

Transfer Dehydrogenative Coupling of Triethylsilane Catalysed by Ruthenium and Rhodium Complexes. A New Si–C Bond Forming Process

Peter I. Djurovich, Alfred R. Dolich and Donald H. Berry*

Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, PA 19104-6323, USA

Four-legged piano stool complexes (η^6 -arene)Ru(H)₂(SiEt₃)₂ and (η^5 -C₅Me₅)Rh(H)₂(SiEt₃)₂ catalyse the transfer dehydrogenative coupling of Et₃SiH in the presence of a hydrogen acceptor such as *tert*-butylethylene to yield the carbosilane dimer, HSiEt₂CHMeSiEt₃, and 2,2-dimethylbutane by a mechanism involving an intermediate η^2 -silene complex, L_nM(Et₂Si=CHMe), generated by β -hydrogen elimination from a silyl group.

Despite considerable effort devoted to exploring the activation of C–H bonds by transition metal complexes, there are only a few examples of systems which catalyse the productive functionalisation of aliphatic C–H bonds.¹ Our interest in C–H bond functionalisation has been concerned with the catalytic formation of Si–C bonds, and we previously reported a series of ruthenium phosphine complexes which catalyse the dehydrocoupling of Me₃SiH to oligomeric carbosilanes, Me₃Si–(CH₂SiMe₂)_n–H.² More recently, a series of new arene ruthenium silyl complexes, (η^6 -arene)Ru(H)₂(SiR₃)₂ has been described which are active catalysts for thermolytic H/D exchange reactions between the C–H bonds of alkylsilanes and deuterated solvents.³ We now report that these (η^6 -arene)Ru complexes and the isoelectronic (η^5 -C₅Me₅)Rh analogues thermally catalyse the dehydrocoupling of Et₃SiH to a carbosilane dimer in the presence of hydrogen acceptors such as alkenes. The dehydrogenation of alkanes with concurrent hydrogen transfer to a different alkene has been described as transfer dehydrogenation;⁴ therefore, the dimerisation of Et₃SiH with concurrent alkene hydrogenation is best described as transfer dehydrogenative coupling.

The complexes (η^6 -arene)Ru(H)₂(SiEt₃)₂ (η^6 -arene = C₆H₆, *p*-cymene) and (η^5 -C₅Me₅)Rh(H)₂(SiEt₃)₂ catalyse the transfer dehydrogenative coupling of Et₃SiH, Scheme 1 and Table 1. In the case of *tert*-butylethylene (3,3-dimethylbut-1-ene) as hydrogen acceptor, the primary products are the carbosilane dimer, HSiEt₂CHMeSiEt₃ **1** and 2,2-dimethylbutane. In addition, typical products of hydrosilylation, *tert*-

BuCH₂CH₂SiEt₃ **2** and (*E*)-*tert*-BuCH=CHSiEt₃ **3** are observed in combined quantities ranging from 4–27% based on Et₃SiH.

Reactions carried out in benzene as solvent also produce phenylsilyl products; details of this process will be described in the future. Carbosilane **1** was isolated as a pure compound by distillation of the reaction mixture. Authentic samples for the identification of **2** and **3** were prepared by the hydrosilylation of *tert*-butylethylene and *tert*-butylacetylene with Et₃SiH catalysed by H₂PtCl₄. The symmetrical dehydrocoupling product, Et₃Si–SiEt₃, was not observed by GC in the reaction mixtures. No conclusive evidence was obtained for higher carbosilane oligomers, as is observed in the dehydrocoupling of Me₃SiH.²

Reactions performed with 2 mol% (η^5 -C₅Me₅)Rh catalyst typically required *ca.* 2 h to reach 80% conversion of Et₃SiH at 150 °C (*ca.* 10 turnovers of dimeric product per h), although reaction times of 12–14 h were usually employed to allow for >95% conversion. Reaction rates for the (η^6 -arene)Ru catalysts are *ca.* one tenth as fast as for the (η^5 -C₅Me₅)Rh catalyst. The corresponding chloride derivatives of the catalysts, [(η^6 -arene)RuCl₂]₂ and [(C₅Me₅)RhCl₂]₂, form the silyls *in situ* under the reaction conditions and can be used directly as catalyst precursors (Table 1). However, carbosilane was not detected with other well-known catalysts such as (PPh₃)₃RhCl or (PPh₃)₃Rh(CO)(H). Furthermore, although (PMe₃)₃Ru(H)₃(SiMe₃) has been shown to be an effective catalyst for the formation of methyl-substituted carbosilanes from Me₃SiH,² this phosphine ruthenium complex catalyses formation of **1** only sluggishly (<5% conversion after 48 h at 150 °C), probably as a result of the different steric constraints of the phosphine complex. In all cases, only traces of carbosilane are observed in the absence of the hydrogen acceptor. Parallel runs employing the (C₅Me₅)Rh catalyst with and without added metallic mercury yielded identical rates and product distributions, which argues against the role of colloidal metal or other heterogeneous catalysts.⁵

Although *tert*-butylethylene was employed as the hydrogen acceptor in most instances, hex-1-ene was also found to be effective, albeit with lower rates and lower selectivity for the carbosilane product. Cyclohexene and cyclooctene were not effective as either hydrogen acceptors or as substrates for

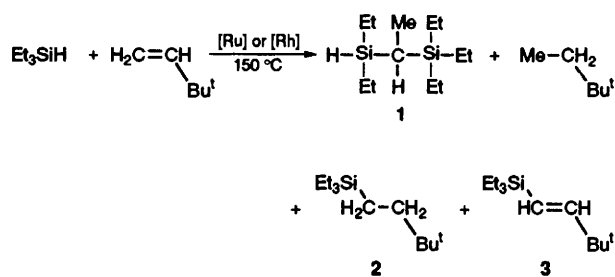
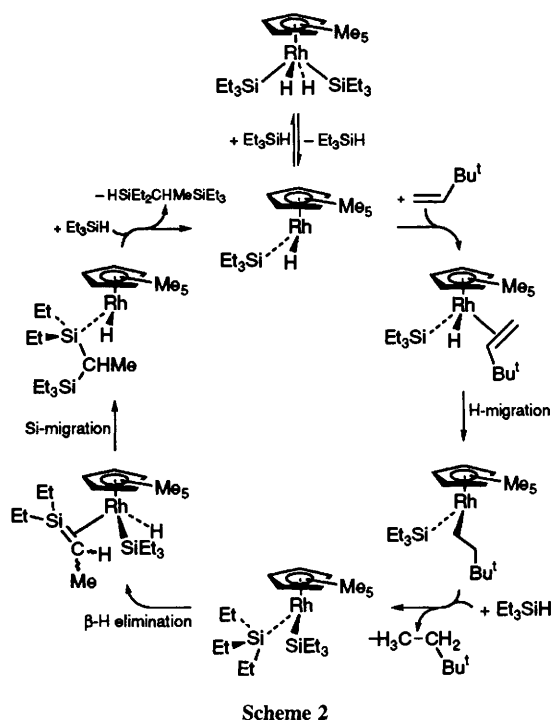


Table 1 Selectivity of dehydrogenative coupling of Et₃Si^a

Catalyst	Et ₃ SiH/ alkene	t/h	Conversion (%)	% 1	% 2	% 3
(η^6 - <i>p</i> -cymene)Ru(H) ₂ (SiEt ₃) ₂	1/1	69	96	78	3	9
(η^6 - <i>p</i> -cymene)Ru(H) ₂ (SiEt ₃) ₂	2/1	71	65	54	1	3
(η^6 - <i>p</i> -cymene)Ru(H) ₂ (SiEt ₃) ₂	1/2	71	100	53	4	23
[(η^6 - <i>p</i> -cymene)RuCl ₂] ₂	1/1	76	94	70	2	9
(η^5 -C ₅ Me ₅)Rh(H) ₂ (SiEt ₃) ₂	1/1	12	99	83	9	3
(η^5 -C ₅ Me ₅)Rh(H) ₂ (SiEt ₃) ₂ (+ Hg ⁰)	1/1	12	99	83	9	3
[(η^5 -C ₅ Me ₅)RhCl ₂] ₂	1/1	12	99	81	8	4
(η^5 -C ₅ Me ₅)Rh(H) ₂ (SiEt ₃) ₂ ^b	1/1	53	65	48	4	13

^a All reactions were conducted at 150 °C with 1–2 mol% catalyst and 2.1 mmol of Et₃SiH; reactions with Ru were conducted in 1 cm³ C₆H₆, those with Rh in 5 cm³ C₆H₁₂. The alkene employed was *tert*-butylethylene, except where noted. Yields were determined by GC relative to an internal standard. ^b Alkene = 1-hexene.



hydrosilylation. Given that **1** is produced by coupling two molecules of Et_3SiH , whereas **2** and **3** arise from the coupling of Et_3SiH with an alkene, it is not surprising that the selectivity for **1** is roughly proportional to the Et_3SiH :alkene ratio (Table 1).

There are two particularly curious points regarding the formation of carbosilane **1** by the dehydrocoupling of Et_3SiH : (i) alkyl group C–H activation is occurring in the presence of the much more reactive Si–H bonds; *i.e.* an Si–C bond is formed instead of a Si–Si bond, and (ii) only regioselective functionalization at the hindered methylene C–H bonds is observed; methyl group activation is not. Both issues are resolved by a mechanism in which the C–H activation occurs by β -hydrogen elimination from a silyl ligand. We have previously presented substantial evidence for this process in ruthenium^{2,3} and osmium⁶ silyl complexes. In the β -hydrogen elimination process, C–H activation is an intramolecular step, always preceded by activation of a silane Si–H bond. The regioselectivity for C–H activation adjacent to silicon is a natural consequence of this process. However, productive C–H activation leading to formation of a new C–Si bond can only occur when there are two silyl groups on the catalyst. In

the proposed mechanism, Scheme 2, a $16e^-$ *cis*-bis(silyl) intermediate is generated by stepwise dehydrogenation of the dihydride catalyst centre by the alkene. Intramolecular activation of a C–H bond by β -H elimination then yields an η^2 -silene, or, if one prefers, a metallated silyl ligand.⁷ Silicon–carbon bond formation is then accomplished by migration of the second silyl to the silene carbon, to yield the $-\text{SiEt}_2\text{CHMeSiEt}_3$ ligand. Addition of Et_3SiH to the metal and elimination of the bulkier silane completes the catalytic cycle.

Many of the steps in the proposed mechanism are identical with those previously suggested for the hydrosilylation of alkenes catalysed by $(\text{C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{H}_4)(\text{SiEt}_3)(\text{H})$ ⁸ and $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}_2]_2$.⁹ The fact that only hydrosilylation products analogous to **2** and **3** were reported by previous researchers may reflect the more hindered alkenes, different solvents and higher temperatures employed in the present studies. The catalytic formation of $\text{HSiEt}_2\text{CHMeSiEt}_3$ by transfer dehydrogenative coupling of Et_3SiH provides a new example of an Si–C bond forming reaction occurring under conditions typically associated with hydrosilylation and silylation chemistry.

Financial support from the US Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, is gratefully acknowledged. D. H. B. also thanks the Alfred P. Sloan Foundation for a research fellowship (1990–1994).

Received, 13th June 1994; Com. 4/03547J

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