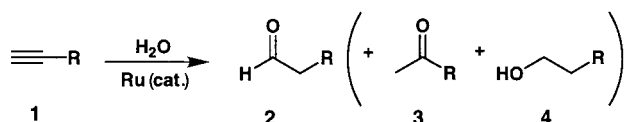


The First Anti-Markovnikov Hydration of Terminal Alkynes: Formation of Aldehydes Catalyzed by a Ruthenium(II)/Phosphane Mixture

Makoto Tokunaga and Yasuo Wakatsuki*

The use of water as a reagent in organic synthesis is an important topic from the viewpoint of economics, safety, and the environment.^[1] For example, metal-catalyzed hydration of alkynes provides an important route to carbonyl compounds. Since all known additions of water to terminal alkynes follow Markovnikov's rule, the hydration of 1-alkynes with Hg^{II}/acid,^[2] Au^{III},^[3] Ru^{III},^[4] RhCl₃,^[5] Pt^{II},^[6] or other metal catalysts^[7] leads exclusively to ketones.^[2] We report herein a novel hydration of terminal alkynes catalyzed by Ru^{II} complexes, which in the presence of appropriate auxiliary phosphane ligands leads to predominantly anti-Markovnikov addition of water and yields aldehydes with only a small amount of ketones (Scheme 1).



a, R = *n*-C₄H₉
b, R = *n*-C₆H₁₃
c, R = *n*-C₁₀H₂₁
d, R = *t*-C₄H₉
e, R = Ph
f, R = CH₂Ph
g, R = (CH₂)₃Cl
h, R = (CH₂)₂OCH₂Ph

Scheme 1. Ru-catalyzed anti-Markovnikov hydration of terminal alkynes.

In preliminary experiments, hydration of 1-octyne (**1b**) in aqueous ethanol in the presence of 5 mol% of [RuCl₂(C₆H₆)(PPh₃)]^[8] as the catalyst precursor gave carbonyl products in 74% yield with an aldehyde/ketone ratio of 1/8 (Table 1, method D). Addition of PPh₃ to the initial reaction mixture inverted the aldehyde/ketone ratio to 5/1 but also lowered the efficiency of the reaction, so that the aldehyde was obtained in less than 10% yield. We investigated about 20 different phosphanes under various reaction conditions, two of which, PPh₂(C₆F₅) and P(3-C₆H₄SO₃Na)₃, led to selective anti-Markovnikov addition of water and satisfactory yields of aldehydes.

The optimum conditions for the reaction with the fluorinated phosphane involve the addition of 10 mol% of [RuCl₂(C₆H₆)(PPh₂(C₆F₅))] and 30 mol% of PPh₂(C₆F₅) to a solution of a 1-alkyne in aqueous 2-propanol (method A). Hydration of **1b** gave 1-octanal (**2b**) in 75% yield together with only 4.5% of methyl hexyl ketone, as determined by GLC analysis (Table 1). This method is applicable not only to other simple 1-alkynes (**1a**, **1c**), but also to substrates with a phenyl (**1f**), chloro (**1g**), or benzyl ether group (**1h**). The highest aldehyde selectivity, (aldehyde/ketone ratio of 67/1) was achieved with **1g**. In contrast, *tert*-butylacetylene (**1d**)

Table 1. Hydration of terminal alkynes **1a–h** under the conditions of methods A–D.

Substrate	Method ^[a]	T [°C]	t [h]	Yield [%] ^[b]			2/3
				2	3	4	
1a	A	65	12	71	3.0		24/1
1b	A	65	12	75	4.5		17/1
1b	B	100	40	45(41)	4.5	8.8	10/1
1b	C	100	40		6.1	61(58)	10/1 ^[c]
1b	D	100	14	8.0	66		1/8
1c	A	80	7	51(50)	3.9		13/1
1c	B	100	36	40	4.4	1.2	9/1
1c	C	100	43		5.3	53(53)	10/1 ^[c]
1d	A	80	18	0.9			1/0
1e	A	80	20	0.7	0.7		1/1
1e	D	100	24		41		0/1
1f	A	70	12	65	7.0	2.8	9/1
1f	C	80	42	2.2	6.3	59	9/1 ^[c]
1f	D	80	22	4.3	58		1/13
1g	A	70	40	60	0.9		67/1
1h	A	80	12	67 (62)	7.2		9/1
1h	D	80	24	3.6	58 (56)		1/16

[a] Method A: [RuCl₂(C₆H₆)(PPh₂(C₆F₅))] + 3 PPh₂(C₆F₅) in 2-propanol. Method B: [RuCl₂(C₆H₆)₂ + 8 P(3-C₆H₄SO₃Na)₃ in 2-methoxyethanol. Method C: [RuCl₂(C₆H₆)₂ + 8 P(3-C₆H₄SO₃Na)₃ in ethanol or 2-propanol. Method D: [RuCl₂(C₆H₆)(PPh₃)] in ethanol or 2-propanol. [b] GLC yield; yield of isolated product in parentheses. [c] 4/3.

and phenylacetylene (**1e**) gave only traces of aldehyde; this shows the steric limitations of this system. When [RuCl₂(C₆H₆)(PPh₂(C₆F₅))] and 3 equiv of PPh₂(C₆F₅) were heated in 2-propanol to the reaction temperature (80 °C), the C₆H₆ ligand was liberated, as monitored by ¹H NMR spectroscopy. Hence, the initial active species in the catalytic cycle under the conditions of method A is probably of the type [RuCl₂{PPh₂(C₆F₅)_x}]^[9]

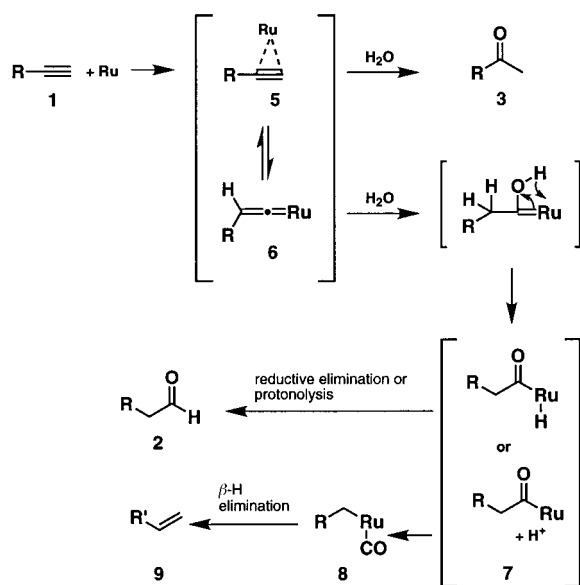
The water-soluble ligand P(3-C₆H₄SO₃Na)₃ (TPPTS) is also a good auxiliary ligand. The use of [RuCl₂(C₆H₆)₂ (5 mol%), TPPTS (40 mol%), and 2-methoxyethanol as the solvent (method B) gave aldehyde/ketone ratios of 9/1 to 10/1 and the hydrated products in 40–45% yield (Table 1). With ethanol or 2-propanol as solvent (method C), the aldehydes were reduced to primary alcohols, while ketones remained inert under these reaction conditions. Detection of acetaldehyde diethyl acetal in the reaction mixture indicates a Meerwein–Ponndorf–Verley type reduction mechanism. Use of the water-soluble phosphane has a practical advantage: The catalyst can easily be recovered after the reaction by using a two-phase system.^[10]

Although this reaction represents, to the best of our knowledge, the first example of the hydration of 1-alkynes to aldehydes, some related stoichiometric reactions are known in the coordination chemistry of vinylidenes, which are tautomers of 1-alkynes.^[11] Bruce et al.^[11b] observed that the reaction of the cationic phenylvinylideneruthenium complex [Ru(C=CHPh)(PPh₃)(L)(η⁵-C₅H₅)]⁺ with water gave the neutral phenylacetyl complex [Ru(COCH₂Ph)(PPh₃)(L)(η⁵-C₅H₅)] (L = CO) or the benzyl carbonyl complex [Ru(CH₂Ph)(CO)(L)(η⁵-C₅H₅)] (L = PPh₃). A similar reaction takes place in a related iron complex.^[11a] The reaction mechanism was recently investigated in detail by Bianchini et al.^[11g] Intramolecular attack of coordinated water on the vinylidene ligand gives a hydroxycarbene, which is deproto-

[*] Dr. Y. Wakatsuki, Dr. M. Tokunaga
 The Institute of Physical and Chemical Research (RIKEN)
 Wako-shi, Saitama, 351-0198 (Japan)
 Fax: (+81) 48-462-4665
 E-mail: waky@postman.riken.go.jp

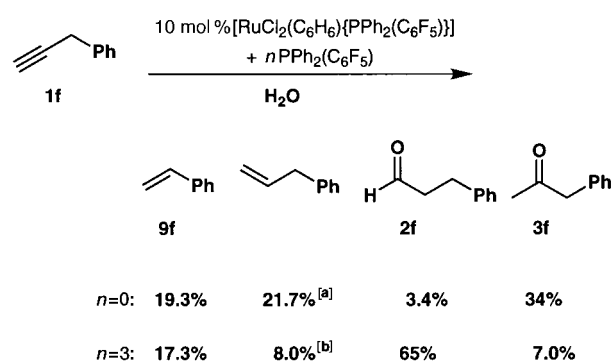
nated to a phenylacetyl ruthenium species, decarbonylation of which gives a benzylruthenium intermediate. Notably, they detected phenylacetaldehyde by GC/MS when the phenyl-vinylidene ruthenium complex was hydrated under CO (30 atm). The highly electrophilic nature of vinylidene C_α atoms and their empty p orbital are well documented by reactions with nucleophiles^[12] and by theoretical studies.^[13]

It is therefore likely that the present ruthenium-catalyzed hydration of terminal alkynes involves the initial tautomerization of 1-alkyne complex **5** to the vinylidene complex **6** followed by the attack of the oxygen atom of water at the vinylidene C_α atom to form the hydroxycarbene intermediate and then the acyl intermediate **7** (Scheme 2). The formation of



Scheme 2. Proposed reaction path for Ru-catalyzed hydration.

ketones by metal-catalyzed hydration of alkynes, on the other hand, involves the nucleophilic attack of H₂O on a η^2 -coordinated alkyne with Markovnikov regioselectivity (**5** $\rightarrow$ **3** in Scheme 2).^[2, 4c, 5, 6b, 7b] The C–C bond cleavage or decarbonylation reaction **7** $\rightarrow$ **8** is expected to occur together with the main reaction, formation of aldehyde, since it is a highly facile reaction path in the stoichiometric systems of Bruce et al. and Bianchini et al. Indeed, olefins with one less carbon atom were always detected by GC in our catalytic system. Most evident in this respect was the hydration of **1f**, which gave up to 17% of styrene (**9f**) as the major by-product under the conditions of method A (Scheme 3). The amount of **9f** increased, albeit by only a few percent, when the reaction was carried out without additional phosphane; the major product was ketone **3f**. We confirmed further that aldehyde **2f**, once formed, is not decarbonylated: When the hydration of **1b** was carried out in the presence of **2f**, the aldehyde remained intact, and no styrene was formed. The ruthenium-containing solid recovered after the reaction showed IR absorption bands for coordinated CO ligands (1970–2070 cm⁻¹). All of these observations are in accord with the proposed reaction path of Scheme 2.



Scheme 3. Influence of the addition of phosphane on the yields of products in the hydration of **1f**. [a] Contains 6.2% β -methylstyrene. [b] Contains 2.1% β -methylstyrene.

We believe that the role of the added phosphane is to shift the equilibrium between **5** and **6** in favor of the vinylidene complex and to retard the decarbonylation of the intermediate **7**. A pronounced effect of the amount and type of added phosphane ligands was noted previously in a Ru^{II}-catalyzed dimerization of a terminal acetylene, in which tautomerization of the 1-alkyne to the corresponding vinylidene plays an important role, as in the present case.^[14]

Experimental Section

All reactions were carried out under an atmosphere of argon. [RuCl₂(C₆H₆)(PPh₂(C₆F₅))] was synthesized by a procedure similar to that for [RuCl₂(C₆H₆)(PPh₃)].^[8] ¹H NMR (270 MHz, CDCl₃): δ = 5.55 (s, 6H, C₆H₆), 7.34–7.50, 7.80–7.92 (m, 10H, PPh₂(C₆F₅)); ³¹P NMR (162 MHz, CDCl₃): δ = 17.0 (t, *J* = 10.3 Hz); elemental analysis calcd for C₂₄H₁₆Cl₂F₅PRu: C 47.85, H 2.68; found C 47.44, H 2.69.

Method A: 1-Octyne (110.2 mg, 1.0 mmol) was added to a mixture of [RuCl₂(C₆H₆)(PPh₂(C₆F₅))] (60.2 mg, 0.1 mmol) and PPh₂(C₆F₅) (105.7 mg, 0.3 mmol) in 2-propanol/water (2.5/0.75 mL). The mixture was stirred for 12 h at 65 °C, then Et₂O (5 mL) was added, and the solution was dried with Na₂SO₄. Yields were determined by GC (nonane as internal standard).

Method C: [RuCl₂(C₆H₆)₂] (25.0 mg, 0.05 mmol) and P(3-C₆H₄SO₃Na)₃ (227.4 mg, 0.4 mmol) were stirred for 3 min at 100 °C in water (1.25 mL), then 1-octyne (110.2 mg, 1.0 mmol) and ethanol (1.25 mL) were added, and the mixture was stirred for 40 h at 100 °C. Et₂O (5 mL) was added, and the organic layer was separated. The products were separated by column chromatography on silica gel (hexane/Et₂O 1/1) to give pure 1-octanol (75.5 mg, 58%).

All the organic products obtained in this study are known. Authentic samples were commercially available for all compounds except for **3f** and **2g** (both synthesized from the corresponding alcohols) and **2h** (characterized by GC/MS and ¹H and ¹³C NMR spectroscopy; data are consistent with those reported in R. Baudouy, P. Prince *Tetrahedron* **1989**, 45, 2067).

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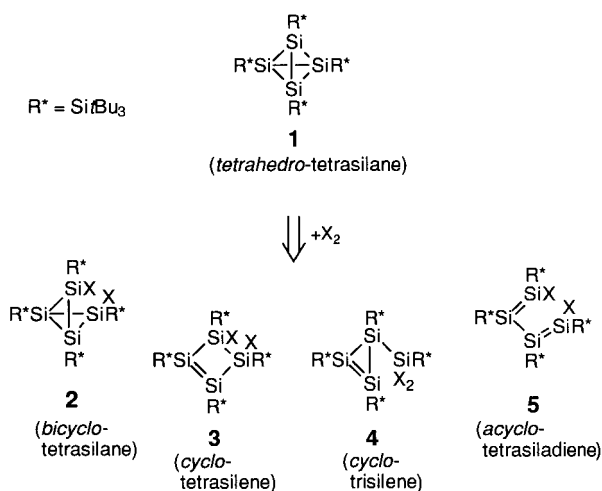
Diiodotetrasupersilylcyclotetrasilene ($(t\text{Bu}_3\text{Si})_4\text{Si}_4\text{I}_2$)—A Molecule Containing an Unsaturated Si_4 Ring**

Nils Wiberg,* Harald Auer, Heinrich Nöth, Jörg Knizek, and Kurt Polborn

A few years ago we were able to synthesize the first molecular silicon compound containing a Si_4 tetrahedron, the orange tetrasupersilyl-*tetrahedro*-tetrasilane R^*_4Si_4 (**1**; $\text{R}^* = \text{tri-}t\text{-tert-butylsilyl}$, $\text{Si}t\text{Bu}_3$, supersilyl).^[1] We noted at the time that **1** is very stable towards water, air, light, and high temperatures and cannot be reduced by sodium even in the presence of [18]crown-6 in benzene under standard condi-

tions. Compound **1** turned out to be more susceptible towards oxidizing agents; initially, however, the tetrahedrane could only be oxidized to complex product mixtures. We have now found that upon reaction with iodine in equimolar amounts at room temperature, **1** quantitatively yields a compound with the molecular formula $\text{R}^*_4\text{Si}_4\text{I}_2$, whose structure, reactivity, and synthesis are described here.

As long as migrations of the supersilyl groups during the iodination of R^*_4Si_4 are excluded, the four isomeric structures **2–5** ($\text{X} = \text{I}$) are possible for $\text{R}^*_4\text{Si}_4\text{I}_2$ (Scheme 1). A *bicyclo*-tetrasilane of type **2** was first proven by Masamune et al. in the



Scheme 1. Possible structural isomers for the molecular formula $\text{R}^*_4\text{Si}_4\text{X}_2$.

form of the pale yellow species $t\text{Bu}_2(2,6\text{-Et}_2\text{C}_6\text{H}_3)_4\text{Si}_4$ (the *t*Bu groups are located on the central Si atoms of the “ Si_4 butterfly”).^[2] We prepared a further species of type **2**, colorless $\text{R}^*_4\text{H}_2\text{Si}_4$ ($\text{X} = \text{H}$ in **2**).^[3] The deep orange, air-sensitive $(t\text{BuMe}_2\text{Si})_6\text{Si}_4$ obtained by Kira et al. in low yields represents a *cyclo*-tetrasilene of type **3**.^[4] Upon irradiation, it is supposed to rearrange to a red-brown *bicyclo*-tetrasilane isomer **2**, which in the dark slowly reverts to **3**. The red-brown species $(2,4,6\text{-}i\text{Pr}_3\text{C}_6\text{H}_2)_6\text{Si}_4$, recently synthesized by Weidenbruch et al.,^[5] represents a tetrasiladiene of type **5**. A *cyclo*-trisilene of type **4** has so far only been obtained as the homologous germanium compound R^*_4Ge_3 (Ge instead of Si and R^* instead of SiX_2R^* in **4**).^[6]

$\text{R}^*_4\text{Si}_4\text{I}_2$ crystallizes from benzene at room temperature in the form of red-orange, light- and moisture-sensitive platelets which are stable in air. They melt with decomposition at 128–130 °C. The structure of this compound is presented in Figure 1. It was obtained by an X-ray structure analysis of a crystal (monoclinic, space group $P2_1/c$) that also contained one molecule of benzene per molecule of $\text{R}^*_4\text{Si}_4\text{I}_2$.^[7] According to the analysis, $\text{R}^*_4\text{Si}_4\text{I}_2$ exhibits the structure **3** ($\text{X} = \text{I}$) and can be termed 1,2-diiodo-1,2,3,4-tetrasupersilylcyclotetrasil-3-ene. The central structural element, which has not been observed before, is a bent unsaturated Si_4 ring with iodine substituents (angle between the planes $\text{Si1-Si2-Si3/Si3-Si4-Si1}$ 27.8° and $\text{Si2-Si3-Si4/Si4-Si1-Si2}$ 28.1°). The $\text{Si}=\text{Si}$ distance is 2.257(2) Å and is therefore similar to that in the disilene $(i\text{Pr}_3\text{Si})_4\text{Si}_2$ (2.251(1) Å), which carries very bulky substitu-

[*] Prof. Dr. N. Wiberg, Dipl.-Chem. H. Auer, Prof. Dr. H. Nöth, Dipl.-Chem. J. Knizek, Dr. K. Polborn
 Institut für Anorganische Chemie der Universität
 Meiserstrasse 1, D-80333 München (Germany)
 Fax: (+49)-89-5902-578

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