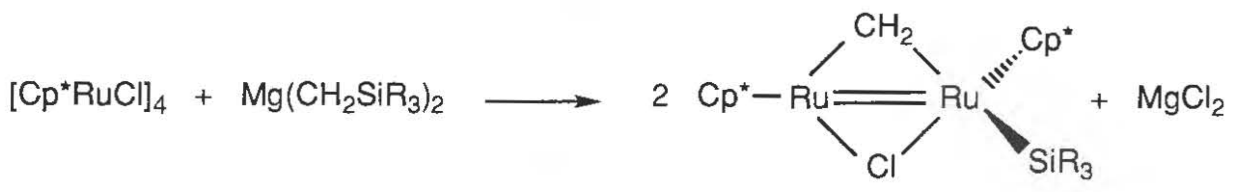
Transition Metal Organosilicon Compounds. Activation of Si-H and Si-C Bonds by Organometallic Complexes

Quinetta D. Shelby Final Seminar October 26, 1998

There is great interest in the activation of Si-H and Si-C bonds by transition metal catalysts because Si-H and Si-C bond cleavage processes are important in reactions involving the functionalization of hydrocarbons (e.g., hydrosilation processes)[1-3] and the catalytic transformation of organosilanes (e.g., silane polymerization and redistribution of substituents on silicon)[4-6]. One of the major goals in catalytic silicon chemistry is to isolate transition metal organosilicon compounds which are proposed as key intermediates in these reactions.[7-10]

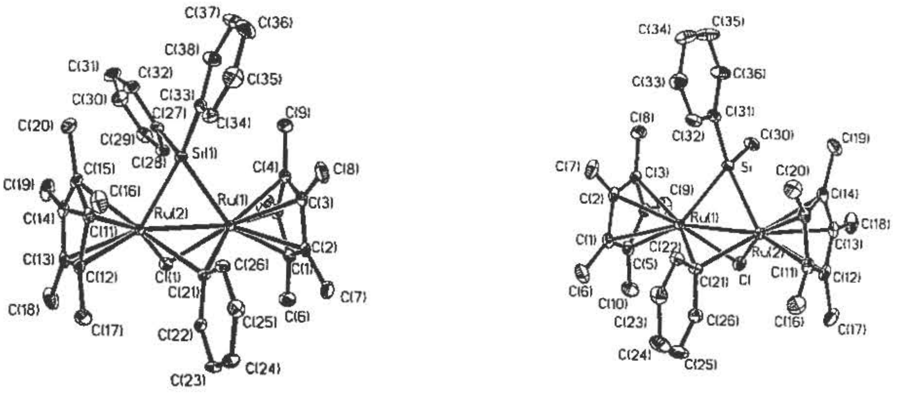
A previous study describes the synthesis of $Cp^*_2Ru_2(\mu\text{-}CH_2)(SiMe_3)(\mu\text{-}Cl)$ from the reaction of $[Cp^*RuCl]_4$ with $Mg(CH_2SiR_3)_2$.[11] This reaction can now be generalized: treatment of $[Cp^*RuCl]_4$ with $Mg(CH_2SiR_3)_2$ affords new methylene/silyl complexes $Cp^*_2Ru_2(\mu\text{-}CH_2)(SiR_3)(\mu\text{-}Cl)$, where $SiR_3 = SiEt_3$, $SiMe_2Et$, or $SiMe_2Ph$:



Variable-temperature ^1H NMR spectroscopy reveals that, similar to $Cp^*_2Ru_2(\mu CH_2)(SiMe_3)(\mu\text{-}Cl)$, each new compound undergoes two fluxional processes. $\Delta G^{\ddagger}$ is 9-10 kcal/mol for the low temperature process and 14-15 kcal/mol for the high temperature process. The activation parameters for the low temperature process, migration of the SiR_3 unit from one Ru center to the other, are sensitive to the nature of the silyl group: $\Delta H^{\ddagger}$ becomes smaller and $\Delta S^{\ddagger}$ becomes more negative if the SiR_3 group bears non-identical or larger, more flexible substituents. The activation parameters for the high temperature process, reversible reformation of the C-Si bond between the silyl group and the bridging methylene unit, are relatively independent of the nature of the silyl ligand. When heated to higher temperatures, these complexes decompose by reformation of the CH_2SiR_3 ligand and abstraction of a hydrogen atom to yield the tetraalkylsilanes $H\text{-}CH_2SiR_3$.

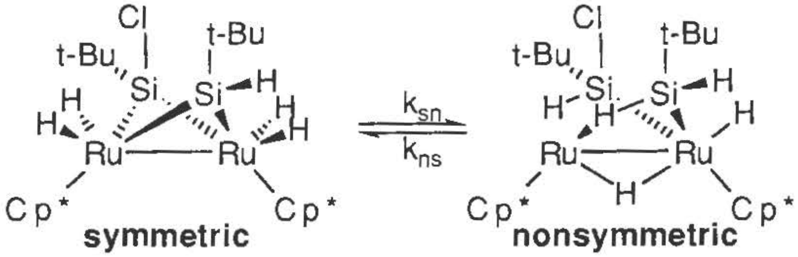
Reaction of $Cp^*_2Ru_2(\mu\text{-}CH_2)(SiMe_3)(\mu\text{-}Cl)$ with tertiary phenylsilanes affords $SiMe_4$ and silylene/phenyl complexes, $Cp^*_2Ru_2(\mu\text{-}SiRR')(\mu\text{-}Ph)(\mu\text{-}Cl)$, where $SiRR' = SiPh_2$ (Figure 1A), SiMePh (Figure 1B), or $SiMe_2$. Treatment of the methylene/silyl compound with Ph_3GeH yields the germylene/phenyl complex. The new ruthenium compounds are generated from oxidative addition of a Si-Ph (or Ge-Ph) bond to the diruthenium framework. ^1H and ^{13}C NMR spectroscopy shows that rotations of the phenyl rings in these compounds are restricted. The high barriers for rotation of the bridging phenyl ring and the Si-Ph (or Ge-Ph) rings are attributed in part to electronic interactions between the metal centers and the π-orbitals of the phenyl rings.

Reaction of $Cp^*_2Ru_2(\mu\text{-}CH_2)(SiMe_3)(\mu\text{-}Cl)$ with $H_3Si(t\text{-}Bu)$ generates $SiMe_4$, the mono-silicon complex $Cp^*_2Ru_2[\mu\text{-}Si(t\text{-}Bu)Cl]H_2$, and the bis-silicon complex $Cp^*_2Ru_2[\mu\text{-}Si(t\text{-}Bu)Cl][\mu\text{-}Si(t\text{-}Bu)H]H_4$; recent studies describe several bis-silicon-bridged diruthenium complexes that are structurally similar.[12] NMR and X-ray crystallographic studies of the bis-silicon compound reveal that this complex exists in solution as a mixture of two trans,cis isomers that differ in the arrangement of the hydride groups: in the nonsymmetric isomer, two agostic hydrides bridge the long Ru-Si bonds, one hydride bridges between the two Ru centers, and one hydride is terminal on the Ru center that forms the short Ru-Si bonds; in the other isomer, the Ru_2Si_2 core is symmetric and each Ru center probably bears two terminal hydride ligands. The two isomers interconvert rapidly and the interconversion process involves pairwise exchange of an agostic hydride ligand with a bridging hydride ligand and of the other agostic hydride ligand with a terminal hydride ligand.

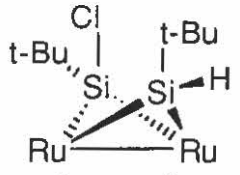


A **B**

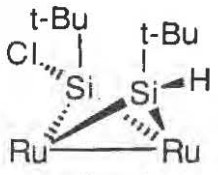
Figure 1



In polar solvents, the *t*-butyl and chloride substituents on the [Si(*t*-Bu)Cl] group quickly exchange places and afford a new cis,cis compound; the new cis,cis compound also exists in solution as a mixture of nonsymmetric and symmetric isomers. In the symmetric cis,cis isomer,



trans,cis



cis,cis

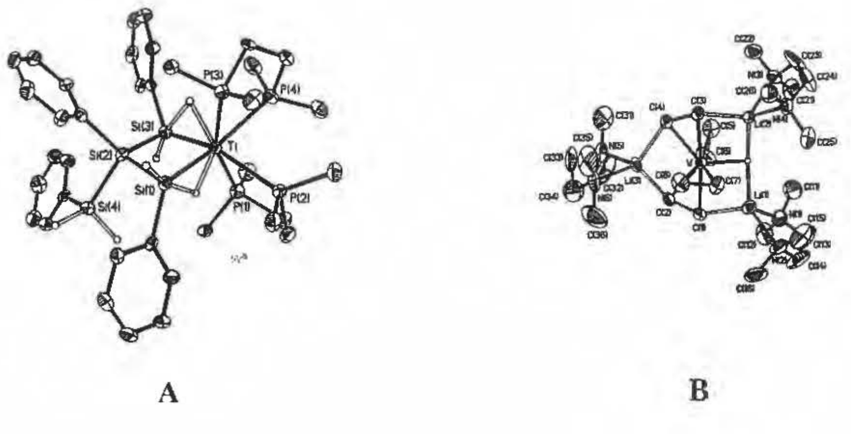
the H-H coupling constant between the two inequivalent terminal hydrogen atoms on each Ru center is large and temperature-dependent owing to quantum exchange coupling. At higher temperatures, the inequivalent hydrides exchange with one another, possibly by means of an η^2-H_2 transition state.

The reaction of $Cp^*{}_2Ru_2(\mu\text{-}CH_2)(SiMe_3)(\mu\text{-}Cl)$ with H_3SiPh gives the bis-silicon complex $Cp^*{}_2Ru_2(\mu\text{-}SiPhCl)(\mu\text{-}SiPhH)H_4$, which exists in solution almost exclusively as a nonsymmetric cis,cis isomer; the four metal-bound hydrogen atoms in this compound exchange with one another, not by a pairwise mechanism, but by a mechanism that permutes all four sites.

The reaction of $Cp^*{}_2Ru_2(\mu\text{-}CH_2)(SiMe_3)(\mu\text{-}Cl)$ with $H_3Ge(t\text{-}Bu)$ yields the bis-germanium complex $Cp^*{}_2Ru_2[\mu\text{-}Ge(t\text{-}Bu)Cl][\mu\text{-}Ge(t\text{-}Bu)H]H_4$, which adopts a cis,cis arrangement of the *t*-butyl substituents, and which also exists in solution as a mixture of nonsymmetric and symmetric isomers. These two isomers interconvert.

Dehydrogenative coupling of $PhSiH_3$ by $TiMe_2(dmpe)_2$ yields the Ti(0) polysilane complex, $Ti(Si_4H_6Ph_4)(dmpe)_2$. X-ray crystallography confirms that the tetrasilane is coordinated to the metal center by two agostic α-Si-H•••Ti interactions (Figure 2A).

Alkylation of $W(OMe)_3Cl_3$ with LiEt followed by addition of N,N,N′,N′-tetramethylethylenediamine (tmed) affords the tungsten ethene/hydride complex $[Li(tmed)]_3$-$[WH(C_2H_4)_4]$. X-ray crystallography shows that the geometry about the tungsten center is a distorted trigonal bipyramid and the hydride ligand occupies one of the equatorial sites (Figure 2B). The ethene groups in the molecule are fluxional.



A

B

Figure 2

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