Rhodium(II) Perfluorobutyrate Catalyzed Hydrosilylation of 1-Alkynes. Trans Addition and Rearrangement to Allylsilanes

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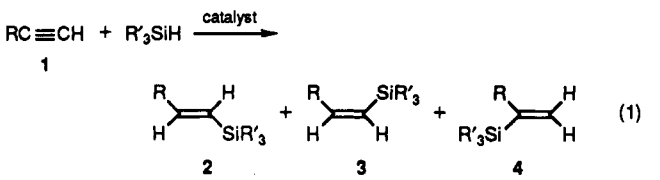
Received January 30, 1991

Summary: Hydrosilylation of 1-alkynes catalyzed by rhodium(II) perfluorobutyrate or chloroplatinic acid forms either allylsilanes or vinylsilanes in moderate to high isolated yields, dependent on the mode of addition of reactants. The duality of these transformations appears to be dependent on coordination of the organosilane or alkyne with the transition-metal catalyst.

Catalytic hydrosilylation of unsaturated organic compounds, a process of substantial importance for the synthesis of organosilicon derivatives, is similar to, but less exothermic than, catalytic hydrogenation.[1-4] Numerous transition-metal compounds, including many that are employed for hydrogenation, are effective catalysts for these addition reactions,[1-11] but hexachloroplatinic acid (Speier's catalyst)[12] is generally recognized to be the catalyst of choice for hydrosilylation of compounds that possess a carbon–carbon multiple bond.[13] Hydrosilylation of alkynes proceeds by preferential cis addition across the carbon–carbon triple bond in chloroplatinic acid and some rhodium catalyzed reactions to yield the corresponding vinylsilanes,[14-17] but limited regiocontrol is observed, and a mixture of isomeric products is obtained (eq 1). In reactions catalyzed by $(Ph_3P)_3RhCl$ and other rhodium catalysts under certain conditions, however, predominant



(1)

trans addition is observed in many cases,[18-20] and the mechanism of this transformation is proposed to involve insertion of an alkyne into a silicon–rhodium bond followed by isomerization of this cis addition product through a zwitterionic carbene complex. We wish to report an unusual and previously unreported duality of transformations for the hydrosilylation of 1-alkynes catalyzed by rhodium(II) perfluorobutyrate[21] and chloroplatinic acid whose success appears to be dependent on coordination of the organosilane at an open coordination site of the transition-metal catalyst.

Addition of 1-octyne to excess triethylsilane in CH_2Cl_2 containing 1.0 mol % $Rh_2(pfb)_4$ produces allylsilanes **6** (eq 2) in high yield together with relatively minor amounts of byproducts that include **2**, **4**, and 1-(triethylsilyl)octane.

$$\underset{\mathbf{5}}{CH_3(CH_2)_5C{\equiv}CH} + Et_3SiH \xrightarrow[CH_2Cl_2]{Rh_2(pfb)_4} \underset{\mathbf{6}}{CH_3(CH_2)_4CH{=}CHCH_2SiEt_3} \quad (2)$$

Although previously unreported, the same mode of addition with chloroplatinic acid (CPA) as the catalyst also results in the predominant formation of allylsilane **6**. Once again, **2** and **4**, but not **3**, are byproducts. In contrast to the moderate degree of stereoselectivity in allylsilane formation with $Rh_2(pfb)_4$, however, stereocontrol with CPA is high, which suggests catalyst involvement in the product-forming step. Comparative results obtained with representative 1-alkynes are presented in Table I. As can be discerned, use of *tert*-butyldimethylsilane increases the *E*/*Z* product ratio, 1-alkoxy-2-propynes give the *Z* isomer preferentially in $Rh_2(pfb)_4$-catalyzed reactions and the *E* isomer in CPA-catalyzed reactions, and overall, $Rh_2(pfb)_4$ appears to be the more suitable catalyst for allylsilane formation. With $(Ph_3P)_3RhCl$ under the same conditions, only a trace amount (<3%) of allylsilane was observed in reactions of triethylsilane with 1-octyne.

In contrast to these results, when the mode of addition is reversed and trialkylsilane is added to the alkyne, "normal" addition (eq 1) occurs to the exclusion of allylsilane products. However, unlike CPA or some rhodium(I) catalysts, which exhibit a commanding preference for cis addition,[1,14-17] $Rh_2(pfb)_4$ catalyzes highly selective trans addition across the carbon–carbon triple bond of linear

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0276-7333/91/2310-1225$02.50/0

Table I. Allylsilane Formation in Reactions of Organosilanes with 1-Alkynes Catalyzed by $Rh_2(pfb)_4$ or H_2PtCl_6[a]

alkyne	silane	catalyst	isolated yield, %[b]	allylsilane	relative yield, %[c]	*E*/*Z*
1-octyne	Et_3SiH	$Rh_2(pfb)_4$	90	$CH_3(CH_2)_4CH{=}CHCH_2SiEt_3$	86	2.0
	Et_3SiH	H_2PtCl_6	92	$CH_3(CH_2)_4CH{=}CHCH_2SiEt_3$	60	11
1-hexyne	Et_3SiH	$Rh_2(pfb)_4$	89	$CH_3(CH_2)_2CH{=}CHCH_2SiEt_3$	72	2.6
	t-$BuMe_2SiH$	$Rh_2(pfb)_4$	79	$CH_3(CH_2)_2CH{=}CHCH_2SiMe_2$-*t*-Bu	68	4.5
	Et_3SiH	H_2PtCl_6	78	$CH_3(CH_2)_2CH{=}CHCH_2SiEt_3$	73	15
1-methoxy-2-propyne	Et_3SiH	$Rh_2(pfb)_4$	74	$MeOCH{=}CHCH_2SiEt_3$	85	0.38
	Et_3SiH	H_2PtCl_6	65	$MeOCH{=}CHCH_2SiEt_3$	49	2.8
1-(benzyloxy)-2-propyne	Et_3SiH	$Rh_2(pfb)_4$	88	$PhCH_2OCH{=}CHCH_2SiEt_3$	92	0.38
	Et_3SiH	H_2PtCl_6	62	$PhCH_2OCH{=}CHCH_2SiEt_3$	57	3.0

[a] Reactions were performed under N_2 at 25 °C with a 60-min addition of 5.0 mmol of alkyne in 3.0 mL of CH_2Cl_2 to 10.0 mmol of silane in 7.0 mL of CH_2Cl_2 containing 0.05 mmol of catalyst. [b] Product yield after distillation. [c] Byproducts are **2**, **4**, and that from hydrogenation of the allylsilane (1–15%).

Table II. Comparative Results from Hydrosilylation of 1-Alkynes Catalyzed by $Rh_2(pfb)_4$ and H_2PtCl_6[a]

				relative yield, %			
alkyne[b]	silane	catalyst	isolated yield, %[c]	**2**	**3**	**4**	**2**/**3**
1-octyne	Et_3SiH	$Rh_2(pfb)_4$	77	13	73	14	0.18
	t-$BuMe_2SiH$	$Rh_2(pfb)_4$	52	5	87	8	0.058
	Et_3SiH	H_2PtCl_6	68	67	6	27	11
1-hexyne	Et_3SiH	$Rh_2(pfb)_4$	56	18	64	18	0.28
	t-$BuMe_2SiH$	$Rh_2(pfb)_4$	25	7	80	13	0.085
	Et_3SiH	H_2PtCl_6	71	87	3	10	29
phenylacetylene	Et_3SiH	$Rh_2(pfb)_4$[d]	48	50	19	25	2.6
	Et_3SiH	H_2PtCl_6[e]	77	75	4	21	19
1-ethynyl-1-cyclohexanol	Et_3SiH[f]	$Rh_2(pfb)_4$	83	78	15	7	5.2
3-phenyl-1-butyn-3-ol	Et_3SiH[f]	$Rh_2(pfb)_4$	84	68	32	0	2.1

[a] Unless specified otherwise, reactions were performed under N_2 at 25 °C with an 80-min addition of 5.0 mmol of silane in 3 mL of CH_2Cl_2 to 10.0 mmol of alkyne in 7 mL of CH_2Cl_2 containing 0.05 mmol of catalyst. [b] Propargyl ethers are not listed because product yields were <20%; in those reactions **2**/**3** = 2.0–2.5. [c] Product yield after distillation. [d] Includes 6% $PhC{\equiv}CSiEt_3$. [e] Reaction performed with a 3-h addition of 1.0 mmol of Et_3SiH in 2 mL of CH_2Cl_2 to 2.0 mmol of phenylacetylene in 3 mL of CH_2Cl_2 containing 0.01 mmol of H_2PtCl_6. [f] Alkyne added to silane; with Et_3SiH addition low product yields were obtained but **2**/**3** was >10.

1-alkynes to yield the thermodynamically less stable *Z* olefin (Table II). Use of *tert*-butyldimethylsilane enhances this stereocontrol and also decreases the yield of regioisomer **4**. As can be seen from results obtained with phenylacetylene and 1-ethynyl-1-cyclohexanol,[22] electronic and steric factors influence stereocontrol in $Rh_2(pfb)_4$-catalyzed reactions. Predominant cis addition that occurs under CPA catalysis also characterizes reactions performed in the presence of $(Ph_3P)_3RhCl$. For example, when triethylsilane is added over 1 h to 1-octyne, **2**/**3** = 1.4 (39% yield); however, at longer addition times the ratio **2**/**3** increases significantly (to 3.2 in a 4-h addition), suggesting that isomerization of the olefin pair is occurring, consistent with observations reported by Watanabe.[24]

The divergent transformations resulting from opposite modes of addition of the reactants suggest that the reaction pathway to products is determined by initial coordination of the alkyne or the organosilane with the catalytically active metal complex. Indeed, like alkenes that form 1/1 coordination complexes with $Rh_2(pfb)_4$,[21,25] alkynes also associate. Equilibrium constants for 1-octyne (65 ± 1), phenylacetylene (18 ± 0.3), and methyl propargyl ether (72 ± 6) were determined. In addition, triethylsilane also forms a coordination complex with $Rh_2(pfb)_4$[23] (K_{eq} = 15 ± 0.8) whose magnitude is only a small fraction of that with alkynes other than phenylacetylene.

Why has this investigation uncovered these divergent pathways for hydrosilylation of alkynes when prior studies have not reported allylsilane formation? The answer to this question lies in the ability of organosilanes to coordinate with the catalytically active metal complex.[26] The low K_{eq} for association of triethylsilane with $Rh_2(pfb)_4$ relative to that with 1-alkynes explains why allylsilanes are not formed when reactions are performed by adding the silane to the alkyne or by combining the reactants in the presence of the catalyst.

The present investigation provides a new and highly effective methodology for allylsilane formation that complements those currently available.[27] The selective formation of vinylsilanes having the *Z* geometry induced by $Rh_2(pfb)_4$ complements results obtained with a select listing of other rhodium catalysts. Our efforts are continuing with emphases on the scope and mechanism of these catalytic transformations.

Acknowledgment. We are grateful to the Robert A. Welch Foundation for their support of this research. Summer support for C.L.N. was received through an NSF-REU grant to Trinity University. T.W.C. gratefully acknowledges fellowship support from the Pew Midstates Science and Mathematics Consortium. We also wish to thank the Johnson Matthey Co. for their loan of rhodium(III) chloride.

Supplementary Material Available: Experimental details and analytical and spectroscopic data for the compounds formed (6 pages). Ordering information is given on any current masthead page.

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