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Reactions of Silanes with the Binuclear Hydride $[\{Pr^i_2PCH_2CH_2PPr^i_2\}Rh]_2(\mu\text{-}H)_2$. Catalytic Deuterium Exchange on Diphenylsilane and X-ray Structure of $[\{Pr^i_2PCH_2CH_2PPr^i_2\}Rh]_2(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}HSiPh_2)$

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Summary: Stoichiometric reactions of diphenylsilane (H_2SiPh_2) with $[(dippe)Rh]_2(\mu\text{-}H)_2$ (**1**; dippe = 1,2-bis(diisopropylphosphino)ethane) have produced the new compounds $[(dippe)Rh]_2(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}HSiPh_2)$ (**2**) and $[(dippe)Rh]_2(\mu\text{-}SiPh_2)_2$ (**3**). An X-ray structure determination of **2** indicates the presence of a three-center, two-electron Rh–Si–H interaction. Deuterium exchange and silicon–silicon coupling to give 1,1,2,2-tetraphenyldisilane are both observed for diphenylsilane in the presence of catalytic amounts of **1**; the isolated silyl–dihydride complex **2** and the bis(silylene) derivative **3** are likely to be active in these catalytic cycles.

The current interest in the preparation of new materials has sparked renewed studies in the formation of polysilanes via reactions of silanes with transition-metal complexes.[1-5] Some hydrosilation catalysts from the platinum-group metals have been reinvestigated to determine their capabilities as silane oligomerization catalysts[6] because of the possibility that dehydrogenative silicon–silicon coupling can occur at the metal center. The catalytic behavior of these complexes stems from their ability to oxidatively add a Si–H bond.[7] In addition, a number of intriguing binuclear complexes having three-center M–Si–H interactions have been isolated from the addition of silanes to mononuclear precursors,[1f,8] and some of these binuclear derivatives are reported to be active in catalytic oligomerization.[1f] As our group has been interested in fundamental reactions promoted by binuclear metal hydrides, it was of interest to examine the reaction of silanes with a *preformed* binuclear rhodium framework.[9] We report here some of our initial structural results and also the catalytic deuterium exchange reaction of diphenylsilane and the catalytic coupling of diphenylsilane to give 1,1,2,2-tetraphenyldisilane.

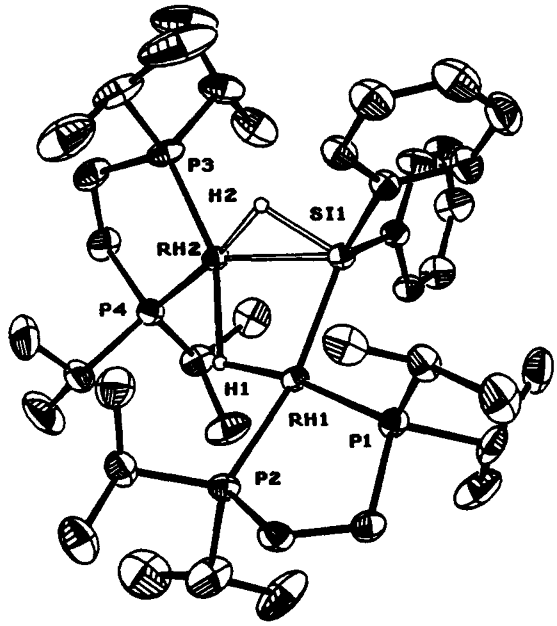

Figure 1. Molecular structure of $[\{Pr^i_2PCH_2CH_2PPr^i_2\}Rh]_2(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}HSiPh_2)$ (**2**). Selected bond lengths (Å) and bond angles (deg) are as follows: Rh(1)–Rh(2) = 2.937 (1), Rh(1)–Si = 2.298 (2), Rh(1)–H(1) = 1.71 (6), Rh(2)–H(1) = 1.90 (6), Rh(2)–H(2) = 1.61 (6), Rh(2)–Si = 2.487 (2), Si–H(2) = 1.66 (6); Rh(1)–H(1)–Rh(2) = 109 (3), Rh(2)–H(2)–Si = 99 (3), Rh(1)–Si–H(2) = 101 (2).

Dropwise addition of 1 equiv of diphenylsilane to a dark green toluene solution of the rhodium dimer $[(dippe)Rh]_2(\mu\text{-}H)_2$ (**1**; dippe = 1,2-bis(diisopropylphosphino)ethane) generates a deep red-orange solution from which red-orange crystals of a compound having the empirical formula $[(dippe)Rh]_2\cdot H_2SiPh_2$ (**2**)[10] were obtained. The X-ray crystal structure[11] of **2** (Figure 1) shows that the binuclear core of **2** is asymmetric, with one bridging hydride and a bridging silyl ligand bound to one rhodium

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(9) Some other examples of the reactions of silanes with preformed binuclear metal centers include: (a) McDonald, R.; Cowie, M. *Organometallics* **1990**, *9*, 2468. (b) Wang, W.-D.; Hommeltoft, S. I.; Eisenberg, R. *Organometallics* **1988**, *7*, 2417. (c) Wang, W.-D.; Eisenberg, R. *J. Am. Chem. Soc.* **1990**, *112*, 1833. (d) Carreño, R.; Riera, V.; Ruiz, M. A.; Jeannin, Y.; Philoche-Levisalles, M. *J. Chem. Soc. Chem. Commun.* **1990**, 15.

(10) Anal. Calcd for $C_{40}H_{76}P_4Rh_2Si$: C, 52.52; H, 8.37. Found: C, 52.32; H, 8.45.

(11) Crystals of $(\mu\text{-}H)(\mu\text{-}Ph_2SiH\text{-}Si{:}H')Rh_2(dippe)_2$ are monoclinic, with $a = 19.338$ (8) Å, $b = 11.223$ (4) Å, $c = 22.934$ (9) Å, $\beta = 112.39$ (3)°, $Z = 4$, $D_c = 1.320$ g cm^{-3}, and space group $P2_1/n$. The structure was solved by the Patterson method and was refined by full-matrix least-squares procedures to $R = 0.037$ and $R_w = 0.043$ for 5752 reflections with $I \geq 3\sigma(I)$. Full details of the crystallographic analysis are included as supplementary material.

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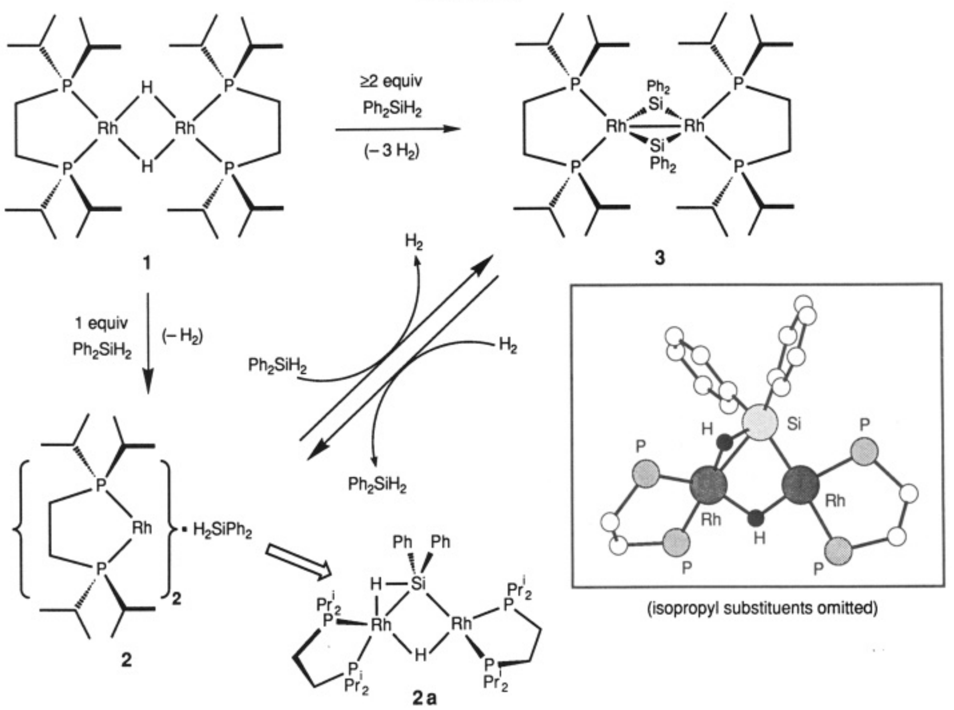
Scheme I

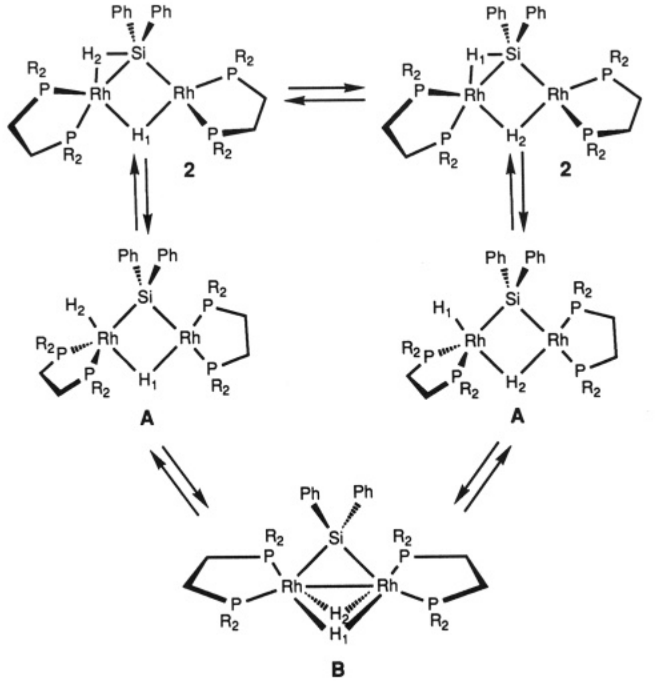


(isopropyl substituents omitted)

atom through the silicon and to the other rhodium atom through a Si–H bond; this is shown in more detail in Scheme I. Observation of this agostic interaction of a Si–H bond with a transition-metal center is becoming less rare, and the subject has recently been reviewed.[12] There are, however, only a few examples of this type of bonding in binuclear complexes.[1f,8]

The room-temperature $^{31}P\{^1H\}$ NMR spectrum[13] of **2** contains a simple doublet whose broadness suggests that the complex is fluxional on the NMR time scale. Variable-temperature ^1H NMR spectroscopy is not very informative, since even at low temperature the resonances are poorly resolved; however, at −95 °C the $^{31}P\{^1H\}$ NMR spectrum shows a complex set of signals attributable to the presence of four inequivalent phosphines. This is consistent with the structure of **2** in the solid state (see **2a** in Scheme I). The presence of a single hydride resonance in the room-temperature ^1H NMR spectrum[13] suggests that the fluxionality in **2** involves exchange of the bridging hydride H(1) and the silicon "hydride" H(2). A possible mechanism for this exchange involves the complete oxidative addition of Si–H(2) to give a bridging silylene fragment and a terminal hydride (A), which subsequently swings into a bridging position, yielding a symmetric intermediate with the structure B (see Scheme II). Such an intermediate would account for the equivalency of the rhodium and phosphorus centers in the high-temperature limiting NMR spectra.[13] A structural precedent for the proposed intermediate B, $[\{(Pr^iO)_3P\}_2Rh]_2(\mu\text{-}H)_2(\mu\text{-}CO)$, has been observed[14] spectroscopically during addition of 1 equiv of carbon monoxide to $[\{(Pr^iO)_3P\}_2Rh]_2(\mu\text{-}H)_2$. The reverse of these steps with H(1) swinging out to the terminal position instead of H(2) would exchange the two hydrides.

Scheme II



Addition of a second equivalent of H_2SiPh_2 to a hexane solution of the silyl–hydride **2** gives a bright orange precipitate, **3**, which has the formula $[(dippe)Rh]_2(\mu\text{-}SiPh_2)_2$.[15] The ^1H and $^{31}P\{^1H\}$ NMR spectra of **3**[16] are consistent with the symmetrical, dimeric structure shown in Scheme I. The reaction of a suspension of the bis(silylene) complex **3** with H_2 (4 atm) in hexane or toluene regenerates the silyl–hydride **2** and 1 equiv of H_2SiPh_2 (as monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy).

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

(13) ^1H NMR (C_6D_6, ppm): H_o, 8.06 (dd, $^3J_{m-o}$ = 7.9 Hz, $^4J_{p-o}$ = 1.4 Hz); H_m, 7.27 (overlapping dd, $^3J_{p-m}$ = 6.6 Hz); Hp, 7.14; ligand resonances, 1.96–0.99; μ-H's, 6.17 ($J_{Rh-H} \approx J_{P-H}$ = 14.5 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, ppm, external reference $P(OMe)_3$ set at +141.0): 94.0 (d, J_{Rh-P} = 154.6 Hz).

(14) Burch, R. R.; Muetterties, E. L.; Schultz, A. J.; Gebert, E. G.; Williams, J. M. *J. Am. Chem. Soc.* **1981**, *103*, 5517.

(15) Anal. Calcd for $C_{52}H_{84}P_4Rh_2Si_2$: C, 57.03; H, 7.73. Found: C, 56.79; H, 7.72.

(16) ^1H NMR (C_6D_6, ppm): H_o, 8.31 (d, J_{m-o} = 9 Hz); H_m, H_p, 7.36–7.16 (overlapping mult); ligand resonances, 1.90–0.75. $^{31}P\{^1H\}$ NMR (C_6D_6, ppm, external reference $P(OMe)_3$ set at +141.0): 79.3 (d mult, J_{Rh-P} = 134 Hz).

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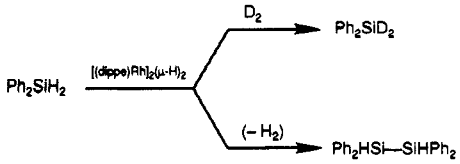
Scheme III



On the basis of the interconvertibility of the silylhydride **2** and the bis(silylene) **3** by either addition of diphenylsilane or addition of H_2, it seemed reasonable that a catalytic cycle could be developed which would allow for the conversion of Ph_2SiH_2 to Ph_2SiD_2 with D_2 (cf. middle of Scheme I). The key to this reaction is that, even in the presence of excess silane, the bis(silylene) **3** reacts with D_2 to generate free Ph_2SiD_2 and the silyl–deuteride $[(dippe)Rh]_2(\mu\text{-}D)(\mu\text{-}\eta^2\text{-}DSiPh_2)$ (**2**-d_2). In the presence of more Ph_2SiH_2, **2**-d_2 is converted to the bis(silylene) **3** and the cycle is complete. This has only been reported previously to occur in the presence of heterogeneous catalysts.[17] Monitoring the reaction under catalytic conditions by ^1H NMR spectroscopy shows the decrease in the intensity of the Si–H resonance with time. If long reaction times are employed, the presence of a new material can be observed; this material has been characterized as 1,1,2,2-tetraphenylsilane, the product of dehydrogenative silicon–silicon coupling of Ph_2SiH_2. The dimerization reaction can be suppressed by dilution and an increase in the pressure of D_2; by the same token, the absence of D_2 (or H_2) favors the formation of $Ph_2HSi\text{-}SiHPh_2$.[18] Further studies on these reactions are in progress.

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Supplementary Material Available: Full details of the crystal structure analysis and tables of crystallographic data, atomic coordinates and equivalent isotropic thermal parameters, bond lengths, bond angles, hydrogen atom parameters, anisotropic thermal parameters, torsion angles, intermolecular contacts, and least-squares planes (30 pages); a table of measured and calculated structure factor amplitudes (71 pages). Ordering information is given on any current masthead page.

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[17] Sommer, L. H.; Lyons, J. E.; Fujimoto, H.; Michael, K. W. *J. Am. Chem. Soc.* **1967**, *89*, 5483.

[18] Typical unoptimized reaction conditions for the production of the disilane are as follows: 254 mg (1.38 mmol) of diphenylsilane was dissolved in 1.25 mL of toluene and placed in a 50-mL round-bottom flask equipped with a stirbar and condenser. The catalyst (1, 1.38 × 10^{-2} mmol, 250 μL of a 0.055 M solution in toluene) was added to the substrate solution by syringe under a strong flow of nitrogen. The solution was degassed and heated to 60 °C under nitrogen open to a Nujol bubbler. After 18–24 h the mixture was taken into a glovebox, where the catalyst was removed on a Florisil column to give 71–77% conversion, as determined by ^1H NMR spectroscopy.

Evidence for the Activation of Thietanes to Ring Opening by Nucleophiles through Bridging Coordination

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Summary: The reaction of $Os_3(CO)_{10}(\mu\text{-}\overline{SCH_2CMe_2CH_2})$ (**1**) with $[Et_4N]^+Cl^-$ in CH_2Cl_2 yielded after acidification the complex $Os_3(CO)_{10}[\mu\text{-}SCH_2CMe_2CH_2Cl](\mu\text{-}H)$ (**3**; 55%), which contains a chloroneopentanethiolato ligand that is believed to have been formed by the nucleophilic ring opening of the thietane ligand in **1**. In contrast, the reaction of the ring-opened complex $Os_3(CO)_{10}[\mu\text{-}SCH_2CMe_2CH_2]$ (**4**) with $[Et_4N]^+Cl^-$ yielded only the cluster-opened product $[Et_4N]^+[Os_3(CO)_9(\mu\text{-}SCH_2CMe_2CH_2)(\mu\text{-}Cl)]^-$ (**5**; 87%). Compounds **3** and **5** were characterized crystallographically.

In recent reports we have described the first examples of the ring-opening reaction of thietane ligands in metal cluster complexes.[1-3] Both thermal[1,2] and photochemical[3] processes have been observed. In some cases these reactions were accompanied by C–H bond cleavage processes.[1,3] We have now discovered an example of facile nucleophilic ring opening of a bridging 3,3-dimethylthietane ligand (DMT) that appears to be promoted by its bridging coordination.

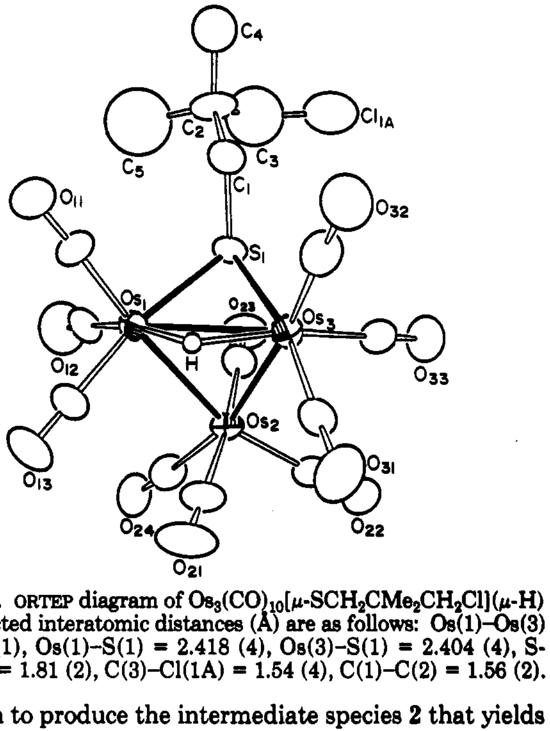

Figure 1. ORTEP diagram of $Os_3(CO)_{10}[\mu\text{-}SCH_2CMe_2CH_2Cl](\mu\text{-}H)$ (**3**). Selected interatomic distances (Å) are as follows: Os(1)–Os(3) = 2.851 (1), Os(1)–S(1) = 2.418 (4), Os(3)–S(1) = 2.404 (4), S(1)–C(1) = 1.81 (2), C(3)–Cl(1A) = 1.54 (4), C(1)–C(2) = 1.56 (2).

The reaction of 45 mg of $Os_3(CO)_{10}(\mu\text{-}\overline{SCH_2CMe_2CH_2})$ (**1**)[1] with 9.0 mg of $[Et_4N]^+Cl^-$ in CH_2Cl_2 proceeds at 25 °C/1.5 h to produce the intermediate species **2** that yields upon protonation (50 μL of acetic acid) the complex $Os_3(CO)_{10}[\mu\text{-}SCH_2CMe_2CH_2Cl](\mu\text{-}H)$ (**3**) in 55% yield.[4]

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[1] Adams, R. D.; Pompeo, M. P. *Organometallics* **1990**, *9*, 2651.
[2] Adams, R. D.; Pompeo, M. P. *J. Am. Chem. Soc.* **1991**, *113*, 1619.
[3] Adams, R. D.; Pompeo, M. P. *Organometallics* **1990**, *9*, 1718.

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