Trans Additions of Silanes to 1-Alkynes Catalyzed by Ruthenium Complexes: Role of in Situ Formed Polynuclear Aggregates

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Received July 2, 2002

Summary: (Z)-Alkenyl ligands are formed by insertion of 1-alkynes into bridging hydrides. The unusual stereoselectivity of this elementary step may account for the selectivity toward (Z)-alkenylsilanes frequently observed in 1-alkyne hydrosilylations catalyzed by basic late-transition-metal complexes.

Homogeneous reactions catalyzed by transition-metal complexes often involve unsaturated metal species with potentially bridging ligands such as hydrides. These are propitious features for the formation of polynuclear compounds,[1] which should be regarded as likely components of catalytic reactions. When observable, such polynuclear aggregates usually play just a marginal role during catalysis, as stable resting states for the catalyst.[2] However, the feasibility of some other catalytic processes seems to rely entirely on the performance of polynuclear species or transition states.[3,4] The catalysis through these polynuclear compounds can involve several types of intermetallic cooperation mechanisms, which may favor faster reaction rates, and selectivities different from those obtained through possible mononuclear catalytic cycles.[3,5]

With regard to the abundance of reported examples, the formation of polynuclear aggregates seems to be specially favored in reactions involving organosilanes.[6,7] Actually, dinuclear species have been recognized to be the true catalysts in reactions such as dehydrogenative dimerizations of silanes and hydrosilylations.[8,9] These latter reactions have also provided numerous examples of another peculiar feature, namely the unusual trans addition of silanes to 1-alkyne triple bonds to give (*Z*)-alkenylsilanes.[10] In this communication, which focuses on ruthenium-catalyzed hydrosilylations of phenylacetylene, we present evidence suggesting that the proclivity of silanes to yield polynuclear compounds and the frequent achievement of unusual stereoselectivities in 1-alkyne hydrosilylations are not independent facts. Actually, they seem to be cause and effect.

Table 1. Addition of $HSiEt_3$ to PhC≡CH Catalyzed by $[RuH(XY)(CO)(PR_3)_2]$ Precursors[a]

					silylated products (%)		
					PhC=CHSiEt$_3$		
	XY	PR_3	*T* (K)	time to 100% yield (h)	Z	E	PhC≡CSiEt$_3$
1	Cl	P^iPr_3	298	1	100	0	0
2	acetate	P^iPr_3	298	1.5	97	2	1
3	acac	P^iPr_3	298	164	95	3	1
4	acetate	PPh_3	353	20	31	10	59
5	Cl, PPh_3	PPh_3	353	20	35	38	27

[a] Conditions: solvent, 1,2-dichloroethane; $HSiEt_3$/PhC≡CH/catalyst 100/100/1; $[Ru]_0 = 2.23 \times 10^{-3}$ M.

The hydrosilylation of alkynes catalyzed by Ru(II)−phosphine compounds has been thoroughly investigated.[11] The selectivity of these reactions has been found to be dependent on, inter alia, the nature of the catalyst precursor, as illustrated in Table 1 for some related five- and six-coordinate Ru(II) complexes in the addition of $HSiEt_3$ to PhC≡CH. It is worth noting that all compounds containing the basic P^iPr_3 phosphine selectively produce the (*Z*)-alkenylsilane, even though their reaction rates are very different, depending on the nature of the other ancillary ligands. On the other hand, the catalysts containing PPh_3 are less selective, producing (*Z*)- and (*E*)-alkenylsilanes together with products of dehydrogenative silylation: PhC≡CSiEt$_3$ and styrene.

A detailed inspection of the course of these latter nonselective processes has revealed strong variations

(1) Venanzi, L. M. *Coord. Chem. Rev.* **1982**, *43*, 251−274.
(2) For examples, see: Chaloner, P. A.; Esteruelas, M. A.; Joó, F.; Oro, L. A. *Homogeneous Hydrogenation*; Kluwer: Dordrecht, The Netherlands, 1993.
(3) *Catalysis by Di- and Polynuclear Metal Clusters Complexes*; Adams, R. A., Cotton, F. A., Eds.; Wiley-VCH: New York, 1998.
(4) See for example: (a) Muetterties, E. L. *J. Organomet. Chem.* **1980**, *200*, 177−190. (b) Esteruelas, M. A.; Oro, L. A.; Valero, C. *Organometallics* **1992**, *11*, 3362−3369. (c) Broussard, M. E.; Juma, B.; Train, S. G.; Peng, W. J.; Laneman, S. A.; Stanley, G. G. *Science* **1993**, *260*, 1784−1788. (d) Grumbine, S. K.; Tilley, T. D. *J. Am. Chem. Soc.* **1994**, *116*, 6951−6952. (e) Torres, F.; Sola, E.; Elduque, A.; Martínez, A. P.; Lahoz, F. J.; Oro, L. A. *Chem. Eur. J.* **2000**, *6*, 2120−2128.
(5) (a) Fryzuk, M. D.; Piers, W. E. *Organometallics* **1990**, *9*, 986−998. (b) Bosnich, B. *Inorg. Chem.* **1999**, *38*, 2554−2562. (c) Sola, E.; Torres, F.; Jiménez, M. V.; López, J. A.; Ruiz, S. E.; Lahoz, F. J.; Elduque, A.; Oro, L. A. *J. Am. Chem. Soc.* **2001**, *123*, 11925−11932.
(6) (a) Braunstein, P.; Knorr, M.; Stern, C. *Coord. Chem. Rev.* **1998**, *178*−*180*, 903−965. (b) Ogino, H.; Tobita, H. *Adv. Organomet. Chem.* **1998**, *42*, 223−290. (c) Braunstein, P.; Boag, N. M. *Angew. Chem., Int. Ed.* **2001**, *40*, 2427−2433.
(7) Osakada, K. *J. Organomet. Chem.* **2000**, *611*, 323−331.
(8) (a) Rosenberg, J.; Fryzuk, M. D.; Rettig, S. J. *Organometallics* **1999**, *18*, 958−969. (b) Fryzuk, M. D.; Rosenberg, L.; Rettig, S. J. *Organometallics* **1996**, *15*, 2871−2880.
(9) Voskoboynikov, A. Z.; Shestakova, A. K.; Beletskaya, I. P. *Organometallics* **2001**, *20*, 2794−2801.
(10) (a) Ojima, I.; Li, Z.; Zhu, J. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Vol. 2, pp 1687−1792. (b) Tanke, R. S.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 7984−7989.
(11) (a) Maruyama, Y.; Yamamura, K.; Sagawa, T.; Katayama, H.; Ozawa, F. *Organometallics* **2000**, *19*, 1308−1318. (b) Maruyama, Y.; Yamamura, K.; Nakayama, I.; Yoshiuchi, K.; Ozawa, F. *J. Am. Chem. Soc.* **1998**, *120*, 1421−1429. (c) Maddock, S. M.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *Organometallics* **1996**, *15*, 1793−1803. (d) Christ, M. L.; Sabo-Etienne, S.; Chaudret, B. *Organometallics* **1995**, *14*, 1082−1084. (e) Esteruelas, M. A.; Herrero, J.; Oro, L. A. *Organometallics* **1993**, *12*, 2377−2379.

10.1021/om0205243 CCC: $22.00
Publication on Web 08/31/2002

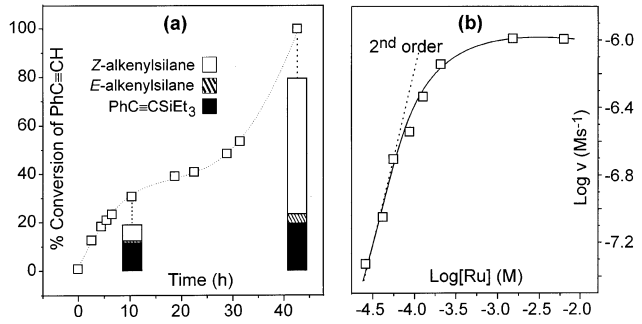
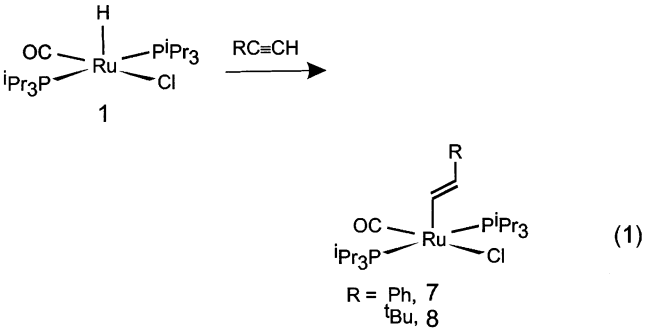


Figure 1. (a) Kinetic profile for the addition of $HSiEt_3$ to PhC≡CH with [RuH(κ^2*O*-O_2C^tBu)(CO)(PPh_3)$_2$] (**6**) as catalyst precursor, under the conditions detailed in Table 1. T = 353 K. (b) Dependence of the initial hydrosilylation rate upon the initial concentration of **1**. T = 298 K.

of the rate and selectivity along the reaction, as shown in Figure 1a for the catalyst precursor [RuH(κ^2*O*-O_2C^t-Bu)(CO)(PPh_3)$_2$] (**6**). The profile of this reaction suggests that the initial active species, which mainly catalyzes dehydrogenative silylation, progressively generates a different catalyst, which is faster and selectively produces the (*Z*)-alkenylsilane. The other PPh_3 precursors in Table 1 have been found to behave in a way similar to **6**, although they require different induction periods to form the second active species.[12] Actually, all compounds in Table 1 can fit within a similar behavior, assuming that formation of the fast and selective catalyst from the P^iPr_3-containing precursors is nearly immediate.

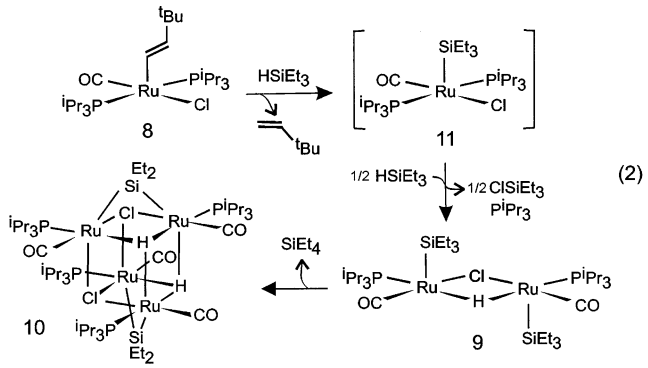
An early reactivity study of precursor **1** under the conditions of this hydrosilylation reaction revealed the presence of the alkenyl complex [Ru((*E*)-CH=CHPh)-Cl(CO)(P^iPr_3)$_2$] (**7**) (eq 1) as the only spectroscopically



(1)

observable species during catalysis.[11e] By using this alkenyl compound as catalyst precursor and the deuterated alkyne PhC≡CD as substrate, we have evidenced that **7** is just a spectator during catalysis, since the catalytic reaction readily produced the deuterated (*Z*)-alkenylsilane without any sign of deuterium incorporation into **7**. It follows from this observation that the true catalyst of this hydrosilylation reaction is formed in amounts not detectable by spectroscopy.

Despite this inconvenience for the identification of the catalytically active species, we searched for possible evolutions of **7** under catalytic conditions, by exploring the reactivity of related alkenyl derivatives. Thus, the complex [Ru((*E*)-CH=CH^{t}Bu)Cl(CO) (P^iPr_3)$_2$] (**8**) was found to react slowly with an excess of $HSiEt_3$ through the reaction sequence depicted in eq 2. Complexes **9** and



(2)

10 have been characterized by X-ray diffraction methods (Figure 2). The organic and silylated products also formed along this reaction sequence have been identified by GC-MS and NMR methods.

Equation 2 shows noticeable similarities with the evolution reported for the rhodium complex [RhCl(P^i-Pr_3)$_2$] in the presence of triarylsilanes,[7] which involved the sequential formation of a five-coordinate hydride silyl compound, a dinuclear complex closely related to **9**, and a silylene-bridged dinuclear species. The similarity between both sequential reactions strongly suggests that reorganization into polynuclear aggregates constitutes a favored alternative for mononuclear silyl complexes that accumulate strong donor ligands. It is worth noting that several stable PPh_3 analogues of the non-observed silyl complex **11** have been reported,[11a−c,13] whereas similar compounds containing both basic silyl ligands and alkylphosphines remain unknown.

The likely formation of polynuclear species suggested by the aforementioned reactivity also provides satisfactory explanations for the kinetic and stereochemical features of these catalytic reactions. Figure 1b illustrates the dependence of the initial hydrosilylation rate upon the initial concentration of precursor **1**. At low precursor concentrations, the experimental data reveal a second-order dependence, which suggests the participation during catalysis of dinuclear intermediates or transition states. The progressive deviation from this second-order dependence at higher precursor concentrations can be rationalized as the result of reversible further aggregations of the active species into compounds of higher nuclearity. In the presence of such aggregates, the concentration of the active species would depend on the stability constants of the aggregates rather than on the concentration of the added precursor. The possible behavior of these proposed aggregates can be illustrated by compound **10**, in which the facile cleavage of the triply (μ_3) bridging hydrides and chlorides has been found to afford unsaturated silylene-bridged dinuclear fragments. The activation parameters for this fragmentation process have been estimated by line-shape analysis of the temperature-dependent $^{31}P\{^1H\}$ NMR spectra of **10** in toluene-d_8 as $\Delta H^{\ddagger} = 19(\pm1)$ kcal mol^{-1} and $\Delta S^{\ddagger} = 22(\pm1)$ eu.

(12) For similar "autocatalytic" kinetic profiles, see: (a) Radu, N. S.; Tilley, T. D. *J. Am. Chem. Soc.* **1995**, *117*, 5863−5864. (b) Fu, P.; Brard, L.; Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 7157−7168.

(13) Clark, G. R.; Rickard, C. E. F.; Roper, W. R.; Salter, D. M.; Wright, L. J. *Pure Appl. Chem.* **1990**, *62*, 1039−1042.

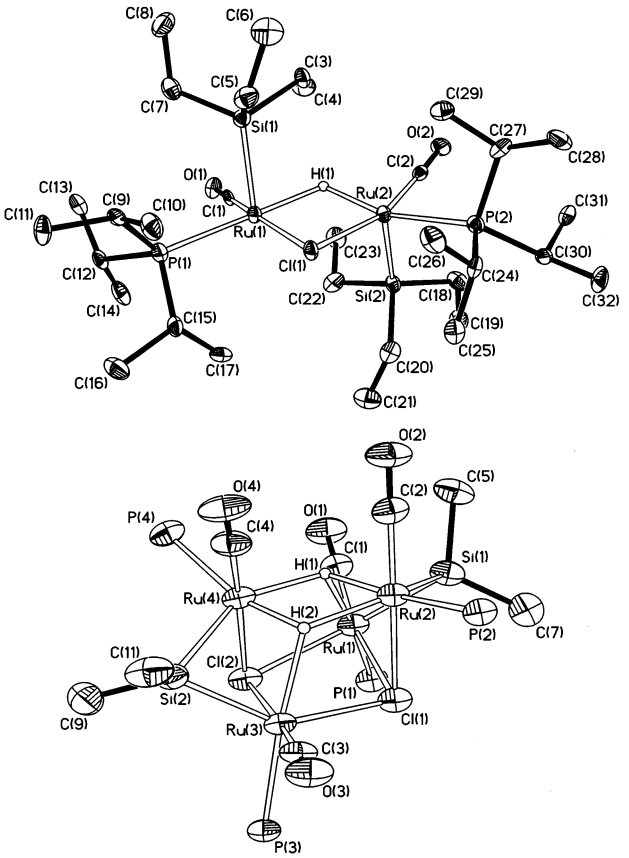
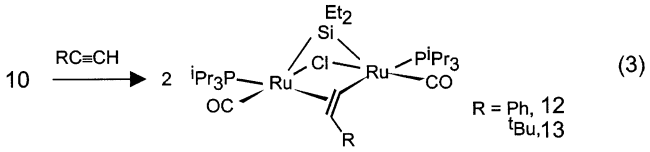


Figure 2. Molecular representations of complexes **9** (above) and **10** (below). The ^{i}Pr groups of the phosphines and the methyl groups of the silylene bridges have been omitted for clarity in the structure of **10**. Selected interatomic distances (Å) and angles (deg): **9**: Ru(1)···Ru(2) = 2.9029(8), Ru(1)−P(1) = 2.3654(18), Ru(1)−Cl(1) = 2.4145(17), Ru(1)−Si(1) = 2.364(2), Ru(1)−H(1) = 1.91(4), Ru(2)−P(2) = 2.3772(19), Ru(2)−Cl(1) = 2.4204(16), Ru(2)−Si(2) = 2.3685(19), Ru(2)−H(1) = 1.80(4); Ru(1)−Cl(1)−Ru(2) = 73.80(5), Cl(1)−Ru(1)−C(1) = 167.4(2), Cl(1)−Ru(1)−Si(1) = 104.13(6), P(1)−Ru(1)−Si(1) = 102.20(7), Cl(1)−Ru(2)−C(2) = 163.9(2), Cl(1)−Ru(2)−Si(2) = 105.18(6), P(2)−Ru(2)−Si(2) = 102.52(7). **10**: Ru(1)···Ru(2) = 2.8222(10), Ru(3)···Ru(4) = 2.8278(10), Ru(1)−Si(1) = 2.363(3), Ru(1)−Cl(1) = 2.511(2), Ru(1)−Cl(2) = 2.686(2), Ru(1)−H(1) = 2.19, Ru(2)−Si(1) = 2.377(3), Ru(2)−Cl(1) = 2.469(2), Ru(2)−H(1) = 1.66, Ru(2)−H(2) = 2.00, Ru(3)−Cl(1) = 2.675(2), Ru(3)−Cl(2) = 2.511(2), Ru(3)−H(2) = 2.09, Ru(4)−Cl(2) = 2.491(2), Ru(4)−H(1) = 1.62, Ru(4)−H(2) = 1.94; Ru(1)−Si(1)−Ru(2) = 73.09(8), Ru(1)−Cl(1)−Ru(2) = 69.03(6), Ru(1)−Cl(1)−Ru(3) = 100.01(8), Ru(1)−Cl(2)−Ru(3) = 99.72(8), Ru(1)−Cl(2)−Ru(4) = 84.60(7), Ru(2)−Cl(1)−Ru(3) = 86.06(7), Ru(3)−Cl(2)−Ru(4) = 68.85(6).

Compound **10** has been found to react with PhC≡CH and ^{t}BuC≡CH, affording the dinuclear alkenyl complexes **12** and **13**, respectively (eq 3). Above 223 K, the spectroscopic data of these compounds indicate symmetric C_s structures, suggesting either symmetric coordination modes for the bridging alkenyl ligands or, most likely, the fast exchange between degenerate structures that contain asymmetric $\mu,\eta^1{:}\eta^2$ alkenyl ligands. Interestingly, the existence of an NOE effect between the ^{1}H NMR signals corresponding to the vinylic hydrogens indicates an unexpected *Z* stereochemistry for the bridging alkenyl ligands.



This stereochemistry could arise from an insertion mechanism comprising the alkyne coordination to one metal center followed by an exo attack of the hydride from the neighboring metal atom, in contrast to the endo attack expected for an insertion into a mononuclear hydride. Such hydride exo attacks have been previously proposed in reactions involving dinuclear complexes or transition states,[5a,14] and precedents for similar trans insertions of alkynes into bridging hydrides are known.[15]

Complexes **12** and **13** have been found to be inert toward triethylsilane, which indicates that compounds **9**−**13** are not true intermediates in the catalytic hydrosilylation reaction. Nevertheless, the formation of such compounds by reaction of the catalyst resting states (e.g. compounds **7** and **8**) with excess silane can be regarded as a sound indication for the proclivity of basic catalyst precursors to furnish polynuclear species under the conditions of catalytic hydrosilylation, even though the actual polynuclear species formed in the presence of 1-alkynes are likely to be different from those described herein, which are formed in the absence of this substrate. Taking into account that participation of polynuclear intermediates or transition states can also provide satisfactory explanations for the observed kinetic and regioselectivity features of these catalytic reactions, we believe that the polynuclear mechanistic approach outlined in this communication could constitute a useful tool for mechanistic understanding and catalyst improvement.

Acknowledgment. We thank the Plan Nacional de Investigación, MCYT (Project No. BQU2000-1170).

Supporting Information Available: Synthesis and characterization data for **6, 8**−**10**, **12**, and **13**, variable-temperature NMR data, X-ray information on **9** and **10**, and details of catalytic and kinetic studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) (a) Jiménez, M. V.; Sola, E.; Martínez, A. P.; Lahoz, F. J.; Oro, L. A. *Organometallics* **1999**, *18*, 1125−1136. (b) Wakatsuki, Y.; Koga, N.; Werner, H., Morokuma, K. *J. Am. Chem. Soc.* **1997**, *119*, 360−366. (c) Xiao, J.; Cowie, M. *Organometallics* **1993**, *12*, 463−472.

(15) (a) Shima, T.; Suzuki, H. *Organometallics* **2000**, *19*, 2420−2422. (b) Conole, G.; Henrick, K.; McPartlin, M.; Horton, A. D.; Mays, M. J. *New J. Chem.* **1988**, *12*, 559.