The Silylformylation of Simple 1-Alkynes Catalyzed by [Rh(cod)][BPh_4] in an Ionic Liquid, [Bmim][PF_6], under Biphasic Conditions: An Efficiently Reusable Catalyst System

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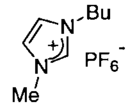
Taking into account the precedent rhodium complex-catalyzed silylformylation of 1-alkynes, an efficient recycling of the catalyst consisting of a zwitterionic rhodium complex, [Rh(cod)][BPh_4] (cod = 1,5-cyclooctadiene) (**2**), in a typical ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF_6] (**1**), under biphasic conditions was easily achieved.

The hydroformylation of alkynes has met limited success due to an inevitable hydrogenation of the alkynes as well as the product enals.[1] While the silylformylation of alkynes with trialkylsilanes and carbon monoxide, which is catalyzed by various rhodium complexes, works well to afford selectively 3-trialkylsilyl-2-alkylpropenals.[2] Zwitterionic rhodium(I) complex-catalyzed intriguing silylhydroformylation of terminal alkynes with trialkylsilanes and synthesis gas (H_2–CO) has also been reported.[3]

Taking into account the conditions of the latter two rhodium-catalyzed silylformylations, on the one hand, and the existing drawback of homogeneous catalysis, i.e., difficulties in the recovery of transition metal complexes as active catalyst, on the other hand, the use of two-phase catalysis in an ionic liquid was examined in order to construct a reusable catalyst system. In recent years, ionic liquids at room temperature have attracted broad attention in organic synthesis, especially in homogeneous catalytic reactions, from the viewpoint of green chemistry.[4] Among many moisture stable ionic liquids, which have specifically unique solvating properties,[5] 1-butyl-3-methylimidazolium hexafluorophosphate, [Bmim][PF_6] (**1**), was selected as a catalyst medium of the present rhodium-catalyzed silylformylation. The dense liquid **1** (d^{20} = 1.36) is known to make a stable solution with the Wilkinson catalyst, but is immiscible with saturated hydrocarbons, diethyl ether, and water.[6] These properties appear to be quite suitable for constructing biphasic conditions between an upper layer of reactants and a lower layer containing the catalyst, and hence for facile product(s)/catalyst separation, which may lead to a recycling of the catalyst.



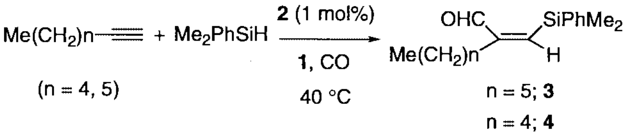
1

[Rh^+(cod)(η^6-$C_6H_5B^-Ph_3$)]
(cod = 1,5-cyclooctadiene)

2

We report herein the silylformylation of simple 1-alkynes under biphasic conditions with efficient catalyst recycling. In a 35-mL glass-lined micro autoclave were placed 1-octyne (2.0 mmol), Me_2PhSiH (2.2 mmol), [Rh^+(cod)(η^6-$C_6H_5B^-Ph_3$)] (**2**)[7] (1 mol%), and **1** (0.5 mL). Then, CO (40 atm) was introduced after flushing three times and the whole mixture was heated at 40 °C for 24 h with magnetic stirring. At an ambient temperature the reaction mixture in the glass tube remained cleanly biphasic and the pale yellow lower layer appeared to contain only the catalyst. The upper layer exhibited practically two peaks by GLC analysis, indicative of complete consumption of 1-octyne, and was decanted after dilution with dry ether (2 mL), and the ether extract was concentrated by evaporation. The residue was separated and purified by flush chromatography on a silica gel column (gradient elution using 2–10% ethyl acetate–haxane) to give recovered Me_2PhSiH, and 3-(dimethylphenylsilyl)-2-hexylpropenal (**3**) (71% isolated yield). On detailed ^1H NMR analysis,[8] **3** was identified to have pure *Z*-configuration (Table 1, run 1).

Table 1. Catalyst recycling in the silylformylation of 1-alkynes



Run	CO/atm	Time/h[a)]	Convn/%	Yield/%[b)]
(n = 5)				
1	40	24	100	71
2	40	24	100	76
3	40	24	100	78
4	40	24	100	67
(n = 4)				
5	20	48	100	52
6	20	48	100	69
7	20	48	100	69

[a)] Not optimized. [b)] Isolated yield by flush chromatography.

Reuse of the lower layer as the catalyst for the second silylformylation of 1-octyne, under otherwise the same conditions as described above, afforded pure (*Z*)-**3** in 76% isolated yield. Furthermore, the catalyst recycling was examined in another two runs, giving (*Z*)-**3** averagely in 73% in each experiment (Table 1, runs 2–4). Thus, formal catalyst turnover number (TON) reached over 290. Use of RhH(CO)(PPh_3)$_3$, instead of the zwitterionic rhodium complex **2**, dissolved in **1** under similar conditions as above but with CO (20 atm) gave also pure (*Z*)-**3** in 65% isolated yield for the first run. However, attempted twice catalyst recyclings exhibited distinct deterioration of the activity, resulting in the lack of reproducible yields of the product. It is conceivable that an air-sensitive rhodium species formed in **1** could not survive under ambient manipulation in the present experiments. By using **2** as a catalyst precursor, 1-heptyne reacted satisfactorily under CO (20 atm) at 40 °C for 48 h under biphasic conditions with three-catalyst recycling, to give exclusively (*Z*)-3-(dimethylphenylsilyl)-2-pentylpropenal (**4**)[8] in 69% average isolated yield (Table 1, runs 5–7).

Application of H_2/CO (1:1) instead of pure CO to the above reaction of 1-octyne with Me_2PhSiH catalyzed by **2** in CH_2Cl_2 would undergo net silylhydroformylation to form (*E*)-2-{(dimethylphenylsilyl)methyl}-2-octenal.[3] However, this was not the case for present biphasic conditions using ionic liquid **1**. Thus, the reaction of 1-octyne with Me_2PhSiH under H_2/CO (1:1) (40 atm) catalyzed by **2** (1 mol%) in **1** at 40 °C for 24 h proceeded smoothly, the product obtained being always pure (*Z*)-**3** in averagely 72% isolated yield of three catalyst recyclings.

Although facile silylformylation in exclusively *Z*-selective manner was observed for the reaction of 1-octyne, Me_2PhSiH, and either CO or synthesis gas under biphasic conditions, Et_2MeSiH was found to undergo the reaction very sluggishly. The product, (*Z*)-3-(diethylmetylsilyl)-2-hexylpropenal (**5**),[9] was obtained in 27% isolated yield at 54% conversion under the same conditions as described above. The diminished reactivity of Et_2MeSiH as compared with Me_2PhSiH has already been pointed out.[2c] The reaction of phenylacetylene with Me_2PhSiH under either CO or synthesis gas gave a mixture of (*E*)- and (*Z*)-3-(dimethylphenylsilyl)-2-phenylpropenal (**6**)[10] in a ratio of 52:48 only in low yields (5.1–18%), while starting material was poorly recovered. The lack of stereoselectivity as well as reactivity in the silylformylation under biphasic conditions makes sharp contrast to the high *Z*-selectivity observed in the homogeneous silylformylation under a CO atmosphere.[2c]

In conclusion, we have found that the zwitterionic rhodium **2** dissolved in ionic liquid **1** constitutes biphasic conditions for the exclusively stereoselective silylformylation of 1-alkynes with Me_2PhSiH under either a CO or synthesis gas atmosphere, and that the catalyst recycling can be acheived with ease. However, the fact that the present silylformylation of phenylacetylene exhibited lack of stereoselectivity and low reactivity, which are not the case for the homogeneous conditions, requires further refinements of the biphasic conditions, study on this line being underway.

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8 ^{1}H NMR (270 MHz, $CDCl_3$, TMS) for **3**: δ 0.50 (s, Si*Me*), 0.88 (t, *J* = 6.6 Hz, CH_2*Me*), 1.28–1.43 (m, $(CH_2)_4$), 2.30 (t, *J* = 7.4 Hz, =CCH_2), 6.92 (t, *J* = 1.2 Hz, =C*H*), 7.36–7.54 (m, *Ph*), and 9.77 ppm (s, C*H*O). ^{13}C NMR (68 MHz, $CDCl_3$, TMS) δ –0.1, 14.0, 22.6, 28.3, 29.0, 31.6, 31.8, 128.2, 129.5, 133.5, 138.0, 149.0, 157.2, and 193.4 ppm. IR (neat) 1687 (C=O), 1427 and 1251 cm^{-1} (SiMe). No trace of (*E*)-isomer was found even in the crude product, contrary to the corresponding data reported for the silylformylation of 1-heptyne with Me_2PhSiH catalyzed by $Rh_4(CO)_{12}$ (0.3 mol%) in benzene solution to afford **4**, a homolog of **3**, in a ratio *Z*:*E* = 87:13 (ref 2c).

9 ^{1}H NMR (270 MHz, $CDCl_3$, TMS) for **5**: δ 0.21 (s, Si*Me*), 0.71 (t, *J* = 7.8 Hz, CH_2*Me*), 0.85–1.00 (m, Si*Et*), 1.28–1.41 (m, $(CH_2)_4$), 2.28 (t, *J* = 7.1 Hz, =CCH_2), 6.77 (t, *J* = 1.2 Hz, =C*H*), and 9.79 ppm (s, C*H*O). ^{13}C NMR (68 MHz, $CDCl_3$, TMS) δ –3.3, 7.2, 7.4, 14.1, 22.6, 28.4, 28.9, 31.6, 31.8, 150.0, 157.4, and 193.6 ppm. IR (neat) 1687 (C=O), 1463 and 1253 cm^{-1} (SiMe).

10 Highly stereoselective silylformylation of phenylacetylene to give **6** (*Z*:*E* = 98:2) was reported in ref 2c.