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SYNTHESIS AND CHARACTERIZATION OF NEW AROMATIC-GROUP SUBSTITUTED SILANES BEARING TRIS (TRIMETHYLSILYL)METHYL BULKY GROUPS

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Reaction of the Grignard reagent, p-ClC_6H_4MgCl, with $SiCl_4$ in toluene gave (p-$ClC_6H_4)_2SiCl_2$, which was treated with KHF_2 to give (p-$ClC_6H_4)_2SiF_2$ (1). Reaction of the latter with $[(Me_3Si)_3C]Li$ in THF leads to the preparation of $[(Me_3Si)_3C]$(p-$ClC_6H_4)_2SiF$ (2). Treatment of (2) with $LiAlH_4$ gave $[(Me_3Si)_3C]$(p-$ClC_6H_4)_2SiH$ (3) and $[(Me_3Si)_3C]$(p-$ClC_6H_4)(C_6H_5)SiH$ (4). $[(Me_3Si)_3C]$(p-$ClC_6H_4)SiCl_2$ (5) was also prepared from the reaction of (p-$ClC_6H_4)SiCl_3$ with $[(Me_3Si)_3C]Li$ in a similar manner. The new highly sterically hindered organosilicon reagents (2) to (5) have been fully characterized by IR, ^1H and ^{13}C NMR, and mass spectrometry as well as elemental analysis.

Keywords Bulky group; Grignard reagent; organosilicon; steric hindrance; trisyl

INTRODUCTION

Considerable novel chemistry has emerged from the studies of compounds in which a highly sterically hindered group, $(Me_3Si)_3C$ (R), is attached to a metal or metalloid.[1–7] This bulky group has successfully been used in the synthesis and characterization of the first derivative of Mg and Mn, i.e., MR_2, shown to be two-coordinate in the solid state,[8] and the first cobalt halide derivatives containing silanolato groups.[9] The first stable silanetriol $RSi(OH)_3$[10] and the first cyanates of silicon, such as $RSiMe_2OCN$, are also prepared by the attachment of $(Me_3Si)_3C$ to the silicon center.[11] It has been shown that this bulky group has a great role in the synthesis of thiocyanate of silicon $(Me_3Si)_2C(MeOMe_2Si)(Me_2SiSCN)$[12] and the first mono-organolead(II) compound $(PbClR)_3$.[13] There are several reports concerning the importance of this methodology in the preparation of the stable organotellurium and organoselenium hydrides,[14,15] the organomanganese and organocobalt halide RMCl as their complexes $[Li(THF)_4][R_3M_3Cl_4(THF)]$,[16] and the solvent-free diorganolanthanides.[17]

Use of the $(Me_3Si)_3C$ group as a bulky ligand in organosilicon chemistry began with the demonstration that $(Me_3Si)_3CH$ could be metallated with MeLi in Et_2O-THF to give the reagent $[(Me_3Si)_3C]Li$,[18] which was found to react with $R'_nSiF_{4\text{-}n}$ to give

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$[(Me_3Si)_3C]R'_nSiF_{4\text{-}n\text{-}1}$ (n = 1–3).[1] The remarkable ability of the $(Me_3Si)_3C$ bulky ligand to induce considerable steric hindrance at a silicon center leads to the observation of a novel competitive mechanism of reactions that are not normally competitive in the absence of the $(Me_3Si)_3C$ bulky group.[19–21]

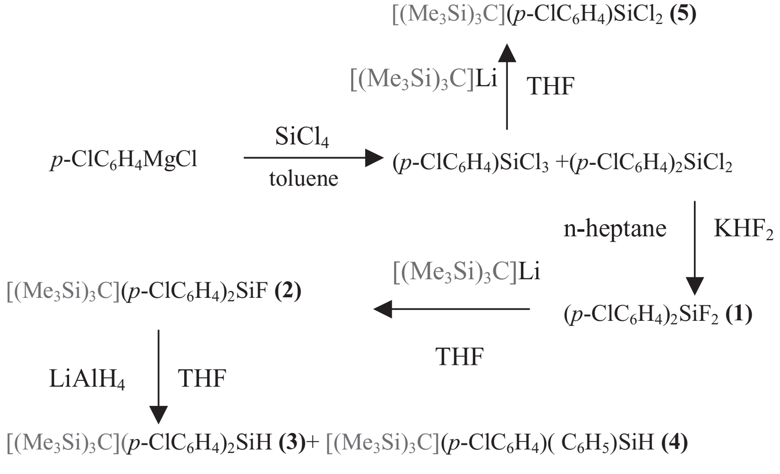
A number of organosilicon compounds bearing tris(trimethylsilyl)methyl, $(Me_3Si)_3C$, frequently denoted by Tsi, of the type $TsiSiR_2X$ (R=Ph, alkyl, X=H or halogen), have been prepared,[22,23] but examples of the type $TsiSi(Y{-}C_6H_4)_2X$ (Y = substituent with electronic effect) are rare.[24]

Thus it seemed of interest to synthesize and fully characterize organosilicon compounds with general formula $TsiSi(p\text{-}ClC_6H_4)_2X$ (X=F or H) (**2** and **3**) along with $TsiSi(p\text{-}ClC_6H_4)_2(C_6H_5)SiH$ (**4**) and $TsiSi(p\text{-}ClC_6H_4)SiCl_2$ (**5**) in order to examine the influence of the electronic effect of chlorine and to introduce these compounds as potential precursors and reagents for the new synthesis. The results of these studies are reported below.

RESULTS AND DISCUSSION

Although highly sterically hindered organosilicon compounds bearing tris (trimethylsilyl)methyl groups are well known and common,[22,23] a few references of the type $[(Me_3Si)_3C](Y{-}C_6H_4)_2SiX$ (X is mainly H or F and Y = substituent with inductive effect) are seen in the chemistry literature.[24] It has been shown that the nature of the substituent has an important influence on direct nucleophilic attack at functional silicon centers containing the $(Me_3Si)_3C$ group.[25–27] In our research work, Y is chlorine and the syntheses of new compounds **2** to **5** were performed by employing Grignard reagents in a similar manner.

The dichlorosilane, $(p\text{-}ClC_6H_4)_2SiCl_2$, usually does not react with TsiLi at all, but sometimes coupling occurs with very low yields. So $(p\text{-}ClC_6H_4)_2SiCl_2$ was prepared from the reaction of the Grignard reagent $(p\text{-}ClC_6H_4)MgCl$ with $SiCl_4$, and was treated with KHF_2 to give the less sterically hindered $(p\text{-}ClC_6H_4)_2SiF_2$ (**1**). The reaction of **1** with TsiLi gave $Tsi(p\text{-}ClC_6H_4)_2SiF$ (**2**) in good yield. Treatment of **2** with $LiAlH_4$ in THF gave a mixture of $Tsi(p\text{-}ClC_6H_4)_2SiH$ (**3**) and $Tsi(p\text{-}ClC_6H_4)\ (C_6H_5)SiF$ (**4**) (Scheme 1).



Scheme 1

These were subsequently separated by fractional crystallization from ethanol. Tsi(p-ClC_6H_4)$SiCl_2$ (**5**) was obtained in low yield when (p-ClC_6H_4)$SiCl_3$ was reacted with TsiLi (Scheme 1). The products **2** to **5** were extensively characterized by MS and IR spectrometry as well as ^{1}H and ^{13}C NMR techniques.

The MS data of **2** to **5** are easily related to the proposed structures, with the normal loss of Me, PhCl, $SiMe_3$, and other silicon moieties (see the Experimental section).

The IR spectra of **2** to **5** exhibit characteristic absorption bands at 850 and 1250 cm^{-1} due to C—Si.[18] The C=C stretching of benzene rings is seen at the range of 1566–1470 cm^{-1}, the Ph—Cl absorption is observed at ~1250 cm^{-1}, and Si—H stretching vibrations due to **3** and **4** appeared at 2095 and 2090 cm^{-1}, respectively.

The ^{1}H NMR spectra of compounds **2** to **5** clearly show a sharp singlet at δ 0.26, 0.24, 0.25, and 0.35 ppm, respectively, which is assigned to trisyl protons $(Me_3Si)_3C$. In the spectra of **2** and **3**, the quintet signal, which is expected for para-substituted rings, is seen at δ 7.26–7.75 ppm, but in that of **4**, a multiplet peak due to the overlap of signals of the two different rings is clearly observed from δ 7.28 to 7.84 ppm with intensity corresponding to 9 protons. The four aromatic protons of **5** are observed at δ 7.35–7.90 ppm. There is also a signal at δ ~5 ppm in **3** and **4**, which is assigned to the Si—H proton.

The ^{13}C NMR spectra of compounds **2** to **5** contain signals at δ ~5.9, 5.3, 4.6, and 4.8 ppm, which belong to $SiMe_3$-carbons, and the aromatic carbons are seen in the range of δ 126.8–137.6 ppm.

It is concluded from MS, IR, ^{1}H, and ^{13}C NMR studies that the four new organosilicon compounds **2** to **5** containing the bulky $(Me_3Si)_3C$ ligand can be prepared with satisfactory yields and fully characterized. In addition, these highly sterically hindered compounds with trisyl group are excellent candidates as starting materials for the reactions with the various suitable reagents in the synthesis of the new compounds based on the novel competitive mechanism at the corresponding silicon centers. Therefore, we strongly recommend them for further research in this field.

EXPERIMENTAL

Materials and Methods

Reactions involving $LiAlH_4$, lithium metal, organolithium, or Grignard reagents were carried out under dry argon. Solvents were dried and other chemicals were purified by standard methods. TsiH,[28] MeLi,[18] TsiLi,[18] and (p-ClC_6H_4)MgCl,[29,30] were prepared using the methods in the literature. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker FT (300 MHz) instrument. The IR spectra were recorded on a Shimadzu IR-470 infrared spectrometer using pressed KBr disks. Mass spectra were obtained at 70 eV Fisnos VG Autospec. Elemental analysis (C and H) was performed by the microanalytical service of N.I.O.C. Research Institute of Petroleum Industry.

Synthesis of (p-ClC_6H_4)$SiCl_3$ and (p-ClC_6H_4)$_2SiCl_2$

A solution of p-ClC_6H_4MgCl in toluene prepared from the reaction of p-ClC_6H_4Cl (73.5 g, 0.5 mol) and Mg turnings (12.15 g, 0.5 mol) was added dropwise to a solution of $SiCl_4$ (34 g, 0.2 mol) in toluene (50 mL). The mixture was stirred under reflux for 3 h and then filtered. Volatile components were removed from the filtrate. The residue was distilled at 119°C/35 mmHg to give (p-ClC_6H_4)$SiCl_3$ and then at 182°C/2 mmHg to give (p-ClC_6H_4)$_2SiCl_2$.

Synthesis of (p-ClC_6H_4)$_2SiF_2$ (1)

KHF_2 (7.8 g, 0.1 mol) was gradually added with stirring to (p-ClC_6H_4)$_2SiCl_2$ (16.1 g, 0.05 mol) at 75°C in a water bath. n-Heptane (50 mL) was added, and the mixture was stirred at 70–80°C for 2 h, then filtered hot. The solvent was removed from the filtrate under vacuum, and the residue was distilled at 127–128°C/3 mmHg. Yield: 11.5 g (79%).

Synthesis of Tsi(p-ClC_6H_4)$_2$SiF (2)

A solution of (p-ClC_6H_4)$_2SiF_2$ (5.78 g, 0.02 mol) in THF was added dropwise with stirring to a solution of TsiLi in THF (50 mL) that had been made by the reaction of TsiH (4.6 g, 0.02 mol) with MeLi generated from the reaction of MeI (3.4 g, 0.024 mol) with Li (0.336 g, 0.048 mol). The mixture was refluxed for 5 h, then aqueous NH_4Cl was added and the organic compounds were extracted with Et_2O. The extract was dried ($MgSO_4$), filtered, and evaporated, and the residue was recrystallized from EtOH to give Tsi(p-ClC_6H_4)$_2$SiF, mp 178°C. Yield: 6.1g (59.8%). Anal. Calcd. For $C_{22}H_{35}Cl_2FSi_4$: C, 52.66. H, 7.03. Found: C, 52.51. H, 6.99. ^{1}HNMR ($CDCl_3$): δ 0.26 (27H, s, $SiMe_3$), 7.29–7.70 (8H, Aromatic-H). ^{13}C NMR: δ 5.9 ($SiMe_3$), 128.3, 129.5, 132.4, 135.7 (Aromatic-C). MS: *m/z* 485 (100, M—Me), 373 (16), 281 (7), 169 (11), 73 (57). IR (KBr, cm^{-1}): ν 850, 1250 (C—Si).

Synthesis of Tsi(p-ClC_6H_4)$_2$SiH (3) and Tsi(p-ClC_6H_4)(Ph)SiH (4)

$LiAlH_4$ (2.5 g, 0.065 mol) was gradually added with stirring to a solution of Tsi(p-ClC_6H_4)$_2$SiF (3 g, 0.006 mol) in dry THF (50 mL). The mixture was refluxed for 10 days. After cooling of the mixture in ice water, aqueous saturated NH_4Cl was slowly added, the solution was extracted with Et_2O, and then the extract was dried ($MgSO_4$), filtered, and evaporated, and the residue was recrystallized from EtOH to give Tsi(p-ClC_6H_4)$_2$SiH, mp 169°C. Yield : 0.8 g (28%). Anal. Calcd. For $C_{22}H_{36}Cl_2Si_4$: C, 54.62. H, 7.50. Found: C, 54.66. H, 7.61. ^{1}H NMR (CD_2Cl_2): δ 0.24 (27H, s, $SiMe_3$), 5.14 (1H, s, Si—H), 7.26–7.75 (8H, Aromatic-H). ^{13}C NMR ($CDCl_3$): δ 5.3 ($SiMe_3$), 127.6, 128.2, 131.2, 137.6 (Aromatic-C). MS: m/z 467 (47), 433 (27), 355 (100), 281 (28), 169 (45), 73 (97). IR (KBr, cm^{-1}): ν 850–1250 (C—Si), 2095 (Si—H). A second crop of crystals was shown to be Tsi(p-ClC_6H_4)(C_6H_5)SiH, mp 158°C. Yield: 0.3 g (11%). Anal. Calcd. For $C_{22}H_{27}ClSi_4$: C, 58.81; H, 8.30. Found: C, 59.03; H, 8.38. ^{1}H NMR (CD_2Cl_2): δ 0.25 (27H, s, $SiMe_3$), 5.17 (1H, s, Si—H), 7.28–7.84 (9H, m, Aromatic-H). ^{13}C NMR ($CDCl_3$): δ 4.6 ($SiMe_3$), 126.8, 127.9, 134.1, 137.0 (Aromatic-C). MS: *m/z* 433 (42 M—Me), 399 (33), 355 (66), 321 (100), 247 (42), 175 (42), 135 (70), 73 (97). IR (KBr, cm^{-1}): ν 850, 1250 (C—Si), 1470 and 1413 (C=C), 2090 (Si—H).

Synthesis of Tsi(p-ClC_6H_4)$SiCl_2$ (5)

A solution of (p-ClC_6H_4)$SiCl_3$ (4.92 g, 0.02 mol) in THF (10 mL) was added dropwise with stirring to a solution of TsiLi (prepared as above) in THF (50 mL). The mixture was refluxed for 4 h, then aqueous NH_4Cl was added and the organic compounds were extracted with Et_2O. The extract was dried ($MgSO_4$), filtered, and evaporated, and the residue was recrystallized from EtOH to give Tsi(p-Cl C_6H_4)$SiCl_2$, mp 187°C. Yield: 3.1 g (35%). Anal. Calcd. For $C_{16}H_{31}Cl_3Si_4$: C, 43.47; H, 7.07. Found: C, 43.59; H, 6.94. ^{1}H NMR ($CDCl_3$): δ 0.35 (27H, s, $SiMe_3$), 7.35–7.90 (4H, Aromatic-H). ^{13}C NMR ($CDCl_3$): δ 4.8 (Me_3Si), δ 127.2, 128.3, 131.2, 137.6 ppm (Aromatic-C). MS: *m/z* 427 (97, M−Me), 389 (93), 332 (24), 317 (30), 221 (52), 73 (100). IR (KBr, cm^{-1}): ν 850, 1250 (C−Si), 1563 and 1471 (C=C).

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