

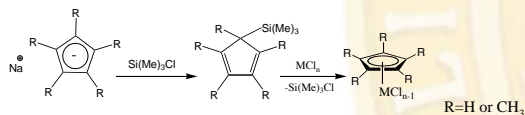
On the Way to Supersized Four Legged Piano Stools: Polyarylcyclopentadienides, $\text{Me}_3\text{E}(\text{H})\text{C}_5\text{Ph}_4$ (E = Si, Sn) and Their Reaction With Group 5 Pentachlorides.

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INTRODUCTION

This group have been active in the use of pentaaryl cyclopentadienyl ligands in group 4 metal complexes by the application of bulky polyphenyl-cyclopentadienyl groups to exploit their steric bulk as facially directing groups. We have successfully prepared pentaphenylcyclopentadienyl zirconium trichloride ($\text{C}_5\text{Ph}_5\text{ZrCl}_3$) as well as some chiral derivatives,^{1,2} and wish to investigate polyphenylcyclopentadienyl complexes with other metals.

Trimethylsilylcyclopentadienes ($\text{C}_5\text{R}_5\text{SiMe}_3$, R=H, alkyl) have been widely used to transfer a cyclopentadienyl ring to a transition metal. Among the trimethylsilyl substituted cyclopentadienes, $\text{C}_5\text{Me}_5\text{SiMe}_3$ has been synthesized to make pentamethylcyclopentadienyl complexes.^{3,4}



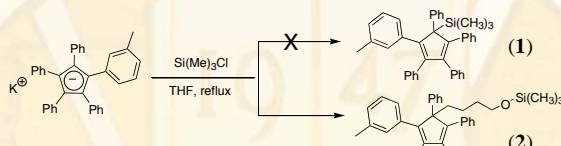
Here we report the synthesis of trimethyl(group14)-polyphenylcyclopentadienes $\text{C}_5\text{Ph}_n\text{EMe}_3$ (E=Si, Sn n=4) and their applications in polyphenylcyclopentadienyl addition to niobium halides.

RESULTS and DISCUSSION

A. The Reaction of potassium *m*-tolyltetraphenylcyclopentadienide (*mt*-Cp) with $\text{Si}(\text{Me})_3\text{Cl}$:

Attempts to prepare trimethylsilyl-*mt*-Cp by the reaction of potassium *mt*-Cp with $\text{Si}(\text{Me})_3\text{Cl}$ in a variety of solvents (polar, nonpolar organics and neat TMS-Cl) returned only starting material with the exception of tetrahydrofuran (THF). Removal of solvent in vacuo, followed by crystallization in heptane gives an off-white solid. The ^{13}C and ^1H NMR spectra as well as HRMS analysis indicate this compound is trimethyl-*m*-tolyltetraphenylcyclopentadienyl-butoxy]-silane(2), the result of THF ring-opening product.

The reaction of potassium *mt*-Cp with SiMe_3Cl :

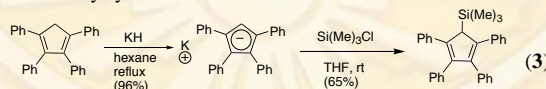


2: ^1H NMR (300MHz, CD_2Cl_2) $\text{Si}(\text{CH}_3)_3$, $\delta=0.1307$ (s), 0.1295 (s); Ph-C-H, 1.919 (s), $\delta=1.911$ (s); C-H, $\delta=1.58$ (m), 1.84 (m), 2.42 (m), 3.51 (m); C_6H_5 , $\delta=6.7$ - 7.6 (m).
HRMS calc'd. for $\text{C}_{43}\text{H}_{44}\text{OSi}$ (M^+) 604.3162, found 604.3292.

Instead of the formation of the expected product $\text{C}_5\text{Ph}_5\text{SiMe}_3$ (1), the reaction gives a product of THF ring-opened ether (2). The scheme only shows one of three isomers of (2).

B. The Reaction of potassium tetraphenylcyclopentadienide (*KCp*) with $\text{Si}(\text{Me})_3\text{Cl}$:

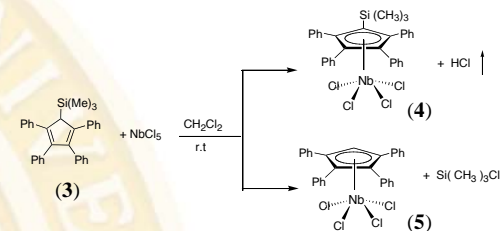
Suspecting that a less sterically encumbered polyarylcyclopentadiene would be more amenable to addition of the TMS group, reaction using a tetra-arylcyclopentadiene was attempted and trimethylsilyltetraphenylcyclopentadien $\text{C}_5\text{Ph}_4\text{HSiMe}_3$ (3) was successfully synthesized.



3: ^1H NMR (300MHz, CD_2Cl_2) $\text{Si}(\text{CH}_3)_3$, $\delta=-0.39$; C-H, $\delta=4.70$; C_6H_5 , $\delta=7.05$ - 7.35 . ^{13}C NMR (300MHz, CD_2Cl_2) $\delta=-2.4$, 54.8 , 126.6 , 126.7 , 127.9 , 128.2 , 129.7 , 130.9 , 137.9 , 138.0 , 142.9 , 143.0 ;
HRMS calc'd. for $\text{C}_{32}\text{H}_{30}\text{Si}$ (M^+) 442.2116, found 442.2107.

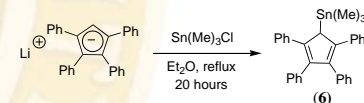
C. The new precursor $\text{C}_5\text{Ph}_4\text{HSiMe}_3$ and its reaction with NbCl_5 :

The reaction of $\text{C}_5\text{Ph}_4\text{HSiMe}_3$ and NbCl_5 was carried out in CH_2Cl_2 as solvent at room temperature. The product of the reaction is a dark red mixture, as illustrated in the following scheme:



Surprisingly, the reaction does not completely follow the regular route to eliminate the TMS group in $\text{C}_5\text{Ph}_4\text{HSiMe}_3$ to form 5, but shows competitive reactions between elimination of TMS and HCl to form both 4 and 5.

D. We have pursued the tin analogue of 3, prepared as shown below.



6: ^1H NMR (300 MHz C_6D_6): C_6H_5 , δ 7.4 (m) δ 7.1 (m); $\text{C}_5\text{Ph}_4\text{H}$, δ 5.05 (s), $^2\text{J}_{\text{Sn-H}} = 91$ Hz; $\text{C}_5\text{Ph}_4\text{H}(\text{Sn}(\text{CH}_3)_3)$, δ -0.19 (s), $^2\text{J}_{\text{Sn-H}} = 53$ Hz.

NMR scale reaction of 6 with NbCl_5 suggest a cleaner reaction as only one trimethyltin signal is observed. Further work in optimization of the synthesis of 6 and its reaction with Group 5 metals is in progress.

ACKNOWLEDGMENTS

Department of Energy:42493
National Science Foundation: CHE-0402718
National Institute of Health

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