled to  $0^\circ C$  was added dropwise a solution of phenyllithium (0.07 mol) in diethyl ether (100 mL) with rapid stirring over a 30-min period. Upon completed addition, the reaction mixture was stirred for an additional 3 h at  $0^\circ C$  prior to addition of a solution of chlorotrimethylsilane (7.6 g, 0.07 mol) dissolved in diethyl ether (50 mL). Subsequent to

being stirred for an additional 8 h at room temperature, the reaction mixture was hydrolyzed by addition to 200 mL of ice-cold 10% aqueous HCl. The organic layer was separated, and the aqueous layer was extracted with diethyl ether (100 mL). The combined organic layers were dried over anhydrous  $CaCl_2$  and filtered, and the volatiles were removed from the filtrate by evaporation on a steam bath, leaving a semisolid residue. The solid that formed upon stirring the residue with 95% ethanol was collected by filtration. Recrystallization from 95% ethanol afforded 13 g (85% yield) of  $(Me_3Si)_3C$ . Distillation of the initial filtrate yielded 9 g (100% yield) of bromobenzene: bp  $156-158^\circ C$ .

**General Preparation of Trisylmagnesium Bromide from Trisyl Bromide and Magnesium Metal.** To magnesium turnings (4.8 g, 0.2 mol) was added with vigorous stirring a solution of 1,2-dibromoethane (2 mL) dissolved in 25 mL of diethyl ether. After the mixture was stirred at room temperature for ca. 15 min to activate the magnesium metal, a solution of trisyl bromide (31 g, 0.1 mol) in 200 mL of diethyl ether was added dropwise to the mixture at reflux over a 45-min period with rapid stirring. Upon completed addition, the reaction mixture was refluxed for an additional 2 h. After this period, the reaction mixture was cooled to room temperature. The unreacted magnesium metal was removed via filtration under nitrogen through a glass-wool-plugged ground glass hose adapter fitted to the three-necked flask into a 250-mL graduated addition funnel. Double titration of a 3-mL aliquot indicated a 75% yield of trisylmagnesium bromide.

(a) **Reaction with Iodine.** Trisylmagnesium bromide (0.08 mol) was added dropwise over a 10-min period to iodine (17.8 g, 0.07 mol) suspended in 50 mL of diethyl ether at room temperature with rapid stirring. An exothermic reaction occurred, and the reaction mixture was stirred for an additional 3 h. After this period, the mixture was hydrolyzed with 200 mL of ice-cold 10% HCl. The organic layer was separated, and the aqueous layer was extracted with 100 mL of diethyl ether. The combined organic extracts were washed with 100 mL of 1 M  $Na_2S_2O_3$  prior to washing with 100 mL of water. The organic layer was dried over molecular sieves and filtered, and the volatiles were removed from the filtrate by evaporation on a steam bath, leaving a solid residue. Recrystallization from 95% ethanol afforded 16.3 g (65% yield) of trisyl iodide, mp  $245-247^\circ C$  (sealed tube) (lit.<sup>5</sup>  $246-247^\circ C$ , dec). Anal. Calcd for  $C_{10}H_{27}Si_3I$ : C, 33.49; H, 7.90. Found: C, 33.61; H, 8.13. The  $^1H$  NMR spectrum showed a sharp singlet at  $\delta$  0.10, which is consistent with that reported in the literature.<sup>5</sup>

(b) **Reaction with Benzyl Chloride.** Trisylmagnesium bromide (0.07 mol) was added dropwise over ca. 10 min to a solution of benzyl chloride (8.9 g, 0.07 mol) dissolved in 200 mL of THF at room temperature with rapid stirring. The reaction mixture was subsequently refluxed for 12 h prior to hydrolysis with 200 mL of 10% aqueous HCl. The organic layer was separated, and the aqueous layer was extracted with 100 mL of diethyl ether. The combined organic layers were dried over anhydrous  $CaCl_2$  and filtered, and the volatiles were removed on a steam bath. The solid residue was recrystallized from 95% ethanol/ethyl acetate, affording 17 g (74% yield) of 1,1,1-tris(trimethylsilyl)-2-phenylethane: mp  $83-85^\circ C$  (lit.<sup>7</sup> mp  $83-84^\circ C$ ). Anal. Calcd for  $C_{17}H_{34}Si_3$ : C, 63.24; H, 10.64. Found: C, 63.22; H, 10.49. The  $^1H$  NMR spectrum showed signals at  $\delta$  0.3 (27 H, s,  $Me_3Si$ ), 2.3 (2 H, s,  $-CH_2-$ ), and 6.2 (5 H, s, Ph).

(c) **Reaction with Mercuric Chloride.** Trisylmagnesium bromide (0.07 mol) was treated with mercuric chloride (10.1 g, 0.04 mol) in the same manner as that described for benzyl chloride (reaction b above). Workup of the reaction mixture in the usual manner afforded 20 g (82% yield) of bis[tris(trimethylsilyl)methyl]mercury (mixed mp  $283-285^\circ C$ ) after recrystallization from 95% ethanol/ethyl acetate.

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