Silylative Dimerization of Aromatic Aldehydes Catalyzed by a Thiolate-Bridged Diruthenium Complex

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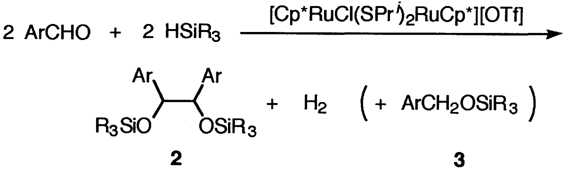
A cationic thiolate-bridged diruthenium complex $[Cp^*RuCl(\mu_2\text{-}SPr^i)_2RuCp^*][OTf]$ ($Cp^* = \eta^5\text{-}C_5Me_5$, $OTf = OSO_2CF_3$) was found to be an efficient catalyst for the reaction of aromatic aldehydes with hydrosilanes in acetonitrile to give 1,2-diaryl-1,2-disiloxyethanes as the major products.

Novel functions of multinuclear complexes in homogeneous catalysis have recently been a major subject of current interest because such complexes can be expected to provide new types of active catalyst sites through accumulation of reactive metal centers.[1] We have been investigating synthesis and reactivities of thiolate- or sulfur-bridged multinuclear complexes,[2-5] and have disclosed that a series of thiolate-bridged diruthenium complexes promote unique transformations of various substrates such as acetylenes,[2a,3] alkyl halides,[4] and hydrazines.[5] Very recently, a cationic thiolate-bridged diruthenium complex $[Cp^*RuCl(\mu_2\text{-}SPr^i)_2RuCp^*][OTf]$[3c] (**1**) has been found to react with ferrocenylacetylene to give a dinuclear butenynyl complex $[Cp^*Ru\{\eta^1{:}\eta^2\text{-}\mu_2\text{-}C(=CHFc)C{\equiv}CFc\}(\mu_2\text{-}SPr^i)_2RuCp^*][OTf]$ (Fc = ferrocenyl) which catalyzes linear di- and trimerization of the acetylene.[3a] Now we wish to report that **1** also works as an effective catalyst for silylative dimerization of aromatic aldehydes with hydrosilanes.

When an acetonitrile solution (10 ml) of benzaldehyde (606 mg, 5.71 mmol), triethylsilane (935 mg, 8.04 mmol), and a catalytic amount of **1** (41.9 mg, 0.0519 mmol) was charged in an autoclave and allowed to react at 120 °C for 24 h, evolution of hydrogen gas (2.50 mmol) was observed. GLC analysis of the resultant solution revealed the formation of 1,2-diphenyl-1,2-bis(triethylsiloxy)ethane (**2a**, threo : erythro[6] = 47 : 53) and benzyl triethylsilyl ether (**3a**) in 78% and 6% yield, respectively (Eq. 1, Ar = Ph, R = Et). A small amount of disiloxane was also detected as a byproduct. Purification of the reaction mixture by silica-gel column chromatography followed by bulb-to-bulb distillation afforded **2a** (961 mg, 76%) as a colorless oil.



(1)

The above observation indicates that the major reaction catalyzed by **1** follows Eq. 1, and the hydrosilylation of benzaldehyde is no more than a side reaction. This type of silylative dimerization of aldehydes is not unprecedented but has rarely been reported so far. The $NiCl_2\text{-}SEt_2$ catalyst is known to be effective for similar selective formation of **2a**,[6] and $Co_2(CO)_8$ gives **2** in a moderate yield from benzaldehyde and diethylmethylsilane under CO.[7] However, there has been reported no ruthenium complex which catalyzes the silylative dimerization of aldehydes.[8]

Catalytic activities of a series of thiolate- or selenolate-bridged diruthenium complexes as well as the effects of reaction conditions in the reaction of benzaldehyde with triethylsilane are summarized in Table 1. Some of the diruthenium complexes exhibited catalytic activity toward the hydrosilylation to give **3a**, and especially, a cationic triply bridged Ru(III)-Ru(III) complex $[Cp^*Ru(\mu_2\text{-}SPh)_3RuCp^*]Cl$ was of high efficiency. In contrast, the formation of **2a** was observed only in the reactions effected by complexes with a cationic $Ru(III)(\mu_2\text{-}SR)_2Ru(III)$ core, and complex **1** was far more active and selective than the SPh analogue. It was also confirmed that common ruthenium complexes such as $RuCl_2(PPh_3)_3$ and $Ru_3(CO)_{12}$ catalyzed only the hydrosilylation to give **3a** under the conditions described above. Reaction temperatures of 100-120 °C were adequate for the selective production of **2a**. The reaction hardly proceeded at 80 °C, while the selectivity was lowered at 140 °C. Acetonitrile was found suitable as the solvent. THF gave a lower yield of **2a** and the reaction failed to occur in benzene or dichloroethane.

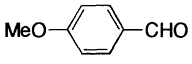
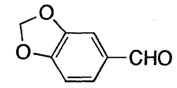
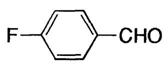
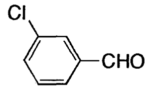
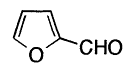
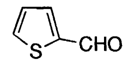
Complex **1** was effective for the silylative dimerization of various aromatic aldehydes as shown in Table 2. In each case

Table 1. Reaction of PhCHO and $HSiEt_3$ by Ru catalysts [a]

Catalyst	Conv. of PhCHO /%	Yield /%[b]	
		2a	**3a**
$[Cp^*RuH(SPr^i)]_2$	27	trace	11
$[Cp^*RuCl(SPr^i)]_2$	29	0	21
$[Cp^*RuCl(SFc)]_2$	25	trace	2
$[Cp^*Ru(SPr^i)_3RuCp^*]$	24	2	8
$[Cp^*Ru(SPh)_3RuCp^*]Cl$	100	0	100
$[Cp^*RuCl(SPr^i)_2RuCp^*][OTf]$	100	78 (76[c])	6
"	100[d]	72[c]	6
"	100[e]	69[c]	18
"	100[f]	51	11
$[Cp^*RuCl(SPh)_2RuCp^*][OTf]$	50	13	37
$[Cp^*RuCl(SePh)_2RuCp^*][OTf]$	21	1	12
$Cp^*Ru(PMe_3)(STol)_2$	0	-	-
$[Cp^*RuCl_2]_2$	97	0	66

[a] Reaction conditions: PhCHO, 5 mmol; $HSiEt_3$, 7.5 mmol; MeCN, 10 ml; catalyst, 0.1 mmol as Ru atom; 120 °C; 24 h. [b] GLC yields based on the starting PhCHO. [c] Isolated yields. [d] At 100 °C. [e] At 140 °C. [f] In THF.

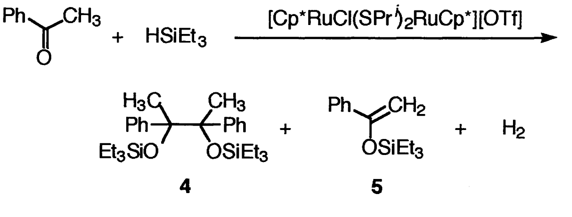
Table 2. Silylation of various aromatic aldehydes catalyzed by **1**^{a}

ArCHO	$HSiR_3$	Yield /%^{b}	
		2	**3**
PhCHO	$HSiEt_3$	76 (78)	(6)
	$HSiMe_2Ph$	74	(25)
m-TolCHO	$HSiEt_3$	82	(5)
	$HSiMe_2Ph$	70	(28)
p-TolCHO	$HSiEt_3$	76	(6)
	$HSiEt_3$	70	(5)
	$HSiEt_3$	66	(5)
 ^{c}	$HSiEt_3$	46	15 (20)
	$HSiEt_3$	71	(12)
	$HSiEt_3$	43	5 (13)
	$HSiEt_3$	51	(7)

^{a}Reaction conditions: aldehyde, 5 mmol; $HSiR_3$, 7.5 mmol; MeCN, 10 ml; **1**, 0.05 mmol; 120 °C; 24 h. ^{b}Isolated (GLC) yields based on the starting aldehydes. Conv. of the aldehydes were essentially 100% in all cases. ^{c}Reaction time, 41 h.

the 1,2-diaryl-1,2-disiloxyethane (**2**, almost 1 : 1 mixture of two stereoisomers) was obtained predominantly with a minor amount of the arylmethyl silyl ether (**3**). The aldehydes with electron donating substituents tend to give **2** in higher selectivity. Use of dimethylphenylsilane instead of triethylsilane also afforded **2** as the major product but less selectively. On the other hand, aliphatic aldehydes such as heptanal and 3-methyl-2-butenal failed to undergo the silylative dimerization.

A similar reaction of acetophenone with triethylsilane also proceeded but at a lower rate (89% conv.). The silylative dimerization product **4** was obtained in a moderate yield (33%) and was accompanied by silyl enol ether **5** (13%) (Eq. 2). The hydrosilylation product, 1-phenylethyl silyl ether, was detected only in a marginal yield.



(2)

We have recently found that a thiolate-bridged diruthenium benzyl complex undergoes facile homolytic cleavage of the Ru-C bond to liberate benzyl radical, which leads to the formation of 1,2-diphenylethane.[4,9] It is assumed that a similar radical formation is included in the present catalytic reaction. The aromatic aldehyde and hydrosilane would react on an active diruthenium center to generate a dinuclear (siloxybenzyl)-ruthenium complex. The siloxybenzyl radical is then released by the homolytic Ru-C bond fission, and couples with each other to yield **2**. Electron withdrawing groups on the aryl group are considered to strengthen the Ru-C bond to prevent the homolytic bond fission and consequently favor the hydrosilylation to give **3**, which is in agreement with the observation shown in Table 2. We must await further investigation to elucidate the detailed mechanism, but it should be emphasized that the diruthenium core in **1** plays a critical role in controlling the reaction paths.

References and Notes

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9 For related reactions, see: a) D. L. Johnson and J. A. Gladysz, *Inorg. Chem.*, **20**, 2508 (1981); b) G. Neumann and W. P. Neumann, *J. Organomet. Chem.*, **42**, 277 (1972).