Synthesis, Structure, and C–H Bond Activation Chemistry of (η^6-arene)Ru(H)$_2$(SiMe$_3$)$_2$ Complexes

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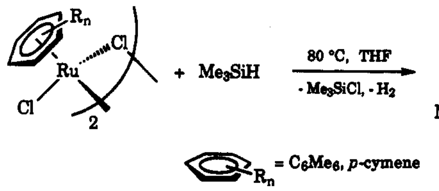
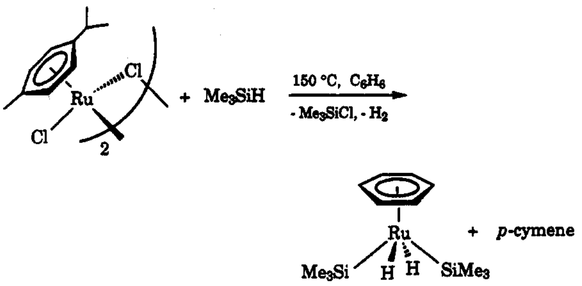
*Summary: The (η^6-arene)Ru(H)$_2$(SiMe$_3$)$_2$ (arene = C_6Me_6 (**1a**), p-cymene (**1b**), C_6H_6 (**1c**)) complexes have been prepared and characterized. The complexes activate both aromatic and aliphatic C–H bonds and catalyze H/D exchange in alkylsilanes upon thermolysis in benzene-d_6. A mechanism based on oxidative-addition/reductive-elimination steps which utilizes a Ru(II)–Ru(IV) cycle is proposed to account for the C–H bond activation and H/D exchange reactions. It is further proposed that H/D exchange into sites adjacent to silicon in alkylsilanes is due to the intermediacy of an η^2-silene complex generated by β-hydrogen elimination from the silyl group.*

Four-legged "piano-stool" transition-metal hydride complexes containing the cyclopentadienyl ligand, $CpML_xH_{4-x}$, have played an important role in the elucidation of a number of catalytic processes including C–H bond activation chemistry.[1] However, there are few examples of (η^6-arene)ML_xH_{4-x} complexes with a similar geometry.[2] Furthermore, although several (η^6-arene)Ru^{II} silyl complexes have been prepared,[3] there are no examples of hydride derivatives. The high reactivity toward arene hydrogenation and C–H bond activation exhibited by the (η^6-arene)Ru^{II} hydrides synthesized by Bennett[4] and Werner[5] prompted us to explore the reactivity of similar (η^6-arene)Ru silyl derivatives. We now report the synthesis and characterization of the first (η^6-arene)Ru(H)$_2$(SiMe$_3$)$_2$ complexes (arene = C_6Me_6 (**1a**), *p*-cymene (**1b**), C_6H_6 (**1c**)). These complexes are isoelectronic analogs of the (η^5-C_5R_5)M(H)$_2$(SiR'$_3$)$_2$ (M = Rh, Ir; R = H, Me; R' = Me, Et) complexes reported by Maitlis[6] and Perutz.[7] We find that **1a–c** activate aromatic and aliphatic C–H bonds upon thermolysis and deuterated solvents and, in addition, catalyze H/D exchange between alkylsilanes and benzene-d_6.

The substituted-arene complexes **1a,b** were prepared by a reaction between excess Me$_3$SiH and the corresponding [(η^6-arene)RuCl$_2$]$_2$ species[8] in THF at 80 °C for 12 h (eq 1).[9] The evolved Me$_3$SiCl was confirmed by ^{1}H NMR and GC, and H$_2$ (0.9 equiv per Ru) was measured by Toepler pump. The benzene derivative **1c** can be prepared directly from the reaction of the (*p*-cymene)ruthenium chloride with Me$_3$SiH at 150 °C for 2 days using benzene as both the solvent and arene source (eq 2). The complexes were isolated as colorless, moderately air-stable solids and were fully characterized.[9]



(1)



(2)

An X-ray structure analysis was carried out for **1a**; the ORTEP and selected geometrical parameters are shown in Figure 1.[10] The hydrides in the molecule were located and refined to chemically reasonable positions. The complex adopts a four-legged piano-stool geometry with a transoid disposition of silyls and hydrides. The metal–silicon and metal–hydrogen bond lengths and angles are similar to the values reported for the (η^5-C$_5$Me$_5$)M(H)$_2$(SiEt$_3$)$_2$ (M = Rh, Ir) complexes.[6b,d] The closest Si···H

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(9) Full details of the synthesis and characterization of **1a–c** by multinuclear NMR, IR, UV, and elemental analysis are provided in the supplementary material.

(10) Crystals of **1a** suitable for X-ray analysis were obtained by slow evaporation of a hexane solution. Crystal data: monoclinic, $P2_1/c$, a = 9.240(1) Å, b = 17.765(2) Å, c = 13.782(3) Å, β = 109.54(2)°, V = 2132(1) Å^3, Z = 4, and d_{calc} = 1.283 g/cm^3. Non-hydrogen atoms were refined anisotropically, Ru hydride hydrogen atoms were refined isotropically, and all other hydrogen atoms were not refined. Final residuals were R = 0.027 and R_w = 0.038 for 3737 unique reflections with $F^2 > 3\sigma(F^2)$.

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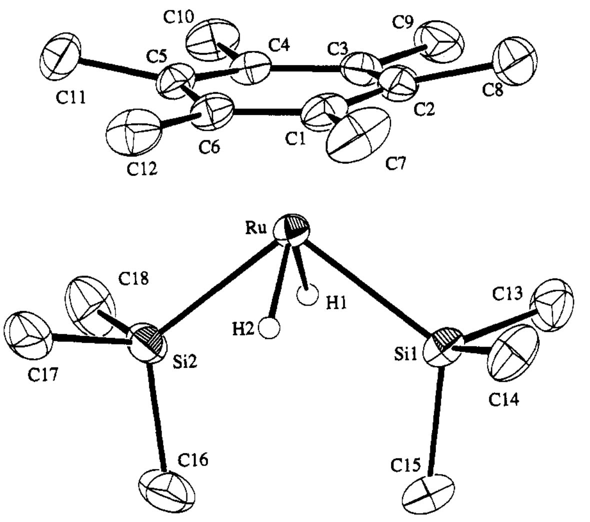
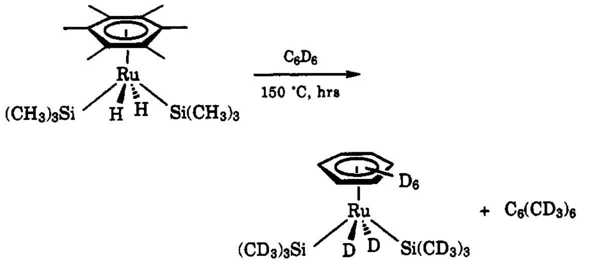


Figure 1. ORTEP drawing of **1a** with thermal ellipsoids drawn at the 30% probability level. Methyl hydrogens are omitted for clarity. Selected bond distances (Å) and angles (deg): Ru-Si1, 2.396(1); Ru-Si2, 2.391(1); Ru-C1, 2.290(2); Ru-C2, 2.288(3); Ru-C3, 2.358(3); Ru-C4, 2.282(3); Ru-C5, 2.282(3); Ru-C6, 2.372(2); Ru-H1, 1.457(30); Ru-H2, 1.407(29); Si1-Ru-Si2, 104.5(1); H1-Ru-H2, 92.8(17).

contact distance is 2.15 Å, clearly too long to suggest nonclassical (η^2) Si–H bonding, as is observed in several (η^6-arene)chromium silyl complexes.[11] Similarly, the intramolecular H···H separation of 2.18 Å indicates there is little interaction between the two hydrides and is thus consistent with the formulation of **1a** as a classical Ru(IV) complex.

Although quite stable compounds, **1a–c** are precursors for highly reactive species capable of activating both aromatic and aliphatic C–H bonds. For example, thermolysis of **1a** in benzene-d_6 at 150 °C leads to H/D exchange between the complex and the solvent. H/D exchange occurs in *all* positions of the molecule, as determined by ^1H and ^2H NMR. Concurrent arene exchange leads to the eventual formation of **1c**-d_{26} and C_6Me_6-d_{18} (eq 3).



(3)

The aliphatic C–H bonds of cyclohexane are also susceptible to attack by **1a–c** under thermal conditions. The thermolysis of **1a–c** in cyclohexane-d_{12} at 150 °C results in >90% D incorporation after 48 h with little or no decomposition. Analysis of the H/D exchange in this instance is not complicated by exchange of the coordinated arene for solvent. Deuteration of the aryl methyl and silyl methyl positions of **1a,b** occurs at comparable rates on the basis of integrated ^1H intensities. However, deuteration of the isopropyl methine and aryl hydrogen positions in **1b** is markedly slower than that of the silyl methyl, aryl methyl, and isopropyl methyl positions. Similarly, deuteration of the aryl hydrogen positions of **1c** is slower than that of the silyl methyl positions. Prolonged thermolysis (weeks) of **1a–c** in either benzene-d_6 or cyclohexane-d_{12} in the absence of added Me_3SiH leads to eventual decomposition of the complexes with formation of deuterated trimethylsilane, arene, and methane as the most prominent products.

The complexes also catalyze the exchange of the C–H and Si–H bonds of silanes with benzene-d_6. The reaction of Me_3SiH with benzene-d_6 solvent in the presence of 5 mol % **1a** at 150 °C results in >90% D incorporation in the silane after 2 weeks (eq 4). Deuteration of the catalyst

$$(CH_3)_3SiH + C_6D_6 \xrightarrow[150\ ^\circ C]{\mathbf{1a}} (CD_3)_3SiD + C_6D_5H \qquad (4)$$

is also observed. The integrated $Si-CH_3$:Si–H ratio remains at ca. 9:1 during the course of the reaction. Arene exchange, which accompanies the reaction, leads to the gradual formation of free C_6Me_6 and **1c**-d_{26}, which is also catalytically active.

Metal silene (silaolefin) complexes have been proposed as reactive intermediates in transition-metal silicon chemistry,[12] and several stable complexes have recently been isolated and structurally characterized.[13] We have previously reported evidence for such an intermediate in the metal-catalyzed H/D exchange between alkylsilanes and benzene-d_6.[14] For example, exchange of benzene-d_6 and $EtMe_2SiH$ catalyzed by $(PMe_3)_4Os(H)(SiMe_2Et)$ is regiospecific for deuteration of C–H bonds adjacent to silicon and leads only to $(CH_3CD_2)(CD_3)_2SiD$. This selectivity has been attributed to exchange via a transient silene complex, $(PMe_3)_3Os(H)(D)(\eta^2\text{-}Me_2Si{=}CHMe)$, formed by β-hydrogen elimination of the coordinated $SiMe_2Et$. Support for the formation of similar coordinated silene intermediates during thermolysis of **1a** is provided by H/D exchange with ethylsilanes. The triethylsilyl complex $(C_6H_6)Ru(H)_2(SiEt_3)_2$ (**2c**)[15] also catalyzes H/D exchange between benzene-d_6 and Et_3SiH, although not as selectively as previously observed with the osmium system. Initially, deuterium is incorporated into the methylene positions of Et_3SiH (eq 5). However, deuterium exchange also occurs in the methyl positions of Et_3SiH, albeit ca. one-fourth as fast as for the methylene positions of the ethyl groups.

$$(CH_3CH_2)_3SiH \xrightarrow[150\ ^\circ C,\ 3\ d]{\mathbf{2c},\ C_6D_6} (CH_3CD_2)_3SiD$$

$$\xrightarrow[150\ ^\circ C,\ 12\ d]{\mathbf{2c},\ C_6D_6} (CD_3CD_2)_3SiD \qquad (5)$$

This regioselective pattern is reversed, however, during H/D exchange in Et_4Si, catalyzed by $(C_6H_6)Ru(H)_2(SiMe_3)_2$ (**1c**) (eq 6). Less than 4% D is incorporated into the methylene positions of Et_4Si. In this case, the

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[15] Prepared analogously to **1c**. See supplementary material.

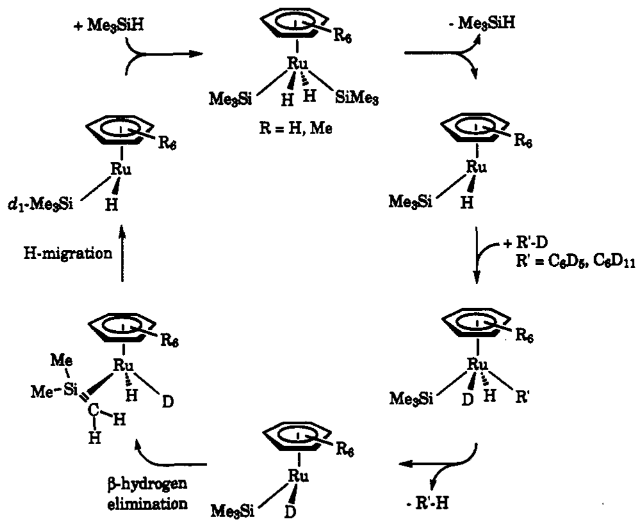
$$(CH_3CH_2)_4Si + (CH_3)_3SiH \xrightarrow[150\ ^\circ C,\ 12\ d]{1c,\ C_6D_6} (CD_3CH_2)_4Si + (CD_3)_3SiD \qquad (6)$$

predominant exchange into the methyl positions of Et_4Si is most likely due to the inability of the silicon to coordinate to the metal; this inhibits the C–H activation of the sterically protected methylene positions and prevents formation of coordinated silene intermediates similar to η^2-$Et_2Si{=}CHMe$, which can be produced during H/D exchange in Et_3SiH by a β-hydrogen-elimination process.

Although conclusively excluding the possibility that metallic ruthenium is responsible for the catalysis would be a very involved procedure, preliminary indications are that these reactions are homogeneous in nature. Essentially no decomposition of the catalyst is observed by NMR during the reactions with excess silanes in benzene, and the reaction mixtures remain colorless or pale yellow and free from visible precipitation even after prolonged thermolysis at 180 °C. Furthermore, the presence of catalytically active colloidal ruthenium is strongly controverted by experiments run in the presence of metallic mercury. Crabtree and co-workers have shown that mercury is an effective poison for colloidal metals and other heterogeneous catalysts.[16] Indeed, we observe that neither the rate nor the regioselectivity of the H/D exchange shown in eq 5 is affected by the presence of metallic mercury; parallel experiments run with and without added mercury proceed indistinguishably. Thus, despite the relatively high temperatures involved, there is no evidence that these reactions are due to heterogeneous impurities or decomposition products.

As **1a–c** are 18e$^-$ complexes, the observed reactions—arene exchange and C–H bond activation—are most likely preceded by the formation of an open coordination site at the metal center, although these processes may or may not utilize a common intermediate. Arene exchange via a ring-slip mechanism, as proposed for (η^6-arene)$M(CO)_3$ (M = Cr, Mo) complexes,[17] involves no change in the oxidation state of the metal but only sequential $\eta^6 \rightarrow \eta^4 \rightarrow \eta^2$ migration of outgoing arene with concurrent $\eta^2 \rightarrow \eta^4 \rightarrow \eta^6$ coordination of the incoming arene. However, H/D exchange with hydrocarbons in late transition metals typically involves an oxidative-addition reaction of the C–H bond with a low-valent, electron-rich metal center.[18] Although a ring-slip process to form (η^4-arene)$Ru(H)_2(SiMe_3)_2$ would open a potential coordination site in the molecule, subsequent oxidative addition would require the complex to adopt the rather high formal Ru(VI) oxidation state. Alternatively, an unsaturated species could also be formed by reductive elimination of Me_3SiH to create a 16e$^-$ Ru(II) intermediate, (η^6-arene)Ru(H)($SiMe_3$). The formation of an isoelectronic 16e$^-$ Rh(III) species by reductive elimination of Et_3SiH has been previously proposed as the first step in the thermolytic H/D exchange reaction of (η^5-C_5Me_5)$Rh(H)_2(SiEt_3)_2$ with benzene-d_6.[19] A possible mechanism for the H/D exchange reaction with Me_3SiH which incorporates this step and utilizes the resultant Ru(II)–Ru(IV) cycle is shown in Scheme 1. That the catalyzed C–H bond activation of alkylsilanes occurs primarily as an intramolecular process involving a metal silene intermediate is indicated by the preferential deuteration of the methylene positions in the catalyzed exchange of Et_3SiH and near-invariance of Si–CH_3:Si–H ratio during the course of the deuteration of Me_3SiH.[14] On the other hand, the regioselective deuteration of the methyl positions in the catalyzed deuteration of Et_4Si clearly suggests that intermolecular C–H activation is also viable; thus, it is difficult to determine whether H/D exchange into the methyl positions of the ethyl group in Et_3SiH occurs via intermolecular C–H activation without prior Si–H addition or via γ-C–H activation (metallacyclobutane formation) in an intermediate Ru—$SiEt_3$ species. Similarly, the observed exchange of free and coordinated arenes in this system makes it difficult to determine whether deuteration of the various arene positions occurs via intra- or intermolecular C–H activation.

Scheme 1



Thexe complexes provide new examples of using silyl ligands to stabilize formally high-oxidation-state metal centers. They also underscore the unusual activity of 16e$^-$ metal silyl complexes toward arene C–H bond activation[20] and metal silene formation.[14] Efforts to exploit this pattern of reactivity are continuing.

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Supplementary Material Available: Textual presentation of synthetic, spectroscopic, and analytical data for **1a–c** and **2c**, text and a table giving details of the X-ray data collection and refinement, and tables of positional parameters, anisotropic thermal parameters, and intramolecular bond distances and angles for **1a** (12 pages). Ordering information is given on any current masthead page.

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