Catalytic Behavior of Rhodium(I) Complexes in Hydrogermylation and Hydrosilylation of Phenylacetylene

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Synopsis. Rhodium complexes, $Rh(L)(C_2H_4)_2$ {L=$(CH_3C{=}O)_2CH$ (acac), and $(CF_3C{=}O)_2CH$ (hfa)}, catalyze hydrogermylation and hydrosilylation of phenylacetylene with Bu_3GeH and R_3SiH (R=Bu, Et), respectively, to produce $Ph(R_3M)C{=}CH_2$ (M=Ge, Si) selectively. Other rhodium complexes, that is, $[RhCl(C_2H_4)_2]_2$, $Rh_2Cl_2(cod)_2$, $Rh(tmhd)(C_2H_4)_2$ {tmhd=$(t\text{-BuC}{=}O)_2CH$}, and $Rh(dbm)(C_2H_4)_2$ {dbm=$(PhC{=}O)_2CH$}, also catalyze these reactions, but with less regioselectivity.

Hydrosilylation, hydrostannylation, and hydrogermylation of terminal acetylenes under transition metal catalysis have been widely studied[1] because of their potential utility in the synthetic organic chemistry of vinylic organometals with 14(IV B) series elements (Eq. 1).

$$R_3MH + R'\text{-}C{\equiv}CH \xrightarrow{cat.} \underset{\text{1 (α-adduct)}}{\overset{R'}{\underset{R_3M}{\diagdown\!\!\diagup}}C{=}CH_2} + \underset{\text{2 (β-adducts, E and Z)}}{\overset{R}{\underset{H}{\diagdown\!\!\diagup}}C{=}CH\sim MR_3} \quad (1)$$

M=Si, Sn, Ge
R,R'=alkyl, phenyl

The selective formation of β-adducts (**2**) has been thoroughly investigated under transition metal catalysis or radical conditions.[1b-e] However, catalysts yielding α-adduct (**1**) selectively have not been well-studied, except for rhodium catalysts used for the hydrostannylation of terminal acetylenes. We report here on a new rhodium catalyst which is effective for the selective formation of an α-adduct in the hydrogermylation and hydrosilylation of phenylacetylene.

Experimental

Materials. The rhodium complexes used in the present study were prepared by using ordinary methods,[2] and were stored at −25 °C. The solvents and other reagents were purified by distillation before use.

General Procedure. All operation were carried out under a nitrogen atmosphere. The typical procedure was as follows. To a mixture of $Rh(hfa)(C_2H_4)_2$ {1.46 mg (4.0×10^{-3} mmol)} and CH_2Cl_2 (10 ml) was added phenylacetylene {0.41 g (4.0 mmol)}, and the mixture was stirred at 40 °C for 10 min. Then, $(n\text{-Bu})_3GeH$ {0.098 g (0.4 mmol)} was added rapidly and the reaction was monitored by GLC. The reaction products were isolated by short-pass distillation. The characterization and the product distribution of products were determined by ^1H NMR and GLC.

Table 1. Rhodium-Catalyzed Hydrogermylation and Hydrosilylation of PhC≡CH[a]

Run	Catalyst[b]	Temp	Time	PhC≡CH/R_3MH	Yield[c]	Products (% ratio)[d]	
		°C	h	(Molar ratio)	%	**1**	**2** (*E*/*Z*)
M=Ge				R=Bu			
1	$RhCl(CO)(PPh_3)_2$	0	6	10	65	7	93 (70/23)
2	$RhCl(CO)(PPh_3)_2$-galvinoxyl	0	2	10	73	1	99 (91/8)
3	$[RhCl(C_2H_4)_2]_2$	0	0.5	1	84	15	85 (36/49)
4	$[RhCl(C_2H_4)_2]_2$	0	1	10	89	61	39 (20/19)
5	$[RhCl(cod)]_2$	40	9	10	88	23	76 (49/27)
6	$Rh(acac)(C_2H_4)_2$	40	0.5	1	89	81	19 (16/1)
7	$Rh(acac)(C_2H_4)_2$	40	0.5	10	91	86	14 (13/1)
8	$Rh(acac)(C_2H_4)_2$-galvinoxyl	40	1	10	96	81	19 (18/1)
9	$Rh(tmhd)(C_2H_4)_2$	40	1	10	96	56	44 (40/4)
10	$Rh(dbm)(C_2H_4)_2$	40	0.5	10	97[d]	54	46 (43/3)
11	$Rh(hfa)(C_2H_4)_2$	40	1	10	100[d]	95	5 (4/1)
M=Si				R=Bu			
12	$Rh(acac)(C_2H_4)_2$	40	22	10	77	75	25 (25/0)
13	$Rh(acac)(C_2H_4)_2$	40	33	1	83[d]	71	29 (25/4)
14	$Rh(tmhd)(C_2H_4)_2$	40	7	10	97	60	40 (39/1)
M=Si				R=Et			
15	$Rh(acac)(C_2H_4)_2$	40	1	10	99[d]	86	14 (14/0)
16	$Rh(hfa)(C_2H_4)_2$	40	1	10	100[d]	96	4 (4/0)

a) The reaction was monitored by GLC for it's completion. Isomerization among the isomers did not observed under the conditions. b) One mol% of a catalyst was used. cod=1,5-cyclooctadiene; acac=$(CH_3C{=}O)_2CH$; tmhd=$(t\text{-BuC}{=}O)_2CH$; dbm=$(PhC{=}O)_2CH$; hfa=$(CF_3C{=}O)_2CH$. c) Isolated yields by short pass distillation based on R_3MH. d) Determined by GLC.

Table 2. Solvent Effects on the Hydrogermylation and the Hydrosilylation

Catalyst[a]	Solvent	Temp °C	Time h	PhC≡CH/R_3MH (Molar ratio)	Yield[b] %	Products (% ratio)[c] 1	2 (*E*/*Z*)
M=Ge				R=Bu			
Rh(acac)$(C_2H_4)_2$	CH_2Cl_2	40	0.5	1	89	81	19 (16/3)
	THF	40	6	1	98	43	57 (38/19)
	C_6H_6	40	9	1	95	41	59 (44/15)
M=Si				R=Et			
Rh(acac)$(C_2H_4)_2$	CH_2Cl_2	40	1	10	99	86	14 (14/0)
	CH_2ClCH_2Cl	65	3	10	94	79	21 (19/2)
	THF	40	1	1	89	48	52 (37/15)
	C_6H_6	65	1	1	86	46	54 (45/9)
	C_6H_6	40	3	1	80	50	50 (40/10)

a) One mol% of the catalyst was used. b) Isolated yields by short pass distilation based on R_3MH. c) Determined by GLC.

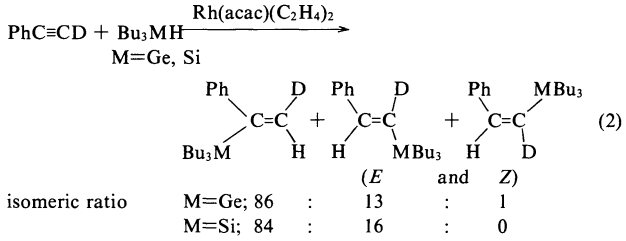
Hydrosilylation was also carried out by the same method mentioned above.

Results and Discussion

Rhodium complexes {$RhClL_3$, $RhCl(CO)L_2$, [RhCl(cod)]$_2$; L=PPh_3} were previously found to catalyze the hydrostannylation of acetylene with Bu_3SnH to produce an α-adduct, $Ph(Bu_3Sn)C=CH_2$ selectively, and a combination of galvinoxyl (radical inhibitor) and $RhCl(CO)(PPh_3)_2$ in the hydrostannylation of phenylacetylene proved to give an α-adduct exclusively in excellent yield.[3] In the hydrogermylation of phenylacetylene, however, these catalysts gave β-adducts (**2**) as the main products, and the presence of the radical inhibitor suppressed the formation of the α-adduct and (*Z*)-β-adduct, as shown in Table 1 (Run 2). When we used a large excess of PhC≡CH to Bu_3GeH (>10), only [RhCl$(C_2H_4)_2]_2$ produced the α-adduct with moderate selectivity (61%), probably because of an effective exchange of the ethylene with PhC≡CH.

Interestingly, Rh(acac)$(C_2H_4)_2$, in which chloride in [RhCl$(C_2H_4)]_2$ is replaced by acetylacetonate, gave the α-adduct in good yields, irrespective of the molar ratio of PhC≡CH/R_3GeH, although the catalytic activity was somewhat less than that of [RhCl$(C_2H_4)_2]_2$. The catalyst also acted as an effective catalyst for the hydrosilylation of PhC≡CH with R_3SiH (R=Bu, Et) under the same conditions as those in hydrogermylation, but not for hydrostannylation. When we used $(CF_3C=O)_2CH$ instead of acac as a β-diketonate ligand, the regioselectivity toward the α-adduct in both reaction systems was greatly improved (select.=ca. 95%). On the other hand, the other complexes with a bulky β-diketonate ligand, that is Rh(tmhd)$(C_2H_4)_2$ and Rh(dbm)$(C_2H_4)_2$, also catalyzed both reactions, but with less selectivity. These results indicate that the regioselectivity in both reaction systems is influenced by both electronic and steric effects of the ligands around the rhodium metal. In this catalyst system, the reaction temperature and solvent also affected the regioselectivity toward the α-adduct. For example, in the Rh(acac)$(C_2H_4)_2$ catalyst system, as shown in Table 2, dichloromethane having a small coordination ability was found to be appropriate as a reaction medium.

Compared with Bu_3GeH, Bu_3SiH required a longer reaction time because of the less reactivity of Bu_3SiH, and the regioselectivity toward the α-adduct was somewhat less than that of Bu_3GeH (Runs 7 and 12). However, with less crowded triethylsilane, Et_3SiH, regioselectivity toward the α-adducct increased, giving almost the same selectivity to that of Bu_3GeH. The solvent effect was almost the same with that in the hydrogermylation as shown in Table 2.



(2)

The Rh(acac)$(C_2H_4)_2$ system proved to give $Ph(Bu_3M)C=CHD$ (M=Ge, Si) stereoselectively in the reaction of PhC≡CD with Bu_3GeH and Bu_3SiH, respectively (Eq. 2).

This result supports the *syn*-addition process in the present α-directive hydrogermylation and hydrosilylation which is generally observed in the transition metal-catalyzed hydrostannylation[4] and hydrosilylation.[5]

The catalytic behaviors of Rh(acac)$(C_2H_4)_2$ and Rh(hfa)$(C_2H_4)_2$ for α-adduct selectivity have not get been clarified. Consequently, Rh(hfa)$(C_2H_4)_2$ is a useful catalyst which provides a simple method for the preparation of $Ph(R_3M)C=CH_2$ (M= Ge, Si; R=Bu, Et) with regard to the starting materials and procedures.

References

1) a) R. J. P. Corriu and J. E. Morean, *J. Organomet. Chem.*, **40**, 73 (1972); b) Y. Ichinose, H. Oda, K. Oshima, and K. Uchimoto, *Bull. Chem. Soc. Jpn.*, **60**, 3468 (1987); c) A. J. Leusink and H. A. Budding, *J. Organomet. Chem.*, **11**, 533 (1968); d) T. K. Gar, A. A. Buyakov, A. V. Kisin, and V. F. Mironov, *Zh. Obsch. Khim.*, **41**, 1589 (1971); e) R. A. Benkeser, M. L. Burrous, L. E. Nelson, and J. V. Swisfer, *J. Am. Chem. Soc.*, **83**, 4385 (1961); f) R. A. Benkeser and R. A. Hickner, *J. Am. Chem. Soc.*, **80**, 5298 (1958); g) J. E. Hill and T. A. Nile, *J. Organomet. Chem.*, **137**, 293 (1977); h) M. Green, J. L. Spences, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, **1977**, 1525; and i) "Comprehensive Organometallic Chemistry," ed by G.

Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, Oxford (1982), Vol. 2.

2) a) $Rh(hfa)(C_2H_4)_2$; B. T. Golding and C. Pierpoint, *J. Chem. Soc., Dalton Trans.*, **1984**, 219. b) $Rh(acac)(C_2H_4)_2$; R. Cramer, *J. Am. Chem. Soc.*, **86**, 217 (1964). c) $RhCl(CO)(PPh_3)_2$; D. Evans, J. A. Osborn, and G. Wilkinson, *Inorg. Synth.*, **11**, 99 (1968).

3) K. Kikukawa, H. Umekawa, F. Wada, and T. Matsuda, *Chem. Lett.*, **1988**, 881.

4) R. A. Benkeser, *Pure Appl. Chem.*, **13**, 133 (1966).

5) K. Tamao, J. Yoshida, M. Yamamoto, T. Kakui, H. Matsumoto, M. Takahashi, A. Kurita, M. Murata, and M. Kumada, *Organometallics*, **1**, 355 (1982).