$$H_2C{=}C(CH_3)_2 \xrightarrow[\text{AIBN, 60 °C}]{CCl_3Br} \underset{\mathbf{6}}{Cl_3CCH_2C(CH_3)_2Br} \xrightarrow[\text{THF, -40 °C}]{\text{KO-}t\text{-Bu}}$$

$$\underset{\mathbf{5}}{Cl_3CCH{=}C(CH_3)_2} \xrightarrow[\text{THF, 35 °C}]{Co_2(CO)_8} \underset{\mathbf{4}}{Co_3(CO)_9CCH{=}C(CH_3)_2}$$

When **4** is dissolved in fluorosulfonic acid, it undergoes protonation and forms $Co_3(CO)_9CCHCHMe_2^+$.[10] As the temperature is lowered, the isopropyl methyl ^{13}C resonance, a single peak at δ 24.2 at room temperature, broadens; at −65 °C two peaks of equal intensity are observed at 25.8 and 22.1 ppm. The barrier to site exchange of the methyl groups can be estimated from the coalescence temperature (−52 ± 2 °C) as $\Delta G^{\ddagger} = 10.5 \pm 0.1$ kcal mol^{-1}.

These results are consistent with **2** as the most stable structure, but not with **1** or **3**.[11] The observed coalescence corresponds to a process of enantiomerization for which two diastereomeric transition states, **3b** and **3′b**, need be considered. The observed barrier corresponds to the one lower in energy; this is presumably **3b** since in **3′b** a bulky *i*-Pr group is compressed against the $Co(CO)_3$ groups. By the same token, the magnitude of the barrier in **3b** should be similar to that in **3a**, since the bulky *i*-Pr group is now out of the range of repulsive nonbonded interactions. The rough agreement between the barriers calculated for **3a** (16 kcal mol^{-1} as an upper limit[4]) and found for **3b** is in accord with this supposition.

It is appropriate to view $Co_3(CO)_9CCH_2^+$ as an electronically driven bevel gear system in which gearing occurs by disrotatory correlated rotation about the two axes, via **3a** (Figure 1).[12] We particularly note the stereochemical correspondence of this system to 9-benzyltriptycene,[13] in which a twofold rotor (benzyl) and a threefold rotor (triptycene) undergo an analogous internal rotation. The major difference between the two systems lies in the coupling mechanism, since the forces governing the internal motions in 9-benzyltriptycene are nonbonded interactions.

The transition-metal-stabilized cations $Co_3(CO)_9CCHR^+$ are thus not true three-coordinate carbenium ions but are stabilized by direct interaction between the cationic carbon and the metal framework. A similar conclusion, suggested by similar use of isopropyl diastereotopism as a chirality probe, has already been reached for the other principal class of transition-metal-stabilized carbocations, the ferrocenyl derivatives $FcCHR^+$,[14] and has been confirmed by X-ray structure determinations.[15]

Acknowledgment. We thank the National Science Foundation (Grant CHE 79-20373 to J.R.N. at Colorado State and Grant CHE 80-09670 to K.M. at Princeton) for support of this work and Professor A. I. Meyers for valuable advice on the dehydrobromination of **6**.

Registry No. **4**, 80662-57-3; **5**, 80658-25-9; **6**, 23153-21-1; $Co_3(CO)_9CCHCHMe_2^+$, 80662-56-2; $Co_2(CO)_8$, 10210-68-1.

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[9] Kharasch, M. S.; Reinmuth, O.; Urry, W. H. *J. Am. Chem. Soc.* **1947**, *69*, 1105. ^1H NMR of **6** (CCl_4): δ 2.08 (s, 6 H), 3.56 (s, 2 H).

[10] ^1H NMR (FSO_3H): δ 1.54 (d, J = 6 Hz, 6 H), 2.18 (m, 1 H), 6.58 (d, J = 9 Hz, 1 H), referenced to CH_2Cl_2 (δ 5.32) as internal standard. $^{13}C\{^1H\}$ NMR (FSO_3H): δ 24.2 (*Me*$_2$CHCH), 42.0 (Me$_2$*C*HCH), 131.6 (Me$_2$CH*C*H), 193 (CO), referenced to CH_2Cl_2 (δ 53.8) as internal standard. At −36 °C another resonance can be seen at δ 272.0 (apical C). Assignments were confirmed by off-resonance decoupling.

[11] There are other possibilities which cannot be ruled out on the basis of the NMR evidence alone (for example, a structure in which the CH_2 group in $Co_3(CO)_9CCH_2^+$ bends toward the center of a Co–Co bond and the σ plane bisects the H-C-H angle), though they are unlikely on theoretical grounds.[4]

[12] The NMR data do not rule out uncorrelated rotation (i.e., rotation of the $CHCHMe_2$ fragment without concomitant rotation of the $Co_3(CO)_9$ moiety), though once again[11] this is unlikely on theoretical grounds.[4]

[13] Yamamoto, G.; Ōki, M. *Chem. Lett.* **1979**, 1251, 1255; *Bull. Chem. Soc. Jpn.* **1981**, *54*, 473, 481.

[14] Sokolov, V. I.; Petrovskii, P. V.; Reutov, O. A. *J. Organomet. Chem.* **1973**, *59*, C27.

[15] Cais, M.; Dani, S.; Herbstein, F. H.; Kapon, M. *J. Am. Chem. Soc.* **1978**, *100*, 5554. Behrens, U. *J. Organomet. Chem.* **1979**, *182*, 89.

Silicon in Synthesis. Ring Expansion and 1,4 Difunctionalization Using Silylcyclopropanes

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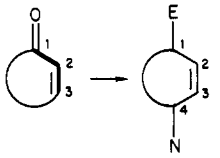
Received October 22, 1981

Summary: Treatment of 7-trimethylsilyl-substituted bicyclo[4.1.0] carbinols with electrophiles leads to ring expansion into an cycloheptenylallylsilane, which can undergo further transformations into substituted cycloheptene derivatives.

The general formulation shown depicts a complicated overall transformation involving one carbon ring expansion of a cyclic enone, combined with the introduction of an electrophile and nucleophile in a 1,4 relationship to one another.



Here we describe a short and flexible way of carrying out this transformation for the cyclohexenone to cycloheptene system, that utilizes the combined chemistry of silylcyclopropanes,[1] cyclopropylcarbinyl rearrangements,[2] and allylsilane electrophilic substitution.[3] It was envisioned that a (silylcyclopropyl)carbinol, **1**, would readily rearrange under electrophilic conditions via **1a** to give **1b**, where the carbenium ion is now situated β to the tri-

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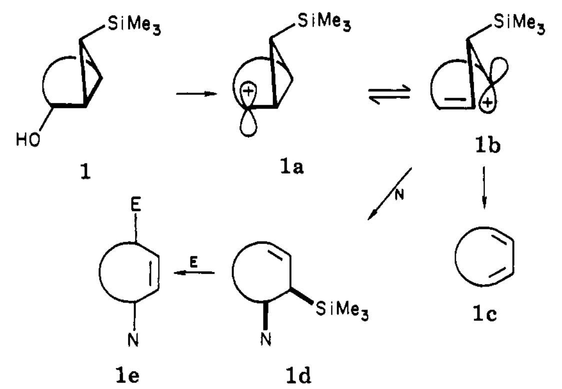
* To whom correspondence should be addressed at the Department of Chemistry, Indiana University, Bloomington, Indiana 47405.

[1] For the synthesis of silylcyclopropyl ketones using the ylide $Me_3SiCHSMe_2$ and references to silylcyclopropanes see: Cooke, F.; Magnus, P.; Bundy, G. L. *J. Chem. Soc., Chem. Commun.* **1978**, 714.

[2] Cyclopropylcarbinyl–cyclopropylcarbinyl cation rearrangements Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1976**, *98*, 7026. Friedrich, E. C.; Jassawalla, J. D. C. *J. Org. Chem.* **1979**, *44*, 4224. For a comprehensive review describing cyclopropane ring opening see: Sarel, S.; Yovell, J.; Sarel-Imber, M. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 577. Hanack, M.; Schneider, H.-J. *Ibid.* **1967**, *6*, 666. Solvolytic rearrangement route to ring-expanded steroids: Steinberg, N. G.; Rasmusson, G. H.; Reamer, R. A. *J. Org. Chem.* **1979**, *44*, 2294. Marshall, J. A.; Ellison, R. H. *Ibid.* **1975**, *40*, 2070. Hudrlik, P. F.; Rudnick, L. R.; Korzeniowski, S. H. *J. Am. Chem. Soc.* **1973**, *95*, 6848. Whalen, D. L.; Cooper, J. D. *J. Org. Chem.* **1978**, *43*, 432. For a general review of cyclopropane chemistry see: Meijere, A.; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 809. Other examples of cyclopropanes in ring expansion reactions: Kohout, L.; Fajkos, J. *Collect. Czech. Chem. Commun.* **1974**, *39*, 1613. Bellamy, A. J.; Whitham, G. H. *Tetrahedron* **1968**, *24*, 247. Caine, D.; Gupton, J. T. *J. Org. Chem.* **1974**, *39*, 2654. Seebach, D.; Braun, M. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 49. Reese, C. B.; Shaw, A. *J. Am. Chem. Soc.* **1970**, *92*, 2566. Parham, W. E.; Schweizer, E. E. *Org. React.* **1963**, *13*, 55. Amice, P.; Blanco, L.; Conia, J. M. *Synthesis* **1976**, 196.

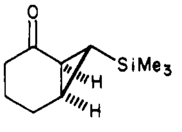
[3] Pillot, J.-P.; Dunogue's, J.; Calas, R. *Tetrahedron Lett* **1976**, 1871. Fleming, I.; Paterson, I. *Synthesis* **1979**, 445. For a recent review see: Chan, T. H.; Fleming, I. *Ibid.* **1979**, 761.

[4] Friedrich, E. C.; Jassawalla, J. D. C. *J. Org. Chem.* **1979**, *44*, 4224. Describe the cyclopropane walk process for a number of bicyclo[4.1.0] systems.



methylsilyl group. It should be noted that whether the trimethylsilyl group is exo or endo[12] the stereoelectronic requirements of the conversion of **1a** into **1b** does *not* initially place the newly developing sp^2 orbital in the same plane as the C–Si bond; and, therefore, the carbenium ion **1b** should not experience the same degree of stabilization as a colinear arrangement of the sp^2 orbital and the C–Si bond. If the β carbenium ion **1b** had a colinear arrangement with the C–Si bond, it would be expected that the trimethylsilyl group would be lost to give a diene, **1c**. As we shall see, this is not the case, and **1b** is intercepted by nucleophiles to give **1d**, an allylsilane. Allylsilanes of the type **1d** can undergo electrophilic substitution with a concomitant double-bond shift to give **1e**.

Reduction of **2** (ca. 9:1 exo/endo)[1] with sodium borohydride in methanol gave the alcohol **2a** as a mixture of cis and transisomers (8:3); the cis-exo[12] epimer slowly crystallized from this mixture, mp 42–44 °C.[6] Treatment of pure **3**, or the cis/trans-exo/endo mixture with acetic acid containing perchloric acid (ca. 5%) at 20 °C for 1 h gave the allylsilane **4** as a mixture of epimers (3:2). Further exposure (2 h) of **4** to the above reagents gave cycloheptenyl acetate **5** in good yield.[5] It should be noted that the ratio of cis and trans epimers **4** does not vary with the composition of **3**. At first sight this seems to be a curious result since it would appear to imply that the carbenium ion **1b** is trapped by the acetic acid in a totally nonstereoselective manner. Furthermore **1b**, if formed, can rapidly undergo conformational inversion to bring the β-carbenium ion into the same plane as the C–Si bond and eliminate "Me_3Si_+" to give **1c**. No cyclohepta-1,3-diene was formed. This would indicate that **4** is formed by concerted attack of AcOH on **3**, which should give clean stereochemical results. In other words, *cis-exo-***3** should yield *trans-***4**. If **3** (exo/endo ratio of the Me_3Si group, 7:1) is exposed to $BF_3 \cdot OEt_2$ at 0 °C and the resulting product oxidized (PCC), *the ketone* **2** *is recovered (84%), but, as a mixture of exo/endo-trimethylsilyl epimers in the ratio of 1:1.* The formation of **4** as a 3:2 cis/trans mixture is a result of *epimerization at the trimethylsilyl group and not the acetoxy group.*[4]



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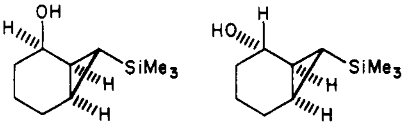

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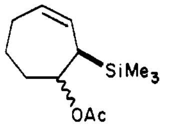
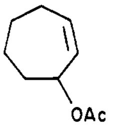


4



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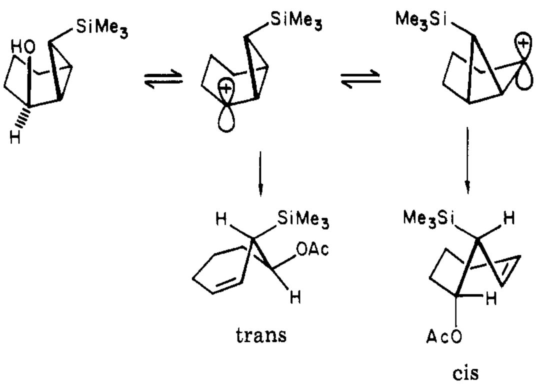
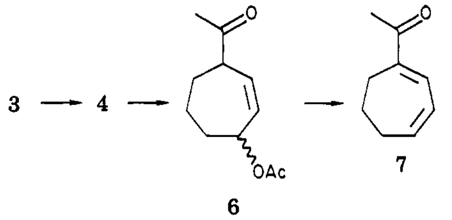
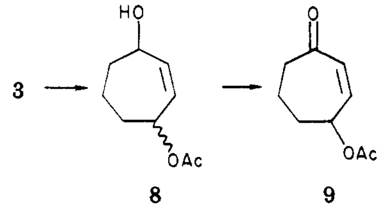


When **3** was treated with acetic anhydride/acetic acid containing perchloric acid (0 °C, 0.5 h), the initially formed allylsilane **4** was acetylated under these mild conditions to give **6** which readily eliminated acetic acid to give the dienone **7** (λ(max) 288, ν(max) 1660, 1595 cm^{-1}). The intermediate **6** is readily observable (ν(max) 1755 and 1735 cm^{-1}). The structure of **7**, and of course, ultimately, the diagnostic proof of this ring expansion, was demonstrated by hydrogenation (H_2/Pd/C) of **7** to give acetylcycloheptane.[7]



Treatment of **3**, in acetic acid with peracetic acid (40% v/v) at 20 °C for 7.5 h, gave a clean conversion into **8** (ν(max) 3400 and 1730 cm^{-1}) as a 3:2 mixture of epimers. Oxidation of **8** with pyridinium chlorochromate gave γ-acetoxycycloheptenone **9**, reinstating the carbonyl group in its original position.



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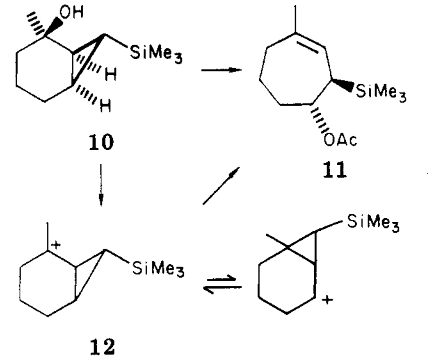
(5) Cope, A. C.; Liss, T. A.; Wood, G. W. *J. Am. Chem. Soc.* **1957**, *79*, 6287.

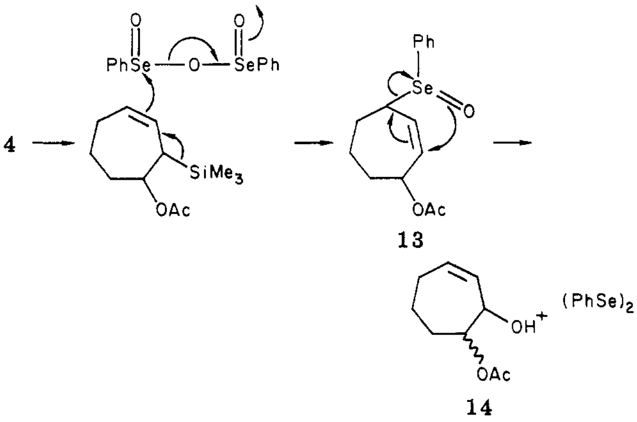
(6) **3**: *p*-nitrobenzoate, mp 122 °C. Anal. Calcd for $C_{17}H_{23}O_4NSi$: C, 61.23; H, 6.95; N, 4.20. Found: C, 61.43; H, 7.08; N, 4.44 (94% yield). **4**: ν(max) 1735, 1230, 1040, 830 cm^{-1}; NMR δ 5.6 (1 H, m), 5.0 (2 H, m), 1.97 and 1.91 (3 H, two singlets for epimers), 2.30–1.1 (7 H, m), 0.19 and 0.08 (9 H, two singlets) (74% yield). **7**: ν(max) 1660 cm^{-1}; λ(max) 288 nm; NMR δ 6.77 (1 H, d, J = 8 Hz), 6.30–5.7 (2 H, m), 2.5 (4 H, m), 2.29 (3 H, s), 1.87 (2 H, m) (80% yield). **8**: NMR δ 5.7 (2 H, m), 5.37 (1 H, m), 4.36 (1 H, m), 2.00 (3 H, s), 2.2–1.7 (6 H, b s), 6.9 (1 H, exchanged by D_2O) (60% yield). **9**: ν(max) 1730, 1670 cm^{-1}; NMR δ 6.31 (1 H, dd, J = 12 Hz and 3 Hz), 5.84 (1 H, dd, J = 12 Hz and 2 Hz), 5.45 (1 H, m), 2.50 (2 H, t, J = 6 Hz), 2.00 (3 H, s), 2.20–1.70 (4 H, m); ^{13}C NMR 202.20, 169.29, 144.13, 131.45, 72.03, 42.90, 31.74, 21.0, 18.15 ppm (80% yield). **11**: NMR δ 5.21 (1 H, d, J = 4.5 Hz), 4.93 (1 H, m), 1.45–2.15 (7 H, m), 1.92 (3 H, s), 0.00 (9 H, s) (70% yield). **14**: NMR δ 5.8–5.6 (2 H, m), 4.4 (1 H, m), 4.0 (1 H, b s), 1.95 (3 H, s), 2.4–1.5 (6 H, b m) (54% yield). **15**: NMR δ 3.28 (J = 3.5 Hz), **7a**, 3.10 (J = 3.5 Hz). (90% yield). **16**: NMR δ 1.2–2.7 (9 H, m), 0.67 (2 H, d, J = 5 Hz), 0.01 (9 H, s) (84% yield). All new compounds gave satisfactory MS and/or microanalytical data.

(7) Comparison with an authentic sample of acetylcycloheptane, prepared from cycloheptanone and $Me_3SiCMeLiCl$, followed by acid hydrolysis, confirmed its identity. Cooke, F.; Magnus, P.; *J. Chem. Soc., Chem. Commun.* **1977**, 513.

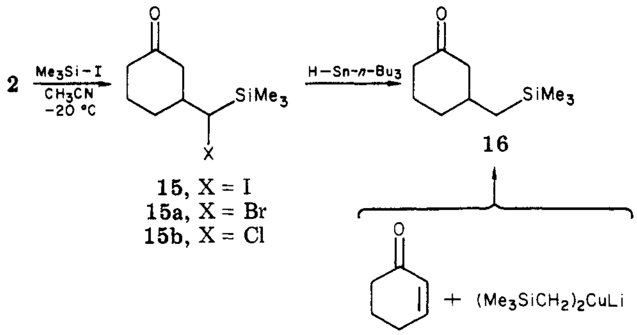
Treatment of 2 with methyllithium in ether at 0 °C gave the tertiary carbinol 10, which when exposed to BF$_3$·OEt$_2$/AcOH/CH$_2$Cl$_2$ at −40 °C for 15 min, was cleanly converted into the allylsilane 11. In this particular case there was no scrambling of stereochemistry, presumably because the tertiary 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$_3$·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$_3$SiCH$_2$)$_2$CuLi.[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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(8) Barton, D. H. R.; Ley, S. V.; Magnus, P.; Rosenfeld, M. N. *J. Chem. Soc., Perkin Trans. 1* 1977, 567.

(9) Olah, G. A.; Narang, S. C.; Gupta, B. G. B.; Malhotra, R. *Synthesis*, 1979, 61.

(10) Miller, R. D.; McKean, D. R. *Tetrahedron Lett.* 1979, 2305.

(11) Lappert, M. F.; Pearce, R. J. *J. Chem. Soc., Chem. Commun.* 1973, 24. Casey, C. P.; Jones, C. R.; Tukada, H. *J. Org. Chem.* 1981, *46*, 2089 and references therein.

(12) The exo/endo terminology refers to the configuration of the trimethylsilyl group with respect to the larger ring. The cis/trans terminology refers to the configuration of the hydroxyl group with respect to the cyclopropane ring.

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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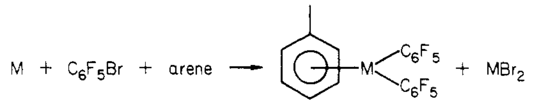
Received October 19, 1981

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$_3$SiSiCl$_3$ + 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$_6$D$_6$ 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.

(2) Gastinger, R. G.; Anderson, B. B.; Klabunde, K. J. *J. Am. Chem. Soc.* 1980, *102*, 4959.

(3) Structural studies have shown that these are η^6 complexes: Radonovich, L. J.; Klabunde, K. J.; Behrens, C. B.; McCollor, D. P.; Anderson, B. B. *Inorg. Chem.* 1980, *19*, 1221.