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# Intramolecular Hydrogen Site Exchange in an HRu($SiHPh_2$) Moiety

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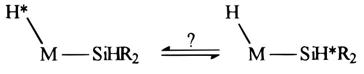
$RuH(Ph)(CO)L_2$ ($L = P^tBu_2Me$) reacts with $SiH_2Ph_2$ to give first benzene and $RuH(SiHPh_2)(CO)L_2$, and then $RuH_3(SiHPh_2)(CO)L_2$ and $Ru(H)_2(CO)L_2$, the trihydride being formed by a dehydrogenative silane coupling reaction when excess $SiH_2Ph_2$ is present. Variable-temperature spin saturation transfer experiments reveal exchange between $H^a$ and $H^b$ in $RuH^a(SiH^bPh_2)(CO)L_2$; this occurs both by an intramolecular mechanism and (when $SiH_2Ph_2$ is present) by a mechanism dependent on $SiH_2Ph_2$ concentration. Spin saturation transfer also reveals exchange between all three of the above complexes via addition/loss of $SiH_2Ph_2$ or $H_2$.

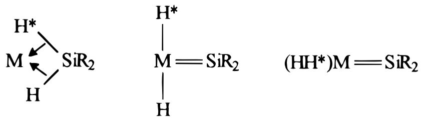
## Introduction

Compounds containing both a hydride and a silyl ligand are of interest for the possibility of their mutual interaction,[1] as well as their reductive elimination. When the silyl ligand in such a complex carries at least one hydrogen substituent (**I**), there arise the interesting questions of possible site exchange (eq 1) *occurrence*, as well as its *mechanism*.[2] In fact, this site exchange is only rarely observed.[3] The significance in observing this exchange is the possibility that it occurs via an $\eta^3$-silane complex (**II**), analogous to an alkane complex. However, two alternative intermediates for accomplishing eq 1 are shown as **III** and **IV** (a dihydrogen complex). Since all of the structures (**II**−**IV**) involve an increase in valence electron count at the metal from that in **I**, *all* therefore require that compound **I** be no more than a 16-electron compound. This valence electron count is unusual in compounds devoid of $\pi$-donor ligands (e.g., halides and pseudohalides), but we have reported such an example: $RuH(SiHPh_2)(CO)L_2$ where $L = P^tBu_2Me$.[4] Our characterization of this molecule included an X-ray diffraction structure determination (**V**, at -174 °C), and $^1H$ NMR detection of the Si−H and Ru−H nuclei as triplets (each coupled to two $^{31}P$ nuclei) at 5.4 and −0.8 ppm, respectively. The presence, in this molecule, of the silyl group in the position *trans* to the empty coordination site (i.e., where hydride is found in all other $RuH(X)(CO)L_2$ molecules) is consistent with this silyl having a strong *trans* effect, probably stronger than that of hydride.[5] It is also clear from the very ordinary silyl hydrogen chemical shift in **V** that there is no α-agostic interaction of this hydrogen with ruthenium in the ground state structure or in any species significantly (>5%) populated at 25 °C. The Si−H hydrogen position observed by X-ray diffraction was consistent with this spectroscopic observation.

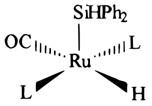


(1)

**I**



**II** **III** **IV**



**V**

We report here on the detection of the hydrogen site exchange process shown in eq 1.

## Experimental Section

**General Data.** All manipulations were done under an atmosphere of dry, $O_2$-free Ar employing a Vacuum Atmospheres inert atmosphere glovebox or standard Schlenk-line techniques. The solvents were reagent grade, distilled from the appropriate drying agents under Ar and degassed by the freeze−pump−thaw method at least three times prior to use. $H_2SiPh_2$ and PhLi were purchased from the Aldrich Chemical Company and used without further purification. The $^1H$ NMR data was recorded on a Varian XL-300 spectrometer operating at 300 MHz or a Bruker AM-500 spectrometer operating at 500 MHz. Spin saturation transfer (SST) and Nuclear Overhauser Effect (NOE) experiments were performed by pre-irradiation of desired resonances utilizing irradiation powers sufficient to completely annihilate the target peak.

**RuHPh(CO)($P^tBu_2Me$)$_2$.** $RuHCl(CO)(P^tBu_2Me)_2$ (540 mg, 1.11 mmol) was suspended in 10 mL of pentane. The mixture was cooled to -30 °C. Then 1.2 equiv of 1.8 M PhLi (0.74 mL, 1.3 mmol) was syringed into the reaction mixture. The reaction was stirred for 2 h and then filtered. The filtrate was placed at -40 °C for 24 h after which time, orange crystalline $RuH(Ph)(CO)L_2$ was recovered. Yield: 47%. $^1H$ NMR ($\delta$, 203 K, $C_7D_8$): Ru*H*, -28.6 (t, 1H, $|J_{P-H}| = 19.6$ Hz). $^{31}P\{^1H\}$ NMR ($\delta$, 298 K, $C_6H_6$): 57.3 (s).

**RuH(HSiPh$_2$)(CO)($P^tBu_2Me$)$_2$.** Ru(H)Ph(CO)$L_2$ (10 mg, 0.019 mmol) was added to 1 mL of toluene-$d_8$ in an NMR tube and the tube fitted with a septum. Then 0.85 equiv (3.0 :l, 0.016 mmol) of $H_2SiPh_2$ was syringed into the solution. Yield: 95% by $^1H$ NMR. $^1H$ NMR ($\delta$, 298 K, $C_6D_6$): Ru*H*, −0.84 (t, 1H, $|J_{P-H}| = 22.5$ Hz); PC*H*$_3$, 0.93

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⊗ Abstract published in *Advance ACS Abstracts*, October 15, 1996.

(1) Schubert, U. *Adv. Organomet. Chem.* **1990**, *30*, 151.

(2) For studies of the analogous process for alkyl hydride complexes, see: Gould, G. L.; Heinekey, D. M. *J. Am. Chem. Soc.* **1989**, *111*, 5502. Bullock, R. M.; Headford, C.; Kegley, S. G.; Norton, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 727. Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332.

(3) For an example of rapid exchange between Rh-H and an *agostic* H (in $SiHPh_2$) of a *di*rhodium complex, see: Fryzuk, M. D.; Rosenberg, L.; Rettig, S. J. *Organometallics* **1991**, *10*, 2537; **1996**, *15*, 2871.

(4) Heyn, R. H.; Huffman, J. C.; Caulton, K. G. *New J. Chem.* **1993**, *17*, 797.

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(br, s, 6H); PCC$H_3$, 1.07 (vt, 36H, $|J_{P-H}| = 5.6$ Hz); RuSi$H$, 5.43 (t, 1H, $|J_{P-H}| = 6.9$ Hz); *p*-C$H$, 7.13 (d, 2H, $|J_{H-H}| = 7.0$ Hz), *m*-C$H$, 7.20 (t, 4H, $|J_{H-H}| = 7.0$ Hz); *o*-C$H$, 8.00 (d, 4H, $|J_{H-H}| = 7.0$ Hz). $^{31}P\{^1H\}$ NMR ($\delta$, 298 K, $C_6H_6$): 59.5 (s).

**Spectral Data for $RuH_3(SiHPh_2)(CO)(P^tBu_2Me)_2$.** $^1H$ NMR ($\delta$, 173 K, $CD_2Cl_2$): Ru$H$, -9.73 (second order four-line pattern, 2H, $|J(1)_{P-H-}| = \pm 28.2$ Hz, $|J(2)_{P-H-}| = \pm 52.5$ Hz); Ru$H$, −8.76 (br, m, 1H). $^1H$ NMR ($\delta$, 253 K, $CD_2Cl_2$): PC$H_3$, 1.00 (d, 6H, $|J_{P-H}| = 13.2$ Hz); PCC$H_3$, 1.24 (d, 36H, $|J_{P-H}| = 12.6$ Hz); RuSi$H$, 5.84 (br, m, 1H), $RuH_3$, −9.35 (br, 3H). $^{31}P\{^1H\}$ NMR ($\delta$, 298 K, $C_6H_6$): 60.5 (s). Our original synthesis of $RuH(SiHPh_2)(CO)L_2$ involved reaction of $SiH_2Ph_2$ with what was then erroneously thought to be "Ru(CO)-$L_2$", but is now known to be $Ru(H)_2(CO)L_2$.[6] The initial product from $Ru(H)_2(CO)L_2$ and $SiH_2Ph_2$ is thus $RuH_3(SiHPh_2)COL_2$, which we confirm here loses $H_2$ in vacuum at 25 °C.

**Spectral Data for $Ru(H)_2(CO)(P^tBu_2Me)_2$.** $^1H$ NMR ($\delta$, 178 K, $C_7D_8$): Ru$H$, -0.12 (d of t, 1H, $|J_{P-H}| = 24.3$ Hz, $|J_{H-H}|, = 6.5$ Hz): Ru$H$, -29.21 (d of t, 1H, $|J_{P-H}| = 19.1$ Hz). $^{31}P\{^1H\}$ NMR ($\delta$, 298 K, $C_7H_8$): 71.5 (s).

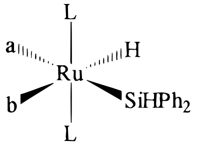
## Results and Discussion

The reaction of $Ru(H)Ph(CO)L_2$ with $H_2SiPh_2$ in toluene (eq 2) was found to be a convenient, high-yield route to RuH-

$$RuH(Ph)(CO)L_2 + SiH_2Ph_2 \rightleftharpoons RuH(SiHPh_2)(CO)L_2 + C_6H_6 \qquad (2)$$

$(SiHPh_2)(CO)L_2$ via the elimination of $C_6H_6$ and the cleavage of a Si−H bond.[7] The present study confirms the earlier spectroscopic parameters, including the absence of any significant line broadening of the Si−H and Ru−H resonances at 25 °C. We have sought to detect any mutual coupling between these two nuclei. Resolution-enhanced $^1H$ NMR spectra at −10 °C, in which the lines within each of the two triplets have a line width of 0.9 Hz, show no mutual coupling.

A standard nuclear Overhauser enhancement (NOE) difference experiment was first attempted for $RuH(SiHPh_2)(CO)L_2$ at 20, −10, and −40 °C. Residual intensity in the difference spectrum can result either from close inter-proton distances (NOE) or from chemical exchange ("spin saturation transfer", SST), or from both mechanisms. These two normally give resonances of opposite phases and additionally can be distinguished by variable temperature studies. At all these temperatures, NOE was clearly observed for the *ortho*-phenyl hydrogens of **V** ($\delta$ 7.95) when irradiating RuH ($\delta$ −0.86) or SiH ($\delta$ 5.37) (and *vice versa*). No detectable NOE was observed between Ru−H and Si−H at −40 °C. The NOE which was detected between Ru−H and the *ortho* phenyl hydrogens establishes the mutual *cis* stereochemistry for the H and $SiHPh_2$ ligands, consistent with the solid-state structure determination. The spectral data indicate that the CO ligand in **VI** must be at



**VI**

site **b** in solution, since the RuH chemical shift (−0.86 ppm) is inconsistent with that (approximately -30 ppm) expected for a hydride *trans* to an empty coordination site. This conclusion about solution phase structure is also consistent with the solid-state structure determination.

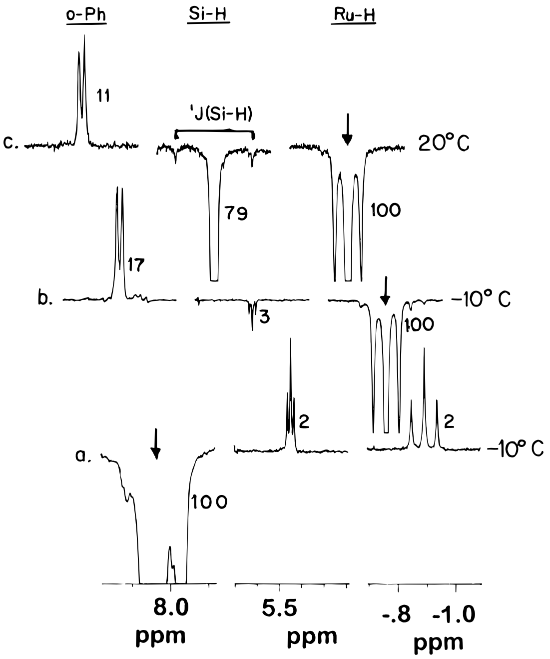


**Figure 1.** Variable-temperature $^1H$ NMR NOE difference experiments on $RuH(SiHPh_2)(CO)(P^tBu_2Me)_2$. Vertical arrow shows signal which was pre-irradiated, and numbers beside signals show relative intensity, as a measure of the magnitude of the NOE. For clarity, the upper spectra are displaced sequentially to the left from the chemical shift scale shown.

At temperatures above −40 °C, difference NOE experiments revealed RuH/SiH saturation transfer (Figure 1). Such transfer was weak at -10 °C but was almost quantitative at +20 °C, indicating that RuH/SiH scrambling (eq 1) has a rate comparable to the relaxation time scale ($\sim 1\ s^{-1}$). For example, Figure 1a (−10 °C) shows the result of preirradiation at the *ortho* phenyl signal to be direct dipolar energy transfer into both the Si−H and Ru−H signals (since the NOE effects are of opposite phase to those of the aryl signal). At this same temperature (Figure 1b), preirradiation of the Ru−H signal gives a direct dipolar (opposite phase) response in the *ortho* phenyl hydrogen signal, but weak spin saturation transfer (same phase) into the Si−H signal. At +20 °C, Figure 1c, pre-irradiation of the Ru−H signal gives nearly quantitative spin saturation transfer (due to chemical exchange) to the Si−H signal, but still only moderate direct dipolar coupling with the *ortho* phenyl signal. The signal-to-noise ratio of the Si−H signal at +20 °C is sufficient to reveal (Figure 1c) the Si−H coupling constant ($^{29}Si$ has 4.67% abundance and $I = {}^1/_2$). The value, 172 Hz, is only moderately diminished from that which we measured (199 Hz) for free $SiH_2Ph_2$, and rules out any α-agostic interaction of this H with ruthenium.

An important observation is that, at room temperature in benzene, if $RuH(Ph)(CO)L_2$ and $SiH_2Ph_2$ are mixed in a 1:1 ratio or with a slight excess of $RuH(Ph)(CO)L_2$, an equilibrium amount (eq 2) of $H_2SiPh_2$ is detectable by $^1H$ NMR. In order to more fully understand the mechanism of this reaction and exchange between the hydride on Ru and the hydrogen on Si, a further set of SST experiments was run at an elevated temperature (30 °C) to enhance the magnitude of any saturation transfer. An SST experiment was performed on a solution which was made by reacting $Ru(H)Ph(CO)L_2$ and $H_2SiPh_2$ in a 1:0.85 ratio. $^1H$ NMR showed the solution to contain >90% $RuH(SiHPh_2)(CO)L_2$ and a small amount of the starting materials. In this case, SST was seen between the hydride and

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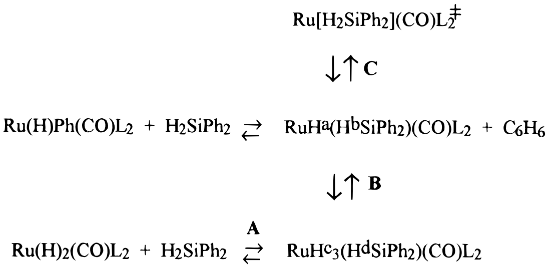
[6] Heyn, R. H.; Macgregor, S. A.; Nadasdi, T. T.; Ogasawara, M.; Eisenstein, O.; Caulton, K. G. *Inorg. Chim. Acta*, submitted for publication.

[7] This synthesis avoids possible contamination by the Li/Ru/Cl/L cluster identified in our earlier study on $RuH(SiHPh_2)(CO)L_2$. See ref 4.

**Scheme 1**



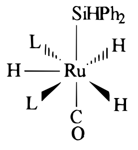
the Si-bound hydrogen in $RuH(SiHPh_2)(CO)L_2$ when irradiating at either site. However, no SST was seen to free $H_2SiPh_2$ when the Ru-bound hydride was irradiated. This indicates that hydrogen scrambling in $RuH(SiHPh_2)(CO)L_2$ occurs intramolecularly, and any dissociation to form free $H_2SiPh_2$ (rate ~5 $s^{-1}$) is slower than the proton relaxation time. A second full equivalent of $H_2SiPh_2$ was then added to this solution. A key feature of this solution is that, in addition to containing free $H_2SiPh_2$ and $RuH(SiHPh_2)(CO)L_2$, it also contains the compound $RuH_3(SiHPh_2)(CO)L_2$ and a small amount of $Ru(H)_2(CO)L_2$. These latter two compounds have been synthesized independently and their chemistry will be discussed elsewhere.[6] Irradiation of the Ru−H signal of $RuH(SiHPh_2)(CO)L_2$ (−0.8 ppm) in this solution at 30 °C then showed saturation transfer to the Si−H signal of *free* $SiH_2Ph_2$ (and also to the Ru−Si−H signal of $RuH(SiHPh_2)(CO)L_2$). This saturation transfer to $SiH_2Ph_2$ implicates a bimolecular mechanism, at this higher concentration of free $SiH_2Ph_2$, for exchange of $H^a$ with $H^c$ in eq 3.

$$RuH^a(SiH^bPh_2)(CO)L_2 + SiH^c{}_2Ph_2 \rightleftharpoons RuH^c(SiH^cPh_2)(CO)L_2 + SiH^aH^bPh_2 \quad (3)$$

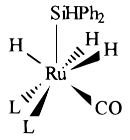
Since $RuH(SiHPh_2)(CO)L_2$ is both unsaturated and devoid of ligands with α-atom lone pairs,[8] a bimolecular mechanism is not implausible. However, in addition, SST was seen for the Ru-bound hydride of $RuH(SiHPh_2)(CO)L_2$ and the Si-bound hydrogen of the $RuH_3(SiHPh_2)(CO)L_2$ present in this solution. These observations can be explained if the equilibria in Scheme 1 are operative. SST is observed from free $H_2SiPh_2$ to $RuH^c$ to $H^dSi$ due to chemical equilibrium **A**. Equilibrium **B** gives the observed SST from $RuH^a$ to $H^dSi$ and $RuH^c$. Equilibrium **C** gives the observed SST from $RuH^a$ and $SiH^b$ when the concentration of free $SiH_2Ph_2$ is low.

This solution also contains $RuH_3(SiHPh_2)(CO)L_2$, the product of $H_2$ addition to $RuH(SiHPh_2)(CO)L_2$. The $H_2$ source is apparently a catalyzed dehydrogenative coupling of the free $SiH_2Ph_2$, to give $H(SiPh_2)_nH$ and $H_2$. The reality of equilibrium **B** is supported by the fact that freeze/thaw degassing of a solution containing $RuH_3(SiHPh_2)(CO)L_2$ three times gives essentially complete conversion to $RuH(SiHPh_2)(CO)L_2$.[9] In addition, a pure sample of $Ru(H)_2(CO)L_2$ reacts with $SiH_2Ph_2$ (equimolar or excess) at −78 °C to give $RuH_3(SiHPh_2)(CO)L_2$.

Spectroscopic studies indicate that $RuH_3(SiHPh_2)(CO)L_2$ is a trihydride (not dihydrogen) molecule with no significant Si/H bond to any of the Ru-bound hydrogens.[10] The molecule has mirror symmetry. While the hydride spectrum is fluxional at higher temperatures, it decoalesces to an AMM′XX′ ($H_3RuP_2$) spin system by 173 K. These data are consistent with either of the two idealized structures shown as **VII** (pentagonal bipyramid) and **VIII** (capped octahedron). An analogous structure (**VIII**) was shown earlier for $RuH_3(SiMe_3)(PMe_3)_3$,[11] although, in the present case, it is less likely than **VII** due to repulsions between the two bulky $P^tBu_2Me$ groups.



**VII**



**VIII**

## Conclusions

These results show that, in spite of the absence of an α-agostic hydrogen in $RuH(SiHPh_2)(CO)L_2$, this unsaturated complex exhibits facile exchange of RuH and SiH at 25 °C. While oxidative addition (**III** or **IV**) cannot be ruled out as the mechanism for this scrambling, we prefer the reductive transient **II** since it nicely explains the rarity of observation of this rearrangement among *saturated* hydrido/silyl compounds.

The facile bimolecular and dissociative scrambling reactions observed in the presence of free $H_2$ or $SiH_2Ph_2$ (Scheme 1) not only show the high reactivity of the unsaturated species $RuH(R)(CO)L_2$ (R = H, Ph or $SiHPh_2$) but also reveal that the saturated $Ru^{IV}$ trihydride species undergoes reductive elimination, to reform an unsaturated molecule, with remarkable ease. This we attribute to the reluctance of the 4d metal (*cf.* Os) to maintain an oxidation state above II, particularly in the presence of a $\pi$-acid CO ligand (*cf.* $Ru(H)_3(SiMe_3)(PMe_3)_3$[11] The high reactivity of the species reported here also derive in part from the absence of $\pi$-donor ligands in the coordination sphere.[8]

Migration of H in an $Ir/SiHR_2$ species from Si to Ir was recently proposed as an essential mechanistic step.[12]

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[12] Okazaki, M.; Tobita, H.; Ogino, H. *Chem. Lett.* **1996**, 477.