An η^2-vinyl pathway may explain net trans hydrosilylation *via* transition metal catalysis even in cyclic cases

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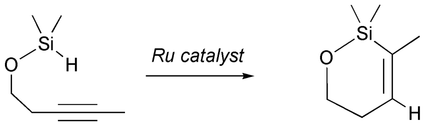
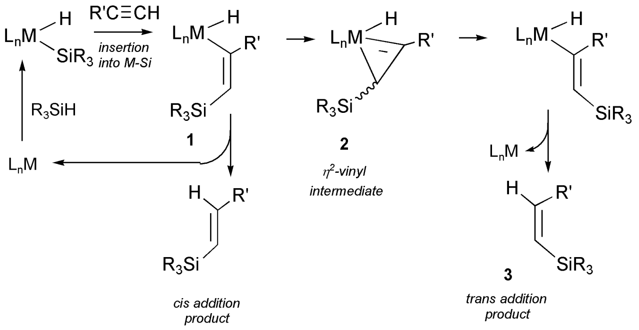
Recently published results seem to rule out the accepted η^2-vinyl pathway for net trans addition in alkyne hydrosilation in cyclic cases. We now suggest how these results can be rationalized on the basis of the accepted mechanism using two concepts: the electrophilic carbene character of η^2-vinyl groups and the tendency of silyl groups to migrate to electron-deficient centers.

Transition metal catalyzed hydrosilylation is not only a useful procedure in synthesis but has also provided a series of interesting mechanistic puzzles. In a recent communication to *J. Am. Chem. Soc.*, Trost and Ball[1] describe an unusual net trans alkyne hydrosilylation (eqn. 1) that seems to rule out the previously accepted mechanism[2,3] for such net trans addition reactions. The purpose of this opinion is to suggest how the new result can indeed be accomodated within the existing mechanism, if an unexpected, but nevertheless plausible, 1,2-silyl shift occurs in the key η^2-vinyl intermediate.



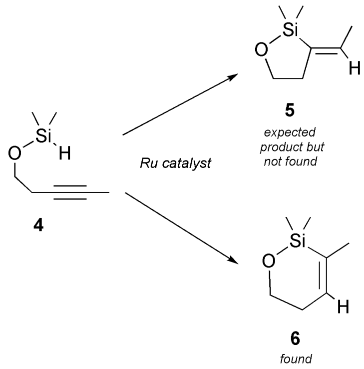
(1)

Net cis addition of R_3Si and H to an alkyne to give the vinylsilane was originally considered as the inevitable outcome of transition metal catalyzed alkyne hydrosilation but Ojima *et al.*found that net anti addition could also occur.[4] Various mechanisms were proposed but these did not prove satisfactory. The currently accepted mechanism was proposed to account for the unexpected predominant (> 99%) net trans hydrosilylation of RC≡CH by a rhodium or iridium catalyst. Both Ojima[3] and Crabtree[2] argued that initial insertion of the C≡C bond takes place exclusively into an Ir–Si bond of the catalyst to give an intermediate **1** [see eqn. (2)] that can rearrange to give the net trans hydrosilylation product, **3**. Tanke and Crabtree [2] proposed that this occurs *via* an η^2-vinyl intermediate **2** while Ojima *et al.*[3] preferred a very closely related zwitterionic form. The bulky L groups on the metal cause the least hindered vinyl isomer to be preferred, and it is this isomer that leads to the trans addition product, **3**, after reductive elimination.

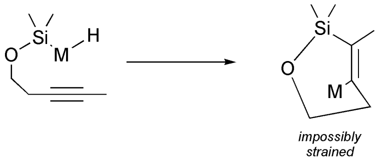


(2)

Trost and Ball[1] now find that in the hydrosilylation of **4** with $[Cp^*Ru(MeCN)_3]BF_4$, the product **5**, expected from the mechanism of eqn. (2), was not formed. Product **6**, with a six-membered ring, is seen instead. The mechanism of eqn. (2), as applied to the reaction of eqn. (3), seems to lead to an absurdity in that its direct application suggests that initial net cis hydrosilylation should give a product with a trans C=C bond within a 6-membered ring, an impossibly strained situation [eqn. (4)], assuming the reaction is intramolecular.



(3)



(4)

The alternative route suggested by Trost and Ball[1] involves M–Si addition across the C≡C bond using orthogonal orbitals of the C≡C bond to give the net trans hydrosilylation product directly.

The original 'η^2-vinyl' pathway can be adapted to the circumstances of eqn. (3), however, if two factors are considered. First, an η^2-vinyl is generally considered[5] to have carbene character at the doubly bonded M=C carbon. Second, 1,2-migrations of silyl groups to electron deficient centers such as carbenes can often occur rather readily.[6,7] Applying these ideas to eqn. (1), initial formation of a 6-membered ring by net cis addition is ruled out because the resulting endocyclic C=C bond cannot be trans, but a 5-membered ring with an exocyclic double bond has no such problem. If the conventional[2] η^2-vinyl intermediate now forms, a simple 1,2-silyl shift to the electron deficient carbon of the carbenoid carbon of the η^2-vinyl leads directly to the observed product **6** without requiring any conformationally strained intermediates [eqn. (5)].

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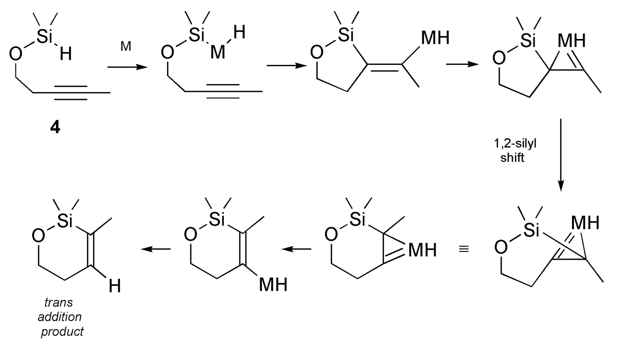
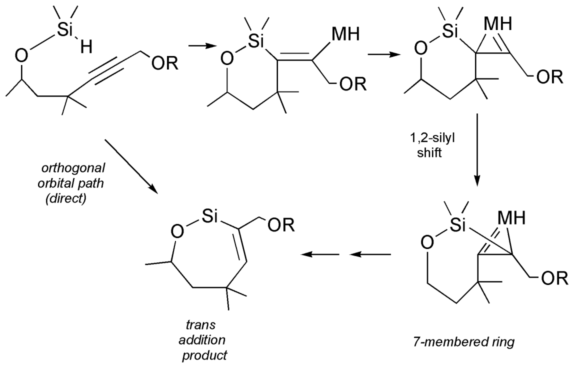


(5)

Such 1,2-shifts—well known for H both in free carbenes[8] and in carbenes coordinated to late transition metals[9] such as Fe(II)—are broadly analogous to Wagner–Meerwein shifts in that H^- migrates to an electrophilic carbene carbon. The cationic character of the metal in this case should favor electrophilicity of the carbene carbon and therefore also favor such rearrangements. Although a silyl version has apparently never so far been seen in a carbene complex, examples where alkyl migration occurs in a carbene complex are long known[5] and 1,2-silyl shifts have been reported[6] or proposed[7] for free carbenes. A 1,2-H shift in an η^2-vinyl has been documented by Casey and coworkers[10] in a cationic $[Cp^*Re(CO)_2(\eta^2\text{-vinyl})]^+$ complex, where it occurs even at −32 °C.

As pointed out by a referee, however, several arguments can be put forward in favor of the orthogonal orbital model. Trost and Ball[1] find that a 7-membered ring is formed in several cases. The driving force for the proposed 1,2-silyl shift is now less obvious and may possibly even be entirely absent because the system would need to go from a six- to a seven-membered ring during any 1,2-shift [eqn. (6)]. In contrast, the orthogonal orbital model is attractive in this case because the longer tether makes achieving the transition state that would lead to the 7-membered ring much easier than in eqn. (1). The 1,2-shift mechanism cannot be entirely excluded, however. Examination of models suggests that the long Si–O and Si–C distances in the relevant intermediates and transition states may permit the 1,2-shift mechanism and favor a seven-membered ring. Indeed, a Wagner–Meerwein 1,2-shift has even been observed[11] to convert a 6- to a 7-membered ring in a case where, as here, a single Si atom is present in the ring, but the formation of a new Si–Cl bond in this process could easily provide extra driving force favoring the 7-membered ring.



(6)

A better analogy may be ring closure of $Me_2HSi(CH)_nCH{=}CH_2$ ($n = 4, 5$) *via* hydrosilation with H_2PtCl_6, which gives both $(n+2)$- and $(n+3)$-membered rings in a 1:1 ratio, while the same silane having $n = 3$ gives mainly the 5-membered ring and $n = 6$ only the 8-membered ring.[12] Differences in the kinetic preferences to form 6-, 7- and 8-membered SiC_5, SiC_6 and SiC_7 rings may therefore be small, and by extension, the same may be true here for $SiOC_4$, $SiOC_5$ and $SiOC_6$ rings.

The orthogonal orbital model also accounts for the reaction taking place for alkynes and allenes but not alkenes; the latter are normally[2] less reactive in hydrosilylation catalysis, however, so this argument is not definitive.

If a 1,2-silyl shift is postulated, the η^2-vinyl mechanism therefore seems adequate to explain the unexpected new result of eqn. (3) and plausibly even that of eqn. (6). If this is correct, other examples of such a shift should be observable in suitable systems. Further work, including experimental tests and theoretical calculations, will be required to definitively distinguish between the η^2-vinyl and orthogonal orbital proposals for this type of alkyne hydrosilation.

Acknowledgements

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