atom removed as in the enolate systems. Further work on the reactions and associated stereochemistry of these acyls is in progress.

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Supplementary Material Available: Spectroscopic data for new compounds, structure determinations for **4a** and **6**, ORTEP drawing and crystal packing diagrams for **4a** and **6**, and tables of crystal data, bond distances and angles, anisotropic temperature factors, and isotropic temperature factors for **4a** and **6** (21 pages); listings of structure factor amplitudes for **4a** and **6** (20 pages). Ordering information is given on any current masthead page.

Formation of Si-Si Bonds from Si-H Bonds in the Presence of Hydrosilation Catalysts

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Summary: **Complexes of Pt, Pd, Rh, and Ir that are known to catalyze the hydrosilation of alkenes are found to also catalyze the formation of Si-Si bonds from Si-H bonds. The relative rates of hydrosilation and Si-Si bond formation are measured for several catalysts.**

The reactivity of Si-H bonds with transition metals is well-established and is frequently exploited to produce Si-C and Si-O bonds via hydrosilation of alkenes and carbonyl compounds, respectively,[1] and as a general synthetic method to produce organometallic complexes containing Si-M bonds.[2] There are, however, few examples of Si-Si bond formation in the presence of transition metals.[3] In fact, the only general method for the synthesis of Si-Si bonds is the Wurtz-type coupling of halosilanes in the presence of alkali metal,[4] in spite of the difficulties frequently encountered in using the method[5] and the currently widespread interest in using polysilanes as precursors to ceramic materials, as photoinitiators for vinyl-free radical polymerization and as photoresist materials.[6] Therefore, the observation in our laboratory of formation of disilane HPhMeSi-SiPhMeH from PhMeSiH$_2$ in the presence of small amounts of (PPh$_3$)$_2$Pt(H$_2$C=CH$_2$) (**1**)[7] warranted further investigation (eq 1).

$$\mathrm{PhMeSiH_2} \xrightarrow{(\mathrm{Ph_3P})_2\mathrm{Pt}(\mathrm{H_2C{=}CH_2})\ (1)} \mathrm{HPhMeSi{-}SiPhMeH}\ (27\%) + \mathrm{H_2} + \mathrm{Ph_2MeSiH}\ (52\%) + \text{others (including Pt compounds)} \qquad (1)$$

Table I. Reaction of R$_3$SiH in the Presence of L$_2$Pt(C$_2$H$_4$) (1)

experiment[a]	silane	R$_3$Si-SiR$_3$,[b] %	others (% yield)[b]
1	PhMeSiH$_2$	27	Ph$_2$MeSiH (52)
2	PhMe$_2$SiH	0[c]	Ph$_2$Me$_2$Si (4)
3	Et$_3$SiH	0[c]	
4	Et$_2$SiH$_2$	95	
5	(EtO)$_3$SiH	0[c]	(EtO)$_4$Si (61)
6	Et$_2$SiH$_2$ + Et$_3$SiH	Et$_4$Si$_2$H$_2$, 58% Et$_5$Si$_2$H, 8%	

[a] 0.03 mmol of **1**, 9 mmol of R$_3$SiH. See footnote 8 for experimental details. [b] Yield as percentage of total products at 75-h reaction time. Products such as trimers, siloxanes (formed from traces of water), other disproportionation products, and unidentified compounds are not included in the table. [c] No reaction within our limits of detection (approximately 0.1%).

Table II. Relative Rates of Disilane Formation and Hydrosilation in the Presence of Various Catalysts

catalyst	A. Si-Si bond formation[a]	B. hydrosilation[b]
(Ph$_3$P)$_2$Pt(C$_2$H$_4$) (**1**)	1.0[c]	0.8
H$_2$PtCl$_6$	0.1	6
(PPh$_3$)$_2$PtCl$_2$	0.1	0.1
Pt(COD)Cl$_2$ (**4**)	0.7	70
(Ph$_3$P)$_3$RhCl (**2**)	31	400
[Rh(CO)$_2$Cl]$_2$ (**6**)	5	60
(η^5-C$_5$H$_5$)Rh(C$_2$H$_4$)	0.2	0.7
RhCl$_3$	0.3	3
[Rh(COD)Cl]$_2$	1	25
[Ir(COD)Cl]$_2$ (**5**)	0.2	3
[Pd(allyl)Cl]$_2$ (**3**)	12	100

[a] 0.01 mmol of catalyst and 1.0 mmol of Et$_2$SiH$_2$. Rate values for disilane formation were obtained from the amount of time necessary to form 0.01 mmol of product. See text for further discussion of kinetics and footnote 9 for experimental details. [b] 0.01 mmol of catalyst, 1.0 mmol of Et$_2$SiH$_2$, and 1.0 mmol of 1-hexene. Values were obtained from the relative amounts of HEt$_2$Si(n-hexyl)/disilane formed for each catalyst, corrected for detector response factors, and multiplied by the relative rate in column A. [c] This rate was arbitrarily assigned a value of 1, and all others are expressed relative to it.

The reactions of various silanes with catalytic amounts of **1** were examined first (Table I).[8] When the silane is

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[7] For a description of the synthesis of Pt-silyl compounds from these reagents, see: Eaborn, C.; Metham, T.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1975**, 2212.

[8] For experiment 1, **1** (22 mg, 0.03 mmol) was placed in a vial in a Vacuum Atmospheres glovebox under a continuously scrubbed nitrogen atmosphere. PhMeSiH$_2$ (1.10 g, 9 mmol, dried over 4A molecular sieves and distilled) was added, and a Teflon-lined cap was placed on the vial. Bubble evolution was immediate, and within minutes all **1** had dissolved/reacted to give a yellow solution. The reaction was allowed to proceed at 18 °C in the closed vial, which was opened periodically to withdraw 1 μL of solution via syringe. The syringe was removed from the glovebox, and its contents were immediately analyzed by gas chromatography. This method minimized introduction of air into even very small samples over long periods of time. The reaction was followed for 75 h, at which point the catalyst activity was greatly reduced and the solution was red. Experiments 2-6 were conducted in a similar manner.

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substituted with aryl or alkoxy groups, disproportionation reactions at the Si–R bond predominate; thus subsequent experimentation was limited to alkylsilanes. Silanes substituted with just one hydrogen do not react to produce disilanes at observable rates (compare experiments 1 and 2 or 3 and 4). This could be due to mechanistic requirements (vide infra) or simply a lowered reactivity due to steric or electronic effects. When a mixture of Et_3SiH and Et_2SiH_2 was allowed to proceed to disilanes in the presence of **1** (experiment 6), $Et_4Si_2H_2$ and Et_5Si_2H were formed in a ratio of 7:1. Et_6Si_2, which could have been detected in amounts 100 times smaller than Et_5Si_2H, was not observed.

A number of late transition-metal catalysts were then tested with Et_2SiH_2 for disilane formation (Table II, column A).[9] The rate of disilane formation varied greatly as the catalyst was changed, although it should be noted that all reactions were performed in the same manner and no attempt was made to individually optimize conditions for each catalyst. $(PPh_3)_3RhCl$ (**2**) is the most effective catalyst found thus far. The rates observed in the presence of **1** and **2** slowed with time and did not fit integral-order kinetics with respect to silane or catalyst, although they did increase as catalyst and/or silane concentration was increased. The number of moles of disilane produced per mole of catalyst has not been optimized, although addition of excess PPh_3 to **1** or to **2** increases this value. At least 650 mol of disilane can be produced per mole of **2**.

Most of the catalysts in Table II did not convert Et_3SiH to disilane. However, Et_6Si_2 could be observed among the products (which included Et_4Si and other silanes arising from reactions with ligands on the catalyst) in reactions containing $[Pd(allyl)Cl]_2$ (**3**), $Pt(COD)Cl_2$ (**4**) (COD = 1,5-cyclooctadiene), $[Ir(COD)Cl]_2$ (**5**), and $[Rh(CO)_2Cl]_2$ (**6**).[10] With **3**, black solids were formed almost immediately in the reaction mixture; similar results have been reported by other workers.[11] No solids were observed with any other catalyst, although the possibility of colloidal heterogeneous catalysis must be considered a possibility in view of a recent report.[12]

Many of the compounds in Table II have been studied by other workers as catalysts for hydrosilation. It was suspected that Si–Si bond formation might occur at rates competitive with hydrosilation, and thus the relative rates of the two reactions were measured. Equimolar amounts of Et_2SiH_2 and 1-hexene were allowed to react in the presence of various catalysts. At low conversions where the concentrations of silane and alkene are essentially unchanged, the relative amounts of $Et_2(n\text{-hexyl})SiH$ and $HEt_2Si\text{–}SiEt_2H$ formed were used as a measure of the relative overall rates of hydrosilation and Si–Si bond formation. The data in Table II, column B, show that these vary considerably for different catalysts, and for many catalysts hydrosilation predominates. Such is the case for **2**, which is an effective catalyst for either process. However, **2** is a useful catalyst for Si–Si bond formation when an alkene is not present. For **1**, Si–Si bond formation is slightly faster.

The experiments described in Tables I and II were run in the absence of water and oxygen. When the reaction was conducted in air, disilane formed in minor amounts, and disiloxane was instead the major product. Experiments in which O_2 or water or both were added to reaction mixtures prepared under nitrogen demonstrate that either can serve as a source of the disiloxane oxygen. Reactions are more rapid in the presence of O_2.[13] When sufficient water is present, silanol also forms. For **1** and **2**, the relative rates of hydrosilation and reaction with ROH (R = H, Et) have been measured, and formation of Si–O bonds is ten to one hundred times faster than hydrosilation.[14,15] This is evidently generally true since with other catalysts, traces of water are scrubbed out of the reaction mixture by the very rapid formation of siloxane, after which the other reactions discussed here proceed.

Little is known about the mechanism of formation of Si–Si bonds in the presence of transition-metal catalysts. Although the observation that Et_2SiH_2 can and Et_3SiH cannot form disilanes in the presence of **1** and **2** seems consistent with a silylene-like intermediate $[Et_2Si{=}M]$ as suggested by Nagai et al.,[3d] the results with **3**–**6** do not support this interpretation and it is premature to make mechanistic conclusions. Investigations into the mechanism continue. These uncertainties notwithstanding, it is established that Si–Si bonds can be formed from Si–H bonds with a variety of transition-metal catalysts, often at rates competitive with hydrosilation. One can generally expect that compounds known to catalyze hydrosilation can be used for the synthesis of Si–Si bonds, within the limitations imposed by the side reactions and any mechanistic constraints.

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(9) For all experiments reported in Table II, experiments were performed in a manner similar to that described for **1** (footnote 8) using amounts of catalyst, silane, and hexene as indicated, with hexadecane as internal standard. Products were analyzed by gas chromatography. In experiments where it was desired to vary concentrations to obtain kinetics data, **1** or **2** and silane were separately dissolved in tetrahydrofuran and mixed at $t = 0$. Relative rates were the same with or without solvent.

(10) For catalysts which are very inefficient (e.g., H_2PtCl_6), the limits of detection preclude observation of Et_6Si_2 at rates that are less than one-tenth that of disilane formation from Et_2SiH_2.

(11) Ssebuwufu, P. J.; Glockling, F.; Harriott, P. *Inorg. Chim. Acta* **1985**, *98*, L35.

(12) Lewis, L. N.; Lewis, N. *J. Am. Chem. Soc.* **1986**, *108*, 7228.

(13) For a discussion of the effect of oxygen on the rate of hydrosilation see: Dickers, H. M.; Haszeldine, R. N.; Malkin, L. S.; Mather, A. P.; Parish, R. V. *J. Chem. Soc., Dalton Trans.* **1980**, 308.

(14) In the glovebox, 1 mmol each of Et_3SiH, 1-hexene, and ROH (R = Et or H) were placed in a vial. For R = H, 0.5 mL of tetrahydrofuran was added to create a homogeneous solution. Catalyst **1** or **2** (0.01 mmol) was then added, and the reaction was monitored by gas chromatography. The ratio area $[Et_3SiOR]$/area $[Et_3Si(n\text{-hexyl})]$, corrected for GC response factors, was used as a measure of the overall rates of reaction. The ratios are as follows: for **1**, R = Et, 10, R = H, >100; for **2**, R = Et, 25, R = H, 110.

(15) For a discussion of mechanistic considerations and the rates of silane reaction with various alcohols, see: Lukevics, E.; Dzintara, M. *J. Organomet. Chem.* **1985**, *295*, 265 and references therein.

Palladium Chloride Catalyzed Olefin–Formate Ester Carbonylation Reactions. A Simple, Exceptionally Mild, and Regioselective Route to Branched Chain Carboxylic Esters

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Summary: Olefins react with formate esters, carbon monoxide, oxygen, hydrochloric acid, copper chloride, and palladium chloride as the catalyst, at room temperature and atmospheric pressure, to give mainly branched chain carboxylic esters in fair to good yields.