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Experimental and Theoretical Studies of Highly Fluxional TpRu(PPh_3)“H_2SiR_3” Complexes (Tp = Hydridotris(pyrazolyl)borate)

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Reactions of $TpRuH(CH_3CN)(PPh_3)$ with free silanes $HSiR_3$ (R_3 = Et_3, $(EtO)_3$, Ph_3, HEt_2, HPh_2, and H_2Ph) in THF yield the complexes $TpRu(PPh_3)(H)(\eta^2\text{-}HSiR_3)$, the formulation of which is inferred from NMR spectroscopic data. The chemical equivalence of the two hydrogen atoms of $TpRu(PPh_3)(H)(\eta^2\text{-}HSiR_3)$ down to −100 °C is attributed to rapid fluxionality between the two, i.e., $TpRu(PPh_3)(H_a)(\eta^2\text{-}H_bSiR_3) \rightleftharpoons TpRu(PPh_3)(H_b)(\eta^2\text{-}H_aSiR_3)$. Molecular orbital calculations at the B3LYP level have been performed to investigate the stereochemistry and the interconversion processes of various structural isomers for $TpRu(PPh_3)(H)(\eta^2\text{-}HSiR_3)$. The results further support the existence of a η^2-silane formulation for these complexes. Two stable structures, with a nonclassical η^2-silane ligand, have been found. These two structural isomers are found to be in equilibrium with a low reaction barrier (7.5 kcal/mol). The interconversion between the enantiomeric pair of the most stable structure has almost no reaction barrier (0.5 kcal/mol). Together with the experimental findings, a mechanistic cycle is proposed. The complexes $TpRu(PPh_3)(H)(\eta^2\text{-}HSiR_3)$ react reversibly with pressurized H_2, CH_3CN, and PPh_3 to give $TpRuH(H_2)(PPh_3)$, $TpRuH(CH_3CN)(PPh_3)$, and $TpRuH(PPh_3)_2$, respectively.

Introduction

The recent work of Kubas on coordination of Si−H, H−H, and agostic C−H σ-bonds to the $[Mo(R_2PC_2H_4PR_2)_2(CO)]$ fragment is interesting, since it is the first system in which comparison between the coordination features of different σ-bonds to the same metal fragment can be made.[1] A complementary approach to this kind of comparison is the study of systems which can tautomerize between different forms of σ-complexes. A complex of the general formula L_nM“H_2SiR_3”, where “H_2SiR_3” stands for $(SiR_3)(\eta^2\text{-}H_2)$ or $(H)(\eta^2\text{-}HSiR_3)$, provides a good example of these systems.

Crabtree reported the synthesis of the complex $[IrH_2(\eta^2\text{-}HSiEt_3)_2(PPh_3)_2]SbF_6$ by addition of excess Et_3SiH to $[IrH_2(CH_3OH)_2(PPh_3)_2]SbF_6$ in CD_2Cl_2 at −80 °C. The complex was stable only at low temperature and extremely sensitive to nucleophiles. Attempted isolation under a variety of conditions led to decomposition to the known $[Ir_2(\mu\text{-}H)_3H_2(PPh_3)_4]SbF_6$.[2] It was also reported that reaction of $OsHCl(CO)(P^iPr_3)_2$ with Et_3SiH gave the silyl η^2-dihydrogen complex $OsCl(SiEt_3)(H_2)(CO)(P^iPr_3)_2$, which was considered as an intermediate in the hydrosilylation of phenylacetylene catalyzed by $OsHCl(CO)(P^iPr_3)_2$.[3] More recently, Chaudret reported the preparation of the highly reactive η^2-silane complex $RuH_2(\eta^2\text{-}HSiPh_3)(H_2)(PCy_3)_2$ by a substitution reaction of the bis(dihydrogen) complex $RuH_2(H_2)_2(PCy_3)_2$ with $HSiPh_3$. $RuH_2(\eta^2\text{-}HSiPh_3)(H_2)(PCy_3)_2$ reacts instantaneously with H_2 or N_2 to give $RuH_2(H_2)_2(PCy_3)_2$ or $RuH_2(N_2)_2(PCy_3)_2$, together with free Ph_3SiH.[4] Theoretically, ab initio MO calculations at the MP2 and MP4 levels on the $OsCl(CO)(PH_3)$“H_2SiH_3” model system predict the existence of two stable octahedral species: the η^2-dihydrogen complex $OsCl(SiH_3)(\eta^2\text{-}H_2)(CO)(PH_3)$ and the η^2-silane complex $OsClH(\eta^2\text{-}HSiH_3)(CO)(PH_3)$.[5]

All the above experimental and theoretical studies indicate a subtle balance of various factors influencing the detailed structures containing the M“H_2SiR_3” unit. We have recently reported the synthesis of $TpRuH(H_2)(PPh_3)$ (**1**) by heating a THF solution of $TpRuH(CH_3CN)(PPh_3)$ (**2**) under 40 atm of H_2. ^{1}H NMR study revealed rapid fluxionality between the hydride and η^2-H_2 ligands in **1** down to −110 °C.[6] In this paper, we report the reactions of **2** with free silanes $HSiR_3$ to form the complexes $TpRu(PPh_3)$“H_2SiR_3” (**3a**−**f**; Tp = hydri-

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Table 1. NMR and IR Spectroscopic Data for TpRu(PPh$_3$)"H$_2$SiR$_3$" (3a−f)

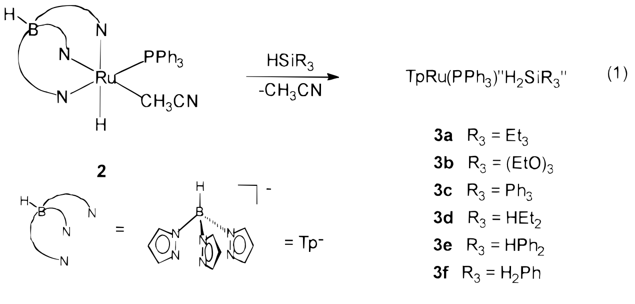
R$_3$	δ(^{1}H) (ppm)^a	J(SiH) (Hz)	δ(^{31}P{^{1}H}) (ppm)^a	δ(^{29}Si{^{1}H}) (ppm)^a	ν(Si−H) (KBr, cm^{-1})	ν(Ru−H) (KBr, cm^{-1})	ν(B−H) (KBr, cm^{-1})
Et$_3$ (**3a**)	−11.62 (d, 2H, ^2J(HP) = 22.8 Hz, Ru−*H*, T_1 = 593 ms); 0.79 (q, 6H, C*H*$_2$CH$_3$); 1.14 (t, 9H, CH$_2$C*H*$_3$); 5.88 (t, 2H), 6.12 (t, 1H), 7.37 (d, 2H), 7.64 (d, 1H), 7.73 (d, 2H), 8.00 (d, 1H) (9H of Tp);^{c} 7.11−7.84 (m, 15H of PPh$_3$)	23.3^b	67.9 (s)	24.7		2044 (w)	2461 (br)
(EtO)$_3$ (**3b**)	−11.41 (d, 2H, ^2J(HP) = 22.4 Hz, Ru−*H*, T_1 = 688 ms); 1.06 (t, 9H, OCH$_2$C*H*$_3$); 3.97 (q, 6H, OC*H*$_2$CH$_3$); 5.90 (t, 2H), 6.07 (t, 1H), 7.07 (d, 2H), 7.61 (d, 1H), 7.76 (d, 2H), 8.51 (d, 1H) (9H of Tp);^{c} 6.06−7.87 (m, 15H of PPh$_3$)	52.8^b	66.4 (s)	−0.72		2057 (w)	2472 (br)
Ph$_3$ (**3c**)	−10.11 (d, 2H, ^2J(HP) = 23.2 Hz, Ru−*H*, T_1 = 436 ms); 5.53 (t, 1H), 5.98 (t, 2H), 7.45 (d, 1H), 7.51 (d, 2H), 7.67 (d, 1H), 7.82 (d, 2H) (9H of Tp);^{c} 5.89−7.69 (m, 30H of Ph)	28.4^b	65.0 (s)	26.9		2040 (w)	2468 (br)
HEt$_2$ (**3d**)	−10.93 (dd, 2H, ^2J(HP) = 22.0 Hz, ^2J(HH) = 2.8 Hz, Ru−*H*, T_1 = 690 ms); 1.08 (m, 6H, CH$_2$C*H*$_3$); 1.21 (m, 4H, C*H*$_2$CH$_3$); 4.60 (m, 1H, Si−*H*); 5.92 (t, 2H), 6.14 (t, 1H), 7.08 (d, 2H), 7.68 (d, 1H), 7.78 (d, 2H), 7.87 (d, 1H) (9H of Tp);^{c} 7.22−7.56 (m, 15H of PPh$_3$)	23.5,^{b} 187.8^d	68.5 (s)	16.9	2194 (w)	2062 (w)	2469 (br)
HPh$_2$ (**3e**)	−9.71 (dd, 2H, ^2J(HP) = 20.8 Hz, ^2J(HH) = 3.0 Hz, Ru−*H*, T_1 = 545 ms); 5.72 (dt, 1H, ^2J(HH) = 3.0 Hz, J(HH) = 10.6 Hz Si−*H*); 5.80 (t, 1H), 5.97 (t, 2H), 7.13 (d, 2H), 7.35 (d, 1H, H), 7.60 (d, 1H), 7.84 (d, 2H) (9H of Tp);^{c} 6.18−7.77 (m, 25H of Ph)	23.5,^{b} 201.5^d	65.6 (s)	9.0	2136 (w)	2082 (w)	2470 (br)
H$_2$Ph (**3f**)	−10.32 (d, 2H, ^2J(HP) = 21.2 Hz, Ru−*H*, T_1 = 615 ms); 5.22 (d, 2H, J(HP) = 3.3 Hz, Si−*H*); 5.98 (t, 1H), 5.99 (t, 2H), 7.08 (d, 1H), 7.37 (d, 2H), 7.67 (d, 1H), 7.84 (d, 2H) (9H of Tp);^{c} 6.32−7.83 (m, 20H of Ph)	27.4,^{b} 195.6^d	67.2 (s)	−17.2	2163 (w)	2029 (w)	2471 (br)

[a] In THF-d_8. [b] Obtained from the ^{29}Si satellites of the upfield hydride signal in ^{1}H NMR; the observed J(SiH) value is an average of the J(SiH) value of the η^2-SiH group and that of the coupling between the silicon and the hydrogen atom not involved in the three-center bond. [c] All coupling constants for pyrazolyl proton resonances were about 2 Hz. [d] Obtained from the ^{29}Si satellites of the terminal Si−H signal.

dotris(pyrazolyl)borate) and show that both the spectroscopic data and theoretical calculations support the hydrido η^2-silane formulation TpRu(PPh$_3$)(H)(η^2-HSiR$_3$) for the complexes.

Results and Discussion

Synthesis of TpRu(PPh$_3$)"H$_2$SiR$_3$". Reactions of TpRuH(CH$_3$CN)(PPh$_3$) (**2**) with free silanes HSiR$_3$ in THF produce the air-sensitive complexes TpRu(PPh$_3$)"H$_2$SiR$_3$" (R$_3$ = Et$_3$ (**3a**), (EtO)$_3$ (**3b**), Ph$_3$ (**3c**), HEt$_2$ (**3d**), HPh$_2$ (**3e**), H$_2$Ph (**3f**)) (eq 1), for which NMR and IR data are collected in Table 1.



The complexes TpRu(PPh$_3$)"H$_2$SiR$_3$" (**3a−f**) could be the silyl η^2-dihydrogen complexes TpRu(PPh$_3$)(SiR$_3$)(η^2-H$_2$), the hydrido η^2-silane complexes TpRu(PPh$_3$)(H)(η^2-HSiR$_3$), or even the seven-coordinate silyl dihydrides TpRu(PPh$_3$)(SiR$_3$)(H)$_2$. Over the past few years, a large number of transition-metal silyl polyhydride complexes have been synthesized and characterized, for example, Re(CO)(PMe$_2$Ph)$_3$(SiPh$_3$)(H)$_2$,[7] Ir(PMe$_3$)$_3$(SiRR'$_2$)(H)(X) (R = H, D, Cl, Ph; R' = Ph, ^{t}Bu; X = H, D),[8] Ir(CO)$_2$(PCy$_3$)(SiR$_3$)(H)$_2$ (R$_3$ = Ph$_3$, Et$_3$, HPh$_2$, (OMe)Ph$_2$, (OEt)Ph$_2$, (O^{i}Pr)Ph$_2$, (OPh)Ph$_2$, (OMe)$_2$Ph, (OEt)$_2$Ph, (O^{i}Pr)$_2$Ph),[9] Os(CO)(P^{i}Pr$_3$)$_2$(SiPhR$_2$)(H)$_3$ (R$_2$ = HPh, Ph$_2$, (OMe)$_2$),[10] Fe(CO)(dppe)(SiR$_3$)(H)$_3$ (SiR$_3$ = Si(OMe)$_3$, Si(OEt)$_3$, SiMe$_3$, SiMe$_2$Ph, SiPh$_3$),[11] and Fe(PR'Ph$_2$)$_3$(SiR$_3$)(H)$_3$ (R' = Et, Bu; SiR$_3$ = Si(OMe)$_3$, Si(OEt)$_3$, SiH$_2$Ph, SiHPh$_2$, SiMePhCl).[11b] It is worth mentioning that the two series of Fe complexes are highly fluxional in solution; low-temperature NMR measurements strongly indicate that the exchange mechanism involves a η^2-silane but not a η^2-H$_2$ ligand. Although seven-coordinate ruthenium silyl polyhydride complexes such as Cp*Ru(PR$_3$)(SiR'$_3$)(H)$_2$[12] and Ru(CO)(P^{t}Bu$_2$Me)$_2$(SiHPh$_2$)(H)$_3$[13] are also known, we believe that a seven-coordinate silyl dihydride structure, which is purely

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classical and does not have any kind of "interligand" bonding interaction, is unlikely to be adopted by **3** since the TpRu fragment strongly prefers to bind three additional ligands to form octahedral complexes, and genuine seven-coordinate ruthenium compounds containing Tp are still unknown.[14] Furthermore, our experiences and those of others have shown that the hydridotris(pyrazolyl)borate and the substituted hydridotris(pyrazolyl)borate ligands have a high propensity to support an η^2-H_2 ligand.[15] In view of the analogy between η^2-dihydrogen and η^2-silane complexes, and the delicate balance between the $L_nM(SiR_3)(\eta^2\text{-}H_2)$ and $L_nM(H)(\eta^2\text{-}HSiR_3)$ structures, we believe that the complexes TpRu(PPh_3)"H_2SiR_3" (**3a**−**f**) are excellent model compounds for comparing the coordinating features of the two forms.

Characterization and Structure of TpRu(PPh_3)"H_2SiR_3". The ^1H NMR spectrum of each of the complexes TpRu(PPh_3)"H_2SiR_3" (**3a**−**f**) shows one hydride signal, which integrates to two hydrogens, in the upfield region. The signal shows coupling to the phosphorus of the triphenylphosphine ligand, with the coupling constant falling in the range of 20.8−23.2 Hz, which is typical for a cis-disposed phosphine ligand. For the secondary silane complexes **3d** and **3e**, the hydride signals show additional couplings to the terminal Si−H hydrogens. It is important to note that all the hydride signals of **3a**−**f** are flanked by ^{29}Si satellites. The observed J(SiH) values, which range from 23.3 to 52.8 Hz, indicate the presence of η^2-silane ligands[16] in these complexes (vide infra). Therefore, it seems appropriate to assign the hydrido η^2-silane structure TpRu(PPh_3)(H)(η^2-$HSiR_3$), rather than the silyl η^2-H_2 structure TpRu(PPh_3)(SiR_3)(η^2-H_2), to TpRu(PPh_3)"H_2SiR_3". The absence of η^2-H_2 coordination is further supported by the relaxation time measurements. The room-temperature T_1 values of the hydride signals of **3a**−**f** (436−690 ms) are well outside the range of T_1 values for nonclassical η^2-dihydrogen complexes.[17] The nondecoalescence of the hydride signals in **3a**−**f** even down to −100 °C can be explained in terms of a rapid fluxionality between H_a and H_b (eq 2). Since the complexes are

$$\text{TpRu}(PPh_3)(H_a)(\eta^2\text{-}H_bSiR_3) \rightleftharpoons \text{TpRu}(PPh_3)(H_b)(\eta^2\text{-}H_aSiR_3) \quad (2)$$

fluxional, the observed J(SiH) value for TpRu(PPh_3)"H_2SiR_3" is an average of the J(SiH) value for the η^2-SiH group and that of the coupling between the silicon and the hydrogen atom not involved in the three-center bond. The latter is expected to be smaller than the former; therefore, the J(SiH) value corresponding to η^2-SiH should be higher than the observed values listed in Table 1. By comparison to the J(SiH) values for known η^2-silane complexes,[16] the J(SiH) values of **3a**−**f** leave no doubt about the presence of the η^2-coordinated silane ligands attached to ruthenium.

The existence of a rapid equilibrium between the enantiomeric pair shown in eq 2 is also in accord with the observation of two sets of resonances (three peaks in each set) for the pyrazole protons of the Tp ligand in the range 5.80−8.00 ppm in the ^1H NMR spectrum. In one set, each peak integrates to 2H, while in the other set each peak corresponds to 1H. This six-peak pattern for the Tp protons is consistent with two of the pyrazole rings being trans to two identical ligands. Should all three pyrazole rings of the Tp ligand in TpRu(PPh_3)"H_2SiR_3" be trans to three different ligands, as in the nonfluxional structure TpRu(PPh_3)(H)(η^2-$HSiR_3$), a nine-peak pattern would have been observed for the Tp protons.

It is of interest to note that the η^2-bound Si−H hydrides H_a and H_b in **3d**−**f** do not interchange with the terminal Si−H on the NMR time scale, even at 50 °C. Brookhart also reported that no such interchange was evidenced in the diastereomeric complexes CpFe(CO)(PEt_3)(η^2-HSiHMePh) (the iron center is chiral), although diastereomeric interconversion was observed.[18] For the complexes *cis*-Mo(CO)($R_2PC_2H_4PR_2$)$_2$(η^2-SiH_4)[19a] and *cis*-Mo(CO)($R_2PC_2H_4PR_2$)$_2$(η^2-$HSiHR'_2$),[19b] Kubas et al. did not mention dynamic interchange of the hydrides in the η^2-silane ligands.

Finally, it is worth commenting on the denticity of the Tp ligand in **3a**−**f**. It is well-known that hydridotris(pyrazolyl)borate has a strong tendency to adopt a facial tridentate coordination mode, and reduced denticity is usually only observed in cases where it is disfavored by the electronic nature of the metal, e.g., d^8-ML_4 square-planar geometry.[20] Recent studies,[21] however, show that bidentate coordination of the hydridotris(pyrazolyl)borate ligand to d^6 Ru(II) and Os(II) centers is also possible. κ^2-Tp Ru(II) and Os(II) complexes were prepared by displacement of a phosphine and a halide ligand from the precursor complexes with hydridotris(pyrazolyl)borate at room temperature; thermolysis of these κ^2-Tp complexes via loss of another phosphine ligand gives the conventional tridentate Tp complexes.[21] The five-coordinate complexes MHCl(CO)(P^iPr_3)$_2$ (M = Os, Ru) have been reported to react with NaTp in methanol at room temperature to give M(κ^2-Tp)H(CO)(P^iPr_3)$_2$, which in toluene under reflux evolves into M(κ^3-Tp)H(CO)(P^iPr_3).[22] A common spectroscopic feature

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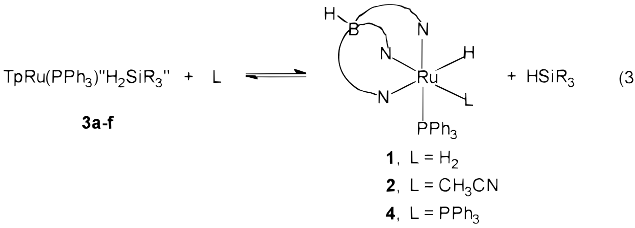
of the κ^2-Tp Ru(II) and Os(II) complexes is that their ν(B−H) bands shift to lower frequencies (~2440 cm^{-1}) compared to those of the κ^3-Tp complexes, which are usually above 2460 cm^{-1}. Perusal of Table 1 reveals that ν(B−H) values of **3a**−**f** are all above 2460 cm^{-1}. Furthermore, complexes **3a**−**f** were prepared by thermal displacement of CH$_3$CN from TpRuH(CH$_3$CN)(PPh$_3$) (**2**), which already contained a tridentate hydridotris(pyrazolyl)borate ligand; therefore, it is very unlikely that the denticity of hydridotris(pyrazolyl)borate would have decreased from 3 to 2 during the reactions. With these facts taken together, it is expected that the tridentate coordination of Tp in **3a**−**f** is maintained and the possibility of having **3a**−**f** to adopt the six-coordinate silyl dihydride structure (κ^2-Tp)Ru(PPh$_3$)(SiR$_3$)(H)$_2$ can be excluded.

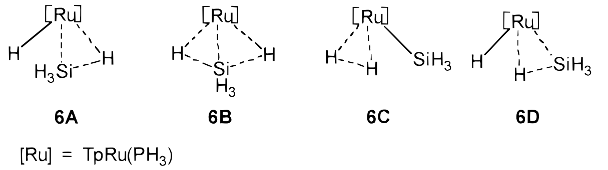
Reactivity of TpRu(PPh$_3$)"H$_2$SiR$_3$". The η^2-silane complexes **3a**−**f** react reversibly with pressurized H$_2$, acetonitrile, and triphenylphosphine to give TpRuH(H$_2$)(PPh$_3$) (**1**), TpRuH(CH$_3$CN)(PPh$_3$) (**2**), and TpRuH(PPh$_3$)$_2$ (**4**), respectively (eq 3). While the dihydrogen complex **1** can be used in place of **2** for the preparation of **3**, it was found that reactions of **4** with excess free silanes only led to partial formation of **3a**−**f**, probably due to stronger coordination of the phosphine ligand.



(3)

Reaction of TpRuCl(CH$_3$CN)(PPh$_3$) with Diphenylsilane. Reaction of TpRuCl(CH$_3$CN)(PPh$_3$) (**5**) with diphenylsilane did not give the chloro η^2-silane complex TpRuCl(PPh$_3$)(η^2-HSiHPh$_2$), and **3e** was formed instead. The formation of **3e** from **5** can be best explained in terms of a Ru−Cl/Si−H exchange to give TpRuH(CH$_3$CN)(PPh$_3$) (**2**), which then reacts with diphenylsilane to form **3e**. M-Cl/Si−H exchange is very often observed when chloro complexes are reacted with H-silanes.[23]

Ab Initio Study on the TpRu(PPh$_3$)"H$_2$SiR$_3$" Complexes. Although the NMR experimental data provide evidence for the formulation of **3a**−**f** as hydrido η^2-silane complexes, the particular stereochemistry around the metal center is still not clear. To provide an insight into the actual structure and bonding situation of **3**, ab initio calculations at the B3LYP level have been performed on the four possible isomeric structures **6A**−**D** (see Computational Details in the Experimental Section for the models used). These structures represent unsymmetric HSiH, symmetric HSiH, and unsymmetric HHSi arrangements, respectively.



6A 6B 6C 6D

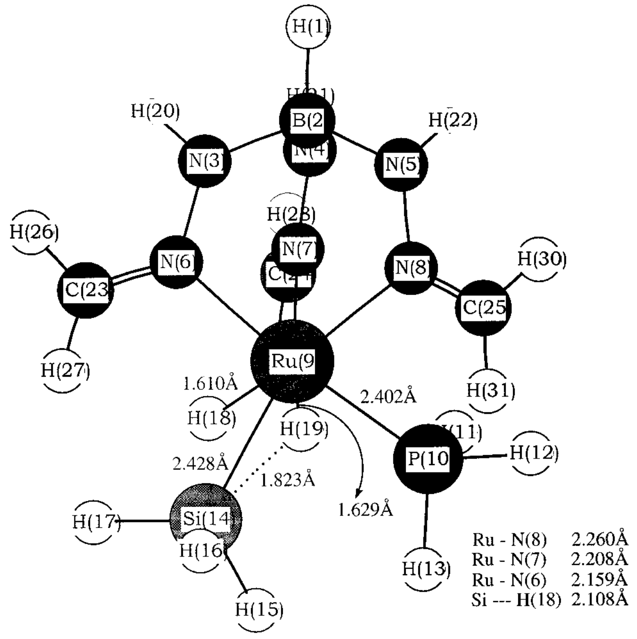


Figure 1. Optimized structure for **6A** showing the nonclassical η^2-silane coordination.

Our previous theoretical study[24] at both B3LYP and MP2 levels has demonstrated that the complex Cp$_2$Ta(SiR$_3$)H(SiR$_3$) adopts a symmetric SiHSi structure. It has been reported that the tantalum dihydride silyl complexes Cp$_2$Ta(H)$_2$(SiR$_3$) exist in two isomeric forms. The major isomer has a symmetrical structure, with the silyl group occupying the central position between two equivalent hydride positions. In the minor isomer, the silyl group occupies a lateral position, giving rise to two inequivalent hydrides.[25] In the present case, however, it turns out that the unsymmetric "*trans*-dihydride" isomer **6A** is the most stable one. Even starting the geometry optimization with a symmetric initial geometry brings the optimized structure back to **6A**. The symmetric structure **6B** can only be obtained with a symmetry constraint, although its energy is only 0.5 kcal/mol higher than that of **6A**. The optimized structure for **6A** is shown in Figure 1. The noticeably short H(19)···Si distance of 1.823 Å indicates the presence of "nonclassical" η^2-silane coordination,[16,26] whereas the long H(18)···Si distance of 2.108 Å shows the absence of significant Si−H interaction. This is further supported by the weakening of the Ru−H(19) bond relative to Ru−H(18) (1.629 vs 1.610 Å). The possibility of a "nonclassical" η^2-H$_2$ coordination can be ruled out on the basis of our calculation of **6C**. Starting from a nonclassical structure of **6C**, the geometry optimization gives **6D** with a H···H distance of 1.707 Å and a Si···H distance of 1.765 Å. The resulting structure **6D** with a nonclassical η^2-silane coordination lies 1.9 kcal/mol

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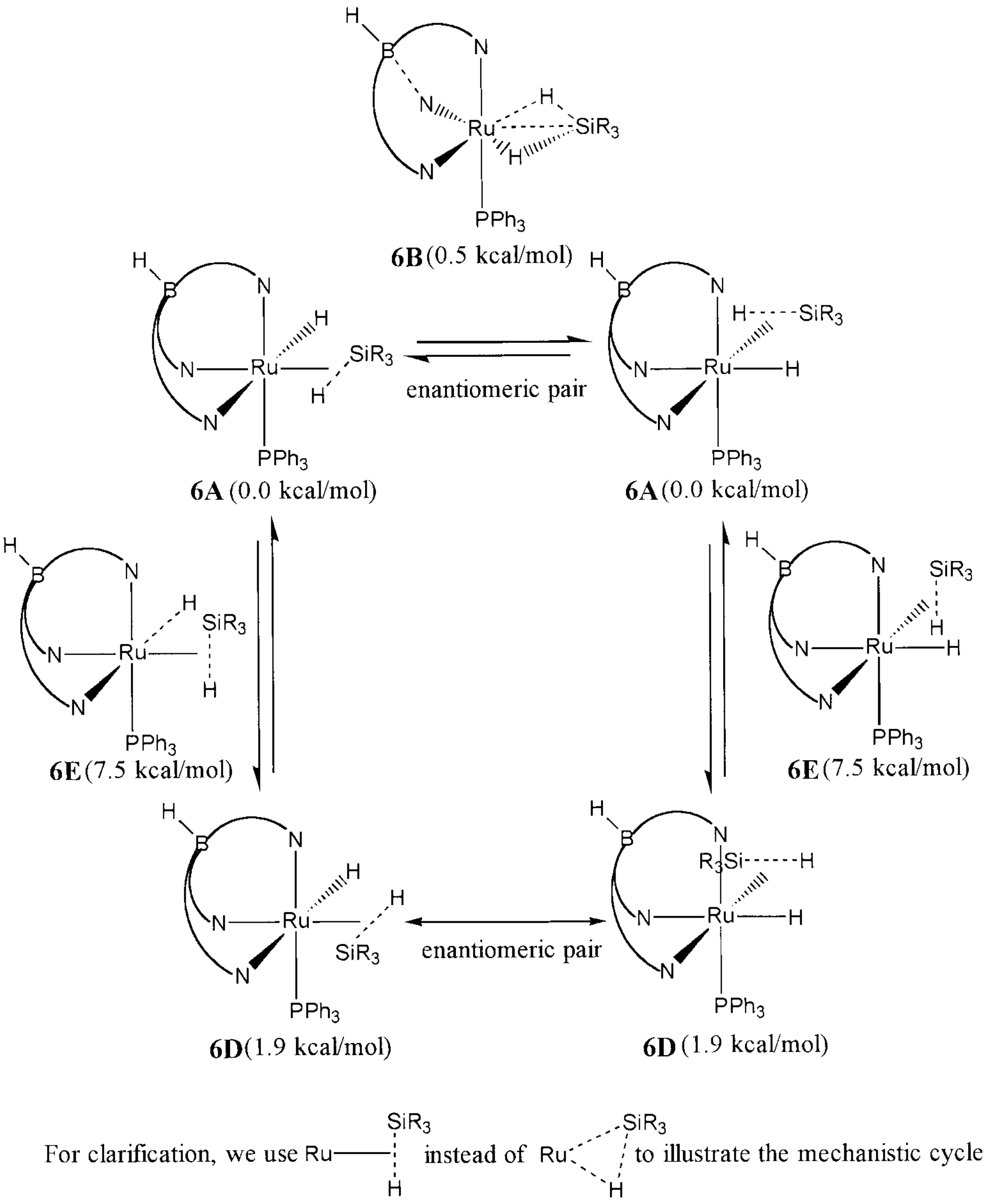

Figure 2. Proposed mechanistic cycle elucidating the interconversion processes among various species.

higher than **6A**. The η^2-(H−Si) coordination in both **6A** and **6D** may point to the role of the Tp ligand in favoring the formation of "nonclassical" H−Si interaction; the analogous ruthenium cyclopentadienyl complexes Cp*Ru-(P^{i}Pr$_3$)H$_2$(SiR$_3$)[12b] have been found to have a symmetric H···Si···H displacement with no significant H−Si interaction.

On the basis of the energetics of the isomeric structures **6A** and **6B**, the proposed mechanism of the equilibrium in eq 2 is justified and can be described as a simple "unsymmetric stretch" of the H···Si···H moiety, passing through the assumed transition state **6B**. The very small reaction barrier (0.5 kcal/mol) is consistent with the rapid fluxionality observed in the variable-temperature NMR experiment. The "unsymmetric stretch" mechanism is similar to the one reported for the exchange of a hydrogen atom between η^2-H$_2$ and H ligands in [Fe(PR$_3$)$_4$(H)(η^2-H$_2$)]$^+$, whose exchange barrier was also found to be quite low (~3.0 kcal/mol).[27]

NMR data suggest that **3a**−**f** are nonclassical η^2-silane complexes and exclude the existence of nonclassical η^2-dihydrogen coordination. Both **6A** and **6D** are consistent with the NMR data. The structure of **6A** can be related to that of **6D** by an approximate 180° rotation of the η^2-silane ligand. The interconversion between **6A** and **6D** passes through a sterically crowded structure, corresponding to an approximate 90° rotation of the η^2-silane ligand, in which N(6), Si, and H(19) are coplanar (see Figure 1 for the numbering scheme). This assumed transition state (**6E**) is calculated to be 7.5 kcal/mol higher in energy than **6A**.

On the basis of all the results of calculations, the schematic mechanistic cycle shown in Figure 2 is proposed to elucidate the interconversion processes of different structural isomers for complexes **3a**−**f**. Equilibrium exists between the enantiomeric pair of **6A** passing through **6B** with a very small energy barrier of 0.5 kcal/mol. The interconversion between **6A** and **6D** requires a higher energy (7.5 kcal/mol). The small barriers calculated for the interconversion processes

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discussed here are consistent with the variable-temperature NMR experiments, showing that **6A** and **6D** are indistinguishable even down to −100 °C. To further comment on the relationship between reaction barrier and variable-temperature NMR, the known process of chair to twist-boat conformation change in cyclohexane has a reaction barrier of ca. 11 kcal/mol, and the two forms are only clearly distinguishable below −100 °C.[28] It should be noted that while the enantiomeric pair of **6D** exist simultaneously, they are not expected to be in direct equilibrium. Rather, the interconversion between the pair passes through **6A**.

The results of calculations suggest that the η^2-SiH coordination is favored over the η^2-H$_2$ coordination for TpRu(PPh$_3$)"H$_2$SiR$_3$". Previous theoretical calculations on the OsCl(CO)(PH$_3$)"H$_2$SiH$_3$" system predict that OsCl(CO)(PH$_3$)(SiH$_3$)(η^2-H$_2$) and OsCl(CO)(PH$_3$)(H)(η^2-H−SiH$_3$) are very close in energy. On the basis of the analysis from thermodynamical values (bond energies), it has been suggested that the relative stability of the two isomeric forms depends essentially on the differences in strength of three bonds, viz. (i) the η^2-binding of X−H (X = SiH$_3$, H) ligand to the metal fragment, (ii) the X−H bond in the isolated fragment, and (iii) the Os−X bond.[5] While a similar analysis based on thermodynamical values may be relevant to TpRu(PPh$_3$)"H$_2$SiR$_3$", we believe that the coordination preference may also be related to the readiness of the Si center to be hypervalent, in which the η^2-SiH coordination is achieved.[29] For the Os system, the stable η^2-H$_2$ structure has the η^2-H$_2$ and silyl ligands trans to each other.[5] For the Ru system studied here, the "η^2-H$_2$" structure would have a cis disposition of the η^2-H$_2$ and silyl ligands due to the presence of the Tp ligand. Clearly, the coordination environment can have a significant impact on the preference of coordination mode.

Reaction energy calculations for the process

$$\mathrm{TpRu(PH_3)(H)}(\eta^2\text{-SiH}_4) + \mathrm{H_2} \rightarrow \mathrm{TpRu(PH_3)(H)}(\eta^2\text{-H}_2) + \mathrm{SiH_4} \quad (4)$$

shows that it is only slightly endothermic by 0.5 kcal/mol. This result is consistent with the experimental observation that complexes **3** react reversibly with H$_2$.

The particularly strong Si−H coupling constant observed for **3b** can be attributed to the more electronegative substituents (R = OEt) in this complex. Indeed, calculation of TpRu(PH$_3$)(H){η^2-H−Si(OH)$_3$} gives a much shorter Si⋯H distance (1.787 Å). The distance between Si and the other coordinated H is significantly shortened (1.985 Å) as well. A previous theoretical study[24] has also shown that Si−H interaction increases with the electronegativity of the substituents on Si.

Conclusion

Reactions of TpRuH(CH$_3$CN)(PPh$_3$) (**2**) with free silanes yielded the complexes TpRu(PPh$_3$)"H$_2$SiR$_3$" (**3a**−**f**). The NMR spectroscopic data support the hydrido η^2-silane formulation TpRu(PPh$_3$)(H)(η^2-HSiR$_3$) for **3a**−**f**. The common feature of these complexes is that the hydride ligand and hydrogen atom of the η^2-(Si−H) bond are chemically equivalent, due to the existence of a rapidly equilibrating pair, i.e., TpRu(PPh$_3$)(H$_a$)(η^2-H$_b$-SiR$_3$) ⇌ TpRu(PPh$_3$)(H$_b$)(η^2-H$_a$SiR$_3$). This fast equilibrium is reminiscent of the rapid fluxionality between the hydride and dihydrogen ligands in TpRu(PPh$_3$)H-(H$_2$). Theoretical calculations further support the existence of a nonclassical η^2-silane formulation for complexes **3a**−**f**. Two stable structures (**6A** and **6D**) representing complexes **3a**−**f** have been found to contain the η^2-silane ligand. These two structural isomers are found to be in equilibrium with a low reaction barrier (7.5 kcal/mol). The interconversion between the enantiomeric pair of **6A** has a very small reaction barrier (0.5 kcal/mol). Together with the experimental findings, a mechanistic cycle is proposed in Figure 2 on the basis of our energetic calculations.

Experimental Section

All reactions were carried out in grease-free glass apparatus under a dry N$_2$ atmosphere using standard Schlenk techniques. All solvents were distilled and degassed prior to use. Dichloromethane and acetonitrile were distilled from calcium hydride; tetrahydrofuran, diethyl ether, and hexane were distilled from sodium benzophenone ketyl. Deuterated tetrahydrofuran was dried on calcium hydride and vacuum-transferred to a flask fitted with a rubber septum for storage. The complexes TpRuH(CH$_3$CN)(PPh$_3$),[6] TpRuH(PPh$_3$)$_2$,[6] TpRuH(H$_2$)(PPh$_3$),[6] and TpRuCl(CH$_3$CN)(PPh$_3$)[6] were synthesized according to literature methods. Triethylsilane, triethoxysilane, triphenylsilane, diethylsilane, diphenylsilane, and phenylsilane were purchased from Fluka and were used as received.

Infrared spectra were obtained from a Nicolet Magna 750 FT IR spectrophotometer. ^{1}H NMR spectra were taken from a Bruker DPX 400 spectrometer; chemical shifts were referenced to the proton residues of the deuterated solvent (C$_4$D$_7$*H* δ 1.85, 3.70 ppm). ^{31}P{^{1}H} NMR spectra were taken on a Bruker DPX-400 spectrometer at 161.98 MHz. ^{31}P chemical shifts were externally referenced to 85% H$_3$PO$_4$ in D$_2$O (δ 0.00 ppm). ^{29}Si-{^{1}H} NMR spectra were taken on a Bruker DPX-400 spectrometer at 79.50 MHz. ^{29}Si chemical shifts were externally referenced to TMS in CDCl$_3$ (δ 0.00 ppm). Relaxation time T_1 measurements were carried out in THF-d_8 at 400 MHz by the inversion−recovery method using a standard 180°−τ−90° pulse sequence. High-pressure NMR studies were performed using a Wilmad pressure-valved NMR tube; the maximum pressure used was 15 atm (room temperature). FAB MS was carried out with a Finnigan MAT 95S mass spectrometer using 3-nitrobenzyl alcohol as matrix. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

NMR and IR spectroscopic data of TpRu(PPh$_3$)"H$_2$SiR$_3$" (**3a**−**f**) are collected in Table 1.

TpRu(PPh$_3$)(H)(η^2-HSiEt$_3$) (3a). A THF solution (10 mL) of TpRuH(CH$_3$CN)(PPh$_3$) (**2**; 0.2 g, 0.32 mmol) and HSiEt$_3$ (0.3 mL, 4 mmol) was stirred under nitrogen at 80 °C for 4 h. The solution was cooled, and the solvent was removed by vacuum. Hexane (10 mL) was added to dissolve the residue, and the solution was cooled to −30 °C to give an orange solid, which was filtered out. The solid was further washed with precooled hexane (5 mL) and then dried under vacuum. Yield: 0.09 g (41%). Anal. Calcd for C$_{33}$H$_{42}$BN$_6$SiPRu: C, 57.14; H, 6.10; N, 12.12. Found: C, 56.93; H, 6.15; N, 11.98. FAB MS (*m*/*z*): 576, [M − HSiEt$_3$]$^+$.

TpRu(PPh$_3$)(H)(η^2-HSi(EtO)$_3$) (3b). This complex was prepared by using the same procedure as for the preparation

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of **3a**, except that $HSi(EtO)_3$ was used. The yield of the orange solid obtained was 0.11 g (46%). Anal. Calcd for $C_{33}H_{42}BN_6O_3SiPRu$: C, 53.44; H, 5.71; N, 11.33. Found: C, 53.13; H, 5.80; N, 11.10. FAB MS (*m*/*z*): 576, $[M - HSi(EtO)_3]^+$.

$TpRu(PPh_3)(H)(\eta^2\text{-}HSiPh_3)$ (3c). This complex was prepared by using the same procedure as for the preparation of **3a**, except that $HSiPh_3$ was used. The yield of the orange solid obtained was 0.13 g (49%). Anal. Calcd for $C_{45}H_{42}BN_6SiPRu$: C, 64.51; H, 5.05; N, 10.03. Found: C, 64.80; H, 5.13; N, 9.89. FAB MS (*m*/*z*): 576, $[M - Ph_3SiH]^+$.

$TpRu(PPh_3)(H)(\eta^2\text{-}HSiHEt_2)$ (3d). This complex was prepared by using the same procedure as for the preparation of **3a**, except that H_2SiEt_2 was used. The yield of the orange solid obtained was 0.13 g (61%). Anal. Calcd for $C_{31}H_{38}BN_6SiPRu$: C, 55.94; H, 5.75; N, 12.63. Found: C, 56.10; H, 5.88; N, 12.40. FAB MS (*m*/*z*): 576, $[M - H_2SiEt_2]^+$.

$TpRu(PPh_3)(H)(\eta^2\text{-}HSiHPh_2)$ (3e). This complex was prepared by using the same procedure as for the preparation of **3a**, except that H_2SiPh_2 was used. The yield of the orange solid obtained was 0.14 g (58%). Anal. Calcd for $C_{39}H_{38}BN_6SiPRu$: C, 61.50; H, 5.03;, N, 11.03. Found: C, 61.24; H, 5.08; N, 10.85. FAB MS (*m*/*z*): 576, $[M - H_2SiPh_2]^+$.

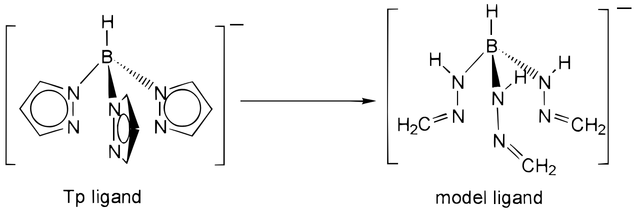
$TpRu(PPh_3)(H)(\eta^2\text{-}HSiH_2Ph)$ (3f). This complex was prepared by using the same procedure as for the preparation of **3a**, except that H_3SiPh was used. The yield of the orange solid obtained was 0.12 g (55%). Anal. Calcd for $C_{33}H_{34}BN_6SiPRu$: C, 57.81; H, 5.00; N, 12.26. Found: C, 57.35; H, 5.10; N, 12.50. FAB MS (*m*/*z*): 576, $[M - H_3SiPh]^+$.

NMR Studies of Reactions of the Ruthenium Complexes. **$TpRu(PPh_3)(H)(\eta^2\text{-}HSiR_3)$ (3) with Hydrogen**. A sample of 10 mg of $TpRuH(HSiR_3)(PPh_3)$ (**3**) was loaded into a 5 mm Wilmad pressure NMR tube. The tube was evacuated and then filled with nitrogen for three cycles. Tetrahydrofuran-d_8 (0.3 mL) was added to the tube to dissolve the sample. The tube was then pressurized with 15 atm of H_2 and heated at 80 °C for 10 h, after which the sample was analyzed by NMR spectroscopy. ^1H NMR indicated the presence of $TpRuH(H_2)(PPh_3)$ (**1**) and a small amount of unreacted **3**.

$TpRu(PPh_3)(H)(\eta^2\text{-}HSiR_3)$ (3) with Acetonitrile. A sample of 10 mg of $TpRuH(HSiR_3)(PPh_3)$ (**3**) was loaded into a 5 mm NMR tube, which was then capped with a rubber septum. The tube was evacuated and then filled with nitrogen for three cycles. Tetrahydrofuran-d_8 (0.4 mL) was added to the tube to dissolve the sample, followed by the addition of 20 μL of acetonitrile. The tube was heated at 60 °C for 10 h, after which the sample was analyzed by NMR spectroscopy. ^1H NMR indicated that **3** was converted to $TpRuH(CH_3CN)(PPh_3)$ (**2**).

$TpRuCl(CH_3CN)(PPh_3)$ (5) with Diphenylsilane. A sample of 10 mg of $TpRuCl(CH_3CN)(PPh_3)$ (**5**) was loaded into a 5 mm NMR tube, which was then capped with a rubber septum. The tube was evacuated and then filled with nitrogen for three cycles. Tetrahydrofuran-d_8 (0.4 mL) was added to the tube to dissolve the sample, followed by the addition of 20 μL of diphenylsilane. The tube was heated at 60 °C for 10 h, after which the sample was analyzed by NMR spectroscopy. ^1H NMR indicated that $TpRuH(H_2SiPh_2)(PPh_3)$ (**3e**) was formed.

Computational Details. Several model isomeric structures representing the possible structures of **3** were considered, namely an unsymmetric structure with one "nonclassical" η^2-(H−Si) coordination **6A**, a similar one with symmetric H···Si···H displacement **6B**, and the other two with adjacent hydrides **6C** and **6D**. The hydridotris(pyrazolyl)borate ligand (Tp) was simplified, as shown in **7** for theoretical simplicity.



Tp ligand

model ligand

7

The simplification has been proven to provide a satisfactory result.[30] It should also be noted that calculations using the actual Tp ligand are also possible for simpler systems such as $TpRhH_4$ and $TpCo(CO)$.[31] In the model complex **6B** an overall C_s symmetry was imposed by placing a symmetry plane defined by Ru, P, and one of the three coordinated N's.

The standard 6-31g basis sets were applied to the first-row elements H, B, and N, with the two hydrides directly bonded to the Ru center augmented by single-ζ polarization functions (i.e. 6-31g**). The atoms Ru, P, and Si were described by the ECPs of Wadt and Hay with double-ζ valence functions,[32] and the Si center was augmented by polarization ($\zeta_d(Si) = 0.262$) functions of Huzinaga.[33] All structures were optimized at the density-functional B3LYP level of theory with no structural constraints (apart from the symmetry plane in **6B**) with the Gaussian94 package[34] on a Silicon Graphics Indigo2 workstation.

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