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Mechanism of Metal-carbenoid Insertion Into the Si-H Bond

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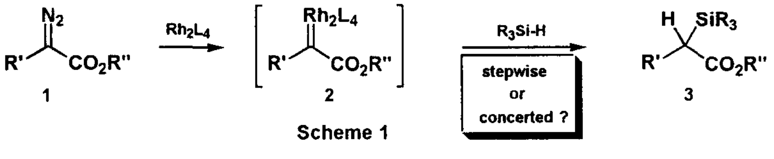
Abstract : Kinetic investigations on the insertion of metal-carbenoid intermediates into the Si-H bond have been carried out. A kinetic isotope effect of 1.5 was found and the plot of log k_X/k_H *vs* σ for the reaction of arylsilanes with EDA, gave a straight line with $\rho = - 0.31$. It was thus concluded that the insertion proceeds through a concerted pathway with development of a small positive charge at the silicon centre and a relatively early transition state.

The metal-catalyzed decomposition of α-diazocarbonyl compounds **1** in the presence of organosilanes is a straightforward and efficient method for the preparation of α-silylcarbonyl substrates **3** (Scheme 1).[1] Doyle introduced $Rh_2(OAc)_4$ as a catalyst with which to perform this reaction under mild conditions and with excellent yields.[2] We have extended this methodology to the synthesis of a variety of α-silyl esters[3] and used this approach in a novel synthesis of allylsilanes via a stereospecific rhodium-vinylcarbenoid insertion in the Si-H bond.[3e] Surprisingly, while the mechanism of the free-carbene insertion into the Si-H bond has been thoroughly studied,[1b,4] little is known about the mode of insertion of the related metal-carbenoid into the Si-H bond. Doyle has suggested that $Rh_2(OAc)_4$-catalyzed decomposition of α-diazocarbonyl compounds leads to an electrophilic metal-carbenoid species (*i.e.* **2**) as a key-intermediate, formed via the reaction of the diazo precursor with the electrophilic rhodium catalyst.[5] The formation of such an intermediate is now generally accepted but its catalytic activity with various substrates (olefins, Si-H, C-H, O-H,...) is not known. During our studies on metal-carbenoid insertion, we suggested that insertion of a rhodium-carbenoid into the Si-H bond occurred via a stepwise mechanism involving an oxidative addition of the Si-H bond to intermediate **2**, followed by a migration of the hydrogen onto the carbenoid centre, the carbon-silicon bond being subsequently formed after reductive elimination.[3d] A similar mechanism was proposed by Taber for the intramolecular insertion of a rhodium-carbenoid into the analogous C-H bond.[6] Later on, however Doyle made the alternative proposition that the insertion into the C-H bond occurred through a concerted pathway.[7]

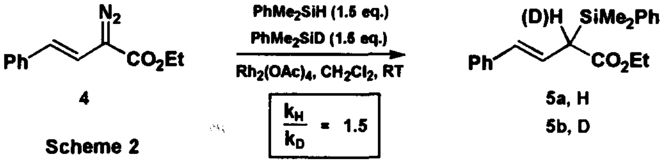


Scheme 1

Both mechanisms might also be invoked for the insertion into the related Si-H bond. While insertion into the C-H bond can be performed only intramolecularly, thus precluding kinetic investigations, the more reactive Si-H bond can react in an intermolecular fashion with diazoesters thus allowing competitive insertion experiments. We thus devised a series of simple competition experiments in order to obtain information on the kinetic of the Si-H bond insertion. We describe herein our experimental evidences that the insertion process occurs through an early transition state in which the silicon group is slightly positively charged. Substituents on the silicon centre which can stabilize this developing positive charge, mainly through inductive effects, accelerate the reaction.

We first investigated the kinetic isotope effect[8] (KIE), running a competition experiment as illustrated in Scheme 2. Reaction of vinyldiazoester **4** in the presence of an equimolar amount of $PhMe_2SiH$ and $PhMe_2SiD$

and $Rh_2(OAc)_4$ as a catalyst afforded the corresponding α-silyl esters **5a** and **5b** in a 6:4 ratio (*i.e.* a KIE of 1.5).[9,10] A variation in the SiH/SiD/diazo ratio (from 1:1:1 to 3:3:1) had no effect on the magnitude of the KIE. This small but significant KIE indicates that *cleavage of the Si-H bond probably occurs in the rate-determining step* and the magnitude of the KIE suggests that the transition state is either very early or very late.



Scheme 2

Further information relating to the mechanism of Si-H insertion were obtained from Linear Free Energy Relationship (LFER) studies using a series of substituted arylsilanes.[11] Competitive insertion reactions were performed starting from an equimolar amount of the arylsilane $PhMe_2SiH$ (1eq.) and various *p*-substituted arylsilanes (p-$XC_6H_4SiMe_2H$) (1eq.) in the presence of ethyldiazoacetate (EDA) (1eq.) and $Rh_2(OAc)_4$. The ratio of the two α-silylacetic esters was measured using 400MHz ^1H NMR. The results of the kinetic studies and the substituent constants σ and σ^+ are summarized in table 1. The relative rates were plotted against Hammett σ constants,[11] affording a ρ value of -0.31 (R=0.993).[12] The negative ρ value using this set of substituent constants indicates that *a small positive charge is developing on the silicon centre at the transition state*. The good correlation observed with σ relative to that of σ^+ (ρ=-0.19, R=0.94) suggests that mesomeric effects are hardly involved in the stabilization of this nascent positive charge. The small polarization of the TS thus indicates *that the cleavage of the Si-H bond and the formation of the new C-Si and C-H bonds are concerted.*

Table 1. Relative rate and σ constants for $Rh_2(OAc)_4$ catalyzed decomposition of EDA in the presence of X-$C_6H_4SiMe_2H$ / $C_6H_5SiMe_2H$ (1:1:1).

X	log k_X/k_H	σ_p	σ_p^+
OCH_3	0.017	-0.28	-0.78
CH_3	-0.017	-0.14	-0.31
F	-0.126	0.15	-0.07
Br	-0.14	0.26	0.15
CF_3	-0.23	0.53	0.61

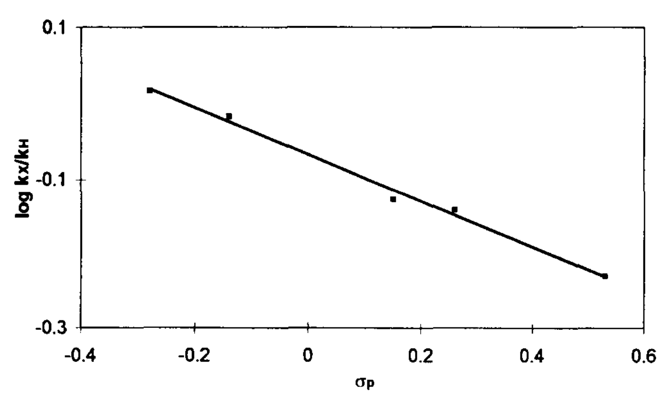


Fig.-1. Plot of log k_X/k_H *vs* σ_p for the reaction of arylsilanes with EDA and $Rh_2(OAc)_4$ at 24°C in CH_2Cl_2.

The above results were further supported by a series of competitive experiments between differently substituted silanes. These have been performed in order to evaluate the electronic and steric influence of the silane on the course of the insertion process. Comparisons have been made within each class of silanes, *i.e.* aryl-, alkyl- and chlorosilanes and crossover experiments between the most reactive of each class of silanes (shaded, Table 2) finally allowed us to set up a silane reactivity scale.

For the alkylsilanes, Et_3SiH was choosen as the reference since Me_3SiH was found difficult to handle under our experimental conditions (25°C). We generally observed a moderate difference of reactivity between the different trialkylsilanes, with Et_3SiH being the most reactive.

Surprisingly, with arylsilanes, addition of an aryl group at silicon decreases the reaction rate. This contrasts with what is known about the stabilization of carbeniums ions.[13] Further studies revealed that Et_3SiH was even more reactive than $PhMe_2SiH$ indicating a predominance of inductive effects over resonance effects, which is in good agreement with the poor correlation observed with σ^+. This parallels some recent studies on hydride transfer reactions from silanes to carbenium ions where alkylsilanes were found to be much more reactive than the aryl analogues indicating the predominance of inductive and field effects over mesomery.[14] The difference of reactivity between aryl- and alkylsilanes is, however, less important in our case due to the occurrence of a partial positive charge instead of a carbenium ion.

The most important and surprising reactivity differences were recorded in the chlorosilane series with the bulky $Cl(t\text{-}Bu)_2SiH$ being the most reactive. For instance, reaction of an equimolar mixture of $ClMe_2SiH$ and $Cl(t\text{-}Bu)_2SiH$ with EDA gave predominantly the α-chlorodi-*t*-butylsilylacetic ester (67:33), indicating that steric hindrance has little effect on the insertion process. The same trend was observed with $Cl(i\text{-}Pr)_2SiH$. *The small influence of steric effects corroborates the assumption that the insertion proceeds through an early transition state in which both protagonists (silane and rhodium-carbenoid) are relatively far away from each other.*[3f,15] Crossover experiments between $PhMe_2SiH$ and Me_2SiClH as before resulted in the unique formation of the α-(phenyldimethylsilyl)acetic ester. This is less surprising since a phenyl group is expected to stabilize much more efficiently the positively charged silicon centre than a chlorine atom (inductive -*I* effect).

This series of experiments finally led to the following reactivity scale for sterically similar silanes towards EDA in the presence of $Rh_2(OAc)_4$: alkyl > aryl > chloro. We noticed that the use of other catalysts such as $Cu(acac)_2$ or $Cu(OTf)_2$ may slightly change the magnitude of k_{rel} but not the order of the silane reactivity.

Table 2. Relative reactivities of organosilanes towards rhodium-carbenoid generated from EDA and $Rh_2(OAc)_4$ at 25°C in CH_2Cl_2.

AlkylSi-H	k_{rel}	**ArylSi-H**	k_{rel}	**ChloroSi-H**	k_{rel}	**Silane-H**	k_{rel}
$Et_3Si\text{-}H$	1	$PhMe_2SiH$	1	$Cl(t\text{-}Bu)_2Si\text{-}H$	1	$Et_3Si\text{-}H$	1
$n\text{-}Hex_3Si\text{-}H$	0.89	Ph_2MeSiH	0.80	$Cl(i\text{-}Pr)_2Si\text{-}H$	0.56	$PhMe_2SiH$	0.78
$n\text{-}Bu_3Si\text{-}H$	0.87	Ph_3SiH	0.64	$Cl(Me)_2Si\text{-}H$	0.49	$Cl(t\text{-}Bu)_2SiH$	0.31
$(i\text{-}Pr)_3Si\text{-}H$	0.75						

In summary, the above results point towards an electrophilic attack of the rhodium-carbenoid species onto the Si-H bond, which would lead to the development of a partial positive charge on silicon at the transition state. Such a picture would closely resemble that proposed for carbomethoxycarbene (ρ=-0.26)[1b] and dichlorocarbene (ρ=-0.632)[4] insertions into the Si-H bond. By analogy with free carbenes, the putative metal-carbenoid species (*i.e.* **2**) can be regarded as an electrophilic species as proposed earlier by Doyle.[5] More recent studies on cyclopropanation of olefins with EDA catalyzed by iron-porphirins also led to low negative ρ values (ρ=-0.68) indicating a deficit of electron density on the alkene moiety at the transition state.[16a] A similar trend was observed in rhodium-catalyzed cyclopropanation using iodonium ylides (ρ = -0.47).[16b]

To conclude, the above observations would support a concerted addition of the Si-H bond onto an electrophilic rhodium-carbenoid centre through a transition state close to that depicted in Figure 2.[17] The retention of configuration at the silicon centre, along with the retention of the geometry of the double bond during vinyl-rhodium carbenoid insertions[3e,18] (R' = vinyl, Fig.-2) seem to be in-keeping with such a mechanism. Moreover, our recent observations that asymmetric insertion into the Si-H bond, using chiral ligands (L*) on rhodium, occurs with high level of enantioselectivity (up to 70% e.e.)[18] suggest that the rhodium and its ligands are bound to the carbenoid centre during the insertion process.

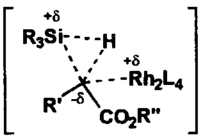


Fig.-2.

This would therefore contradict the mechanism which we have proposed earlier on the basis of experimental data available at that time.[3d,19] However, further studies now underway in our laboratory will be required to provide more definitive conclusions.

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References and Notes

1. (a) Rijkens, F.; Janssen, M.J.; Drenth, W.; VanDerKerk, G.J.M. *J. Organomet. Chem.*, **1964**, *2*, 347-356; (b) Watanabe, H.; Kakano, T.; Araki, K.; Matsumoto, H.; Nagai, Y. *J. Organomet. Chem.*, **1974**, *69*, 389-396; (c) Barnier, J.-P.; Blanco, L. *J. Organomet. Chem.*, **1996**, *514*, 67-71.
2. Bagheri, V.; Doyle, M.P.; Taunton, J.; Claxton, L.E. *J. Org. Chem.*, **1988**, *53*, 6158-6160.
3. (a) Andrey, O.; Landais, Y.; Planchenault, D. *Tetrahedron Lett.*, **1993**, *34*, 2927-2930; (b) Andrey, O.; Landais, Y.; Planchenault, D.; Weber, V. *Tetrahedron,* **1995**, *51*, 12083-12096; (c) Landais, Y.; Planchenault, D. *Tetrahedron,* **1995**, *51*, 12097-12108; (d) Landais, Y.; Planchenault, D. *Tetrahedron Lett.*, **1994**, *35*, 4565-4568; (e) Landais, Y.; Planchenault, D.; Weber, V. *Tetrahedron Lett.*, **1994**, *35*, 9549-9552; (f) Landais, Y.; Planchenault, D. *Tetrahedron*, **1996**, (In press).
4. Seyferth, D.; Damrauer, R.; Mui, J.Y.-P.; Jula, T.F. *J. Am. Chem. Soc.*, **1968**, *90*, 2944-2948.
5. Doyle, M.P. *Recl. Trav. Chim. Pays-Bas*, **1991**, *110*, 305-316.
6. Taber, D.F. in *Comprehensive Organic Synthesis*; Trost, B.M., Fleming, I., Ed.; Pergamon Press: Oxford, U.K. 1991; Vol. 4, pp 1045-1062 and references cited therein.
7. Doyle, M.P.; Westrum, L.J.; Wendelmoed, N.E.W.; See, M.M.; Boone, W.P.; Bagheri, V.; Pearson, M.M. *J. Am. Chem. Soc.*, **1993**, *115*, 958-964.
8. (a) Wiberg, K.B. *Chem. Rev.*, **1955**, *55*, 713-743; (b) Westheimer, F.H. *Chem. Rev.*, **1961**, *61*, 265-273.
9. We first carried out the reaction between **4** and $PhMe_2SiD$ and found that **5b** was obtained in 90% yield, with complete incorporation of deuterium.
10. Independently, KIE were also observed during rhodium-carbenoid insertion into O-H bonds of EtOH/EtOD and H_2O/D_2O which gave KIE values of 2.57 and 1.7 respectively.
11. Hansch, C.; Leo, A.; Taft, R.W. *Chem. Rev.*, **1991**, *91*, 165-195.
12. A strong deviation with X=H is observed. Introduction of this value in the plot of $k_{rel}=f(\sigma_p)$ little affects the ρ value, *i.e.*, $\rho=-0.32$ (R=0.92) for σ and $\rho=-0.18$ (R=0.72) for σ^+.
13. Streitwieser, A., Jr. *Solvolytic Displacement Reactions*; Mc Graw Hill : New-York, 1962, 43.
14. Mayr, H.; Basso, N.; Hagen, G. *J. Am. Chem. Soc.*, **1992**, *114*, 3060-3066 and references cited therein.
15. We have observed previously during diastereoselective insertions using menthol diazoesters, that changing the size of the substituents on silicon and on the diazoesters had little effect on the stereocontrol,[3d,f] again supporting the occurrence of an early transition state.
16. (a) Wolf, J.R.; Hamaker, C.G.; Djukic, J.-P.; Kodadek, T.; Woo, L.K. *J. Am. Chem. Soc.*, **1995**, *117*, 9194-9199; (b) Müller, P.; Fernandez, D. *Helv. Chim. Acta*, **1995**, *78*, 947-958.
17. A three-centered transition state (Fig.-2) is also consistent with the small primary KIE in Scheme 2.[8] It is noteworthy that primary KIE of similar magnitude have been observed for hydride transfer from silanes to carbenium ions.[14] A polar mechanism with rate determining formation of silicenium ion was proposed ($\rho=-2.46$). Such a polar mechanism would imply more charge development at the transition state than that suggested by the LFER studies (Fig.-1) and therefore can be ruled out.
18. Bulugahapitiya, P.; Landais, Y.; Parra-Rapado, L.; Planchenault, D.; Weber, V. *J. Org. Chem.*(Submitted).
19. The oxidative addition of the Si-H bond to a Rh(I)-carbenoid was proposed on the basis of the results obtained from a competition experiment : olefin hydrosilylation-carbenoid insertion.[3d] The hydrosilylation product observed in this case might be formed through an ionic pathway and not via oxidative addition, as suggested by some recent investigations carried out in our laboratories which will be reported in a forthcoming article.

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