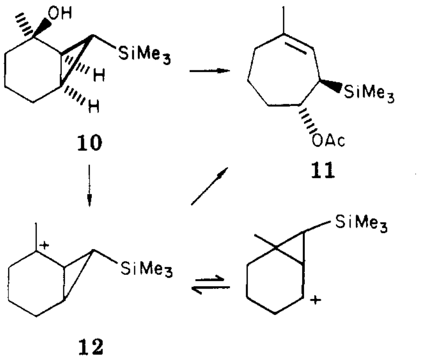
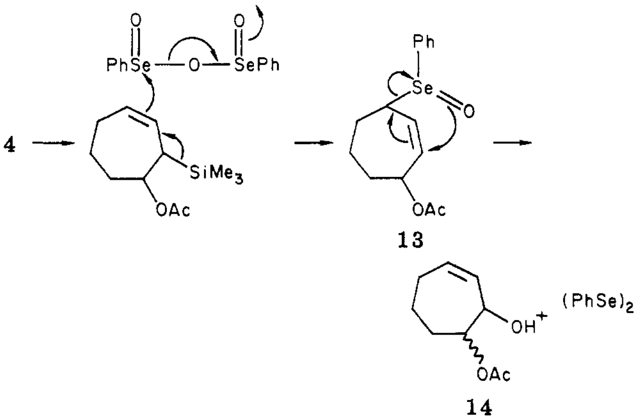
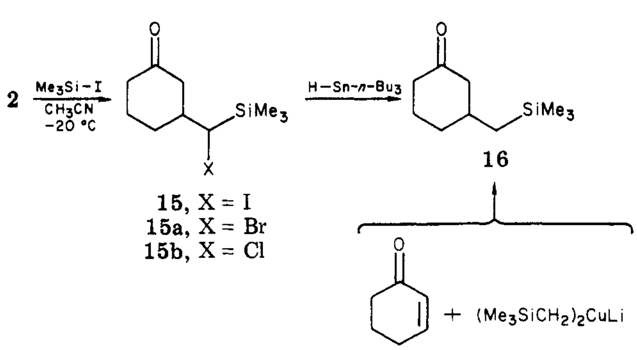
Treatment of **2** with methyllithium in ether at 0 °C gave the tertiary carbinol **10**, which when exposed to $BF_3 \cdot OEt_2/AcOH/CH_2Cl_2$ at -40 °C for 15 min, was cleanly converted into the allylsilane **11**. In this particular case there was no scrambling of stereochemistry, presumably because the tertiary carbenium ion **12** has nothing to gain in stabilization by entering into cyclopropane migration in the way that **3** does.[4]



The allylsilane **4**, on treatment with diphenylseleninic anhydride[8] in dichloromethane at 20 °C containing a catalytic amount of $BF_3 \cdot OEt_2$, gave the α-acetoxyalcohol **14** (3:2 cis/trans), via a [2.3] sigmatropic rearrangement of the intermediate **13**.



To demonstrate that the cyclopropylcarbinyl system is necessary to ring expansion and the $-SiMe_3$ group cannot direct this alone, we treated the ketone **2** with trimethylsilyl iodide in acetonitrile[9] at 20 °C for 1.5 h. The iodide **15** was the only product formed.[10] Its structure was demonstrated by removal of the iodine atom with tri-*n*-butyltin hydride to give **16**. An authentic sample of **16** was prepared from cyclohexenone and the cuprate $(Me_3SiCH_2)_2CuLi$.[11] Similarly the ketone **2** gave the adducts **15a** and **15b**, respectively, on treatment with HBr and HCl.



The ring expansion-functionalization sequences (e.g., **3** → **9**), where no stereochemistry evolves, provide a new method of converting cyclohexenone into γ-acetoxycycloheptenone. We anticipate that the conversion of the tertiary carbinol **10**, with control of stereochemistry into **11**, will have synthetic promise in the construction of seven-membered rings with substitutents in fixed relative stereochemistry.

Acknowledgment. The National Science Foundation and National Institute of Health are gratefully thanked for their support of this work.

Registry No. *exo*-**2**, 69152-98-3; *endo*-**2**, 69177-43-1; **3** isomer 1, 80540-14-3; **3** isomer 2, 80540-15-4; **4** isomer 1, 80540-16-5; **4** isomer 2, 80540-17-6; **5**, 826-13-1; **6**, 80540-18-7; **7**, 1124-23-8; **8** isomer 1, 80540-19-8; **8** isomer 2, 80540-20-1; **9**, 74982-28-8; **10**, 80540-21-2; **11**, 80540-22-3; *cis*-**14**, 80540-23-4; *trans*-**14**, 80540-24-5; **15**, 80540-25-6; **15a**, 80540-26-7; **15b**, 80540-27-8; **16**, 77644-39-4.

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Preparation of (η^6-Toluene)bis(trichlorosilyl)nickel(II) by Oxidative Addition of Silicon-Silicon and Silicon-Hydrogen Bonds to Nickel Atoms and Bis(1,5-cyclooctadiene)nickel(0). Extreme Lability of the π-Toluene Ligand[1a]

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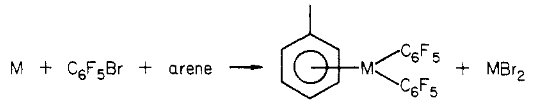
Summary: A new π-arene complex, (η^6-toluene)$Ni(SiCl_3)_2$ (**1**), was prepared by three methods: the reaction of (1) Ni vapor + $Cl_3SiSiCl_3$ + toluene, (2) Ni vapor + $HSiCl_3$ + toluene, and (3) $Ni(COD)_2$ + $HSiCl_3$ + toluene. Complex **1** possesses a very labile π-toluene ligand which can be exchanged with C_6D_6 at room temperature.

For several years we have been investigating the syntheses and chemistry of π-arene complexes of Co(II) and Ni(II).[1b,2]



These complexes are rare and Ligand for two reasons: (1) they are unique structures[3] and, until now, only stable

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(1) (a) This research was supported by the National Science Foundation. (b) Anderson, B. B.; Behrens, C. L.; Radonovich, L. J.; Klabunde, K. J. *J. Am. Chem. Soc.* **1976**, *98*, 5390.

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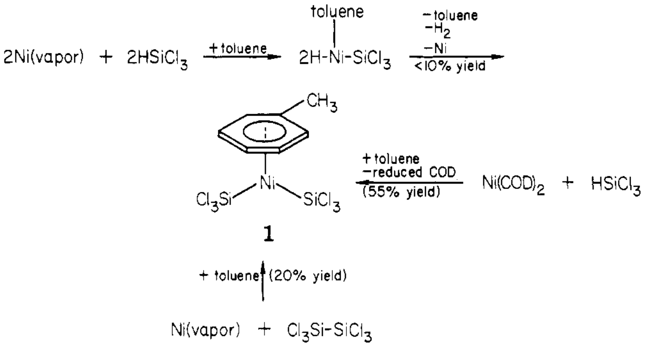
when C_6F_5 σ-bonding ligands were present, even though the π-arene could be varied at will, and (2) the π-arene lability is very high, probably higher than any other π-arene complex known.[4]

After considerable effort we have now found another σ-bonding ligand, $SiCl_3$, that imparts good thermal stability to the (π-arene)NiX_2 system. The impetus for using $SiCl_3$ as a σ-bonding ligand comes from the interesting work of Pomeroy and co-workers in (π-arene)Ru chemistry,[5] Lappert and co-workers on the reactivity of metal atoms and silanes,[6] and Uhlig and co-workers on the studies of Ni complexes with anionic ligands.[7] Of course, the method of introduction of the $SiCl_3$ groups into a Ni system was the most critical problem, and we report herein the first examples of oxidative addition of Si–H and Si–Si bonds to Ni atoms.[8] We also report that bis(1,5-cyclooctadiene)nickel(0), [$Ni(COD)_2$],[9] can be used for the preparation of π-arene complexes containing $SiCl_3$ ligands.

Codeposition of the vapors of Ni, toluene, and $HSiCl_3$ at −196 °C, followed by slow warming to room temperature, led to the production of H_2 and (π-toluene)$Ni(SiCl_3)_2$ (1). In the absence of toluene as a stabilizing ligand (Ni vapor + $HSiCl_3$) hydrogen was produced but no stable complex was isolable. Preparation of a Ni atom–toluene matrix (toluene-solvated Ni atoms) followed by $HSiCl_3$ addition did not lead to 1, which suggests that Ni atoms first attack the Si–H bond. Stabilization of the initially formed Si–Ni–H species by toluene seems likely, and upon warming and meltdown, two such molecules could combine (or another $HSiCl_3$ molecule could react) to release H_2 and form the product.



A more direct route to 1 is by oxidative addition of $Cl_3Si–SiCl_3$ to Ni atoms in the presence of toluene. This reaction is more efficient and even small amounts of $Cl_3Si–SiCl_3$ are utilized well.

A third method to obtain 1 can be used, not employing Ni vapor, but $Ni(COD)_2$ instead. The success of this method is dependent on at least one COD ligand being converted to reduced and/or silylated derivatives. (About 50% of the COD is converted to cyclooctene during the reaction.) Furthermore, addition of COD to 1 causes the displacement of toluene, showing that 1 cannot exist in the presence of an excess of COD. Lastly, $Ni(COD)_2$ + $Cl_3Si–SiCl_3$ does not yield 1. Therefore, by ensuring that COD will be simultaneously destroyed during the reaction by adding adequate amounts of $HSiCl_3$, we can obtain convenient yields of 1 from $Ni(COD)_2$.

The ^1H NMR spectrum of 1 has absorptions at δ 2.7 (s, CH_3) and 6.7 (m, aromatic H), indicating a substantial upfield shift for the aromatic protons and a slight downfield shift for the CH_3 group. The toluene ligand is highly labile: addition of C_6D_6 to the NMR sample caused the immediate release of toluene (as detected by NMR). In addition, pure (η^6-benzene)$Ni(SiCl_3)_2$ was synthesized by exhaustive arene displacement exchange.

Further studies of the exchange process, arene displacement reactions, and catalysis studies of 1 will be reported later.

Procedure. I. Nickel vapor (0.532 g, 9.06 mmol) was cocondensed with a mixture of 10 mL of $Cl_3Si–SiCl_3$ in 10 mL of toluene at −196 °C over a 1-h period.[9] The resulting dark red-brown matrix turned black with some gold areas on warming. The excess ligand was recovered by trap-to-trap distillation in vacuo. The residue was flushed with nitrogen and washed three times with 10-mL portions of toluene, and the washings were filtered under nitrogen through a medium porosity glass frit. The dark red filtrate was reduced to 5 mL in vacuo and 20 mL of purified, deoxygenated pentane was added to precipitate a yellow-orange powder (1). The solid was washed three times with 3.5-mL portions of pentane and dried under vacuum (17% yield based on Ni vaporized), mp 140 °C; the solubility of 1 is high in toluene and CH_2Cl_2 but low in CCl_4 and pentane; it has long term stability in the solid or dissolved state (slight decomposition of the solid in a 4-week period while under nitrogen at room temperature) and is moderately air sensitive. NMR (CCl_4): δ 2.70 (CH_3, s), 6.70 (C_6H_5, m).

Anal. Calcd for ($C_7H_8Cl_6NiSi_2$): C, 20.03; H, 1.92; Cl, 50.68; Si, 13.38. Found: C, 20.14; H, 2.03; Cl, 50.25; Si, 12.90.

II. Addition of a solution of 15 mL of $HSiCl_3$ in 20 mL of purified, deoxygenated toluene at −95 °C to a solution of 1 g of $Ni(COD)_2$ (3.6 mmol) in 80 mL of toluene at −95 °C under nitrogen resulted in no color change. The mixture was allowed to warm slowly, and at about −65 °C it started to turn red-brown. At −45 °C it was red-black. The mixture was filtered under nitrogen at room temperature, the filtrate was concentrated under vacuum, and pentane was added as in procedure I. The yield of pure 1 was 0.84 g (55% based on $Ni(COD)_2$).[11]

Registry No. 1, 80410-01-1; $Ni(COD)_2$, 1295-35-8; $Cl_3SiSiCl_3$, 13465-77-5; $HSiCl_3$, 10025-78-2; Ni, 7440-02-0.

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(11) We thank Dr. Thomas Murdock for a pure sample of $Ni(COD)_2$.

Reactivity of Bridged Dinuclear Transition-Metal Complexes of the Type $Me_2Si[C_5H_4Fe(CO)(L)I]_2$, L = PPh_3 and $P(OPh)_3$. Synthesis and Characterization of the Mixed Iodo–Alkyl Complex $Me_2Si[C_5H_4Fe(CO)(PPh_3)(\eta^1\text{-butyl})]–[C_5H_4Fe(CO)(PPh_3)I]$

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Summary: Dinuclear diiron transition-metal complexes of the type $Me_2Si[C_5H_4Fe(CO)(L)I]_2$, L = Ph_3P and $(PhO)_3P$, have been synthesized and characterized. Alkylation of