Heterogeneous Dinuclear Rhodium(II) Hydroformylation Catalysts—Performance Evaluation and Silsesquioxane-Based Chemical Modeling**

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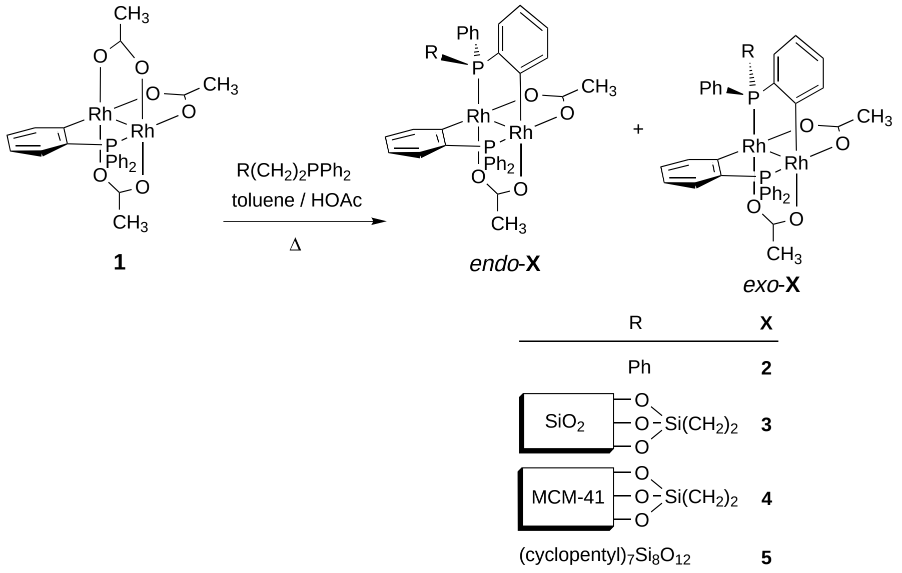
The extensive use of homogeneous transition metal catalysts in industrial hydroformylation processes is affected by a number of disadvantages, such as the problem of the recovery of the metal from the reaction products, expensive metal losses, and solubility limitations.[1] Many attempts have been made to overcome these drawbacks by immobilizing metal complex catalysts on various supports, with inorganic oxide carriers being considered the most promising.[2] Catalysts prepared by coordinative anchoring of metal complexes on a chemically modified support containing donor functions possess superior activities to those which are prepared by means of physical adsorption (supported liquid-phase catalysts, deposited catalysts, etc.), although the achievable activities are still inferior to those of the corresponding homogeneous systems because of mass-flow restrictions.[2d, 3] Another severe problem of coordinatively anchored catalysts is their limited stability towards metal leaching. However, the exceptional stability of a rhodium catalyst that had been immobilized on a silica support by a *trans*-chelating bidentate phosphane tether has recently been reported.[4]

Dinuclear rhodium(II) complexes $[Rh_2(\mu\text{-}\widehat{PC})_2(\mu\text{-}O_2CR)_2]$ ($\mu\text{-}\widehat{PC}$ = bridging *ortho*-metalated arylphosphane ligand) catalyze the hydroformylation of styrene with high efficiency.[5] The immobilization of these catalysts on amorphous silica supports as well as on MCM-41 by surface-tethered phosphane ligands appeared desirable, since a) the bridging bidentate coordination of the *ortho*-metalated phosphane ligands promises firm anchoring of the catalyst on the support (thereby reducing the problem of catalyst leaching without problems arising from *cis*-chelation[6]) and b) the open mesoporous support structures should avoid mass-transfer problems.[7] This objective was approached by an acid-assisted cyclometalation reaction[8] between a surface-grafted phenylphosphane tether and the catalytic precursor **1**.[9] Compound **1** is known to react cleanly with one equivalent of PPh_3 to give **2** (Scheme 1). The phosphane-modified silica supports were prepared by grafting $Ph_2P(CH_2)_2SiCl_3$[10] on both amorphous silica gel and on MCM-41. In case of the mesoporous support MCM-41, protection of the external surface with a layer of grafted $Si(CH_3)_2$ groups under nondiffusive conditions prior to the introduction of the phosphane tethers guaranteed the location of the tethers within the mesoporous channels.[11] Heating **1** with an excess of phosphane-grafted silica or MCM-41 dispersed in toluene in the presence of acetic acid resulted in complete adsorption of **1** with formation of the immobilized catalysts **3** and **4**, respectively (Scheme 1).



Scheme 1. From **1** to dinuclear rhodium(II) complexes bearing two *ortho*-metalated phosphane ligands. Axial acetic acid ligands are omitted for clarity.

Incompletely condensed polyhedral oligosilsesquioxanes (OSS) can be used to model the surface chemistry of silica involved in organometallic grafting reactions.[12] Hence, for a better understanding of the processes that take place during the immobilization of the catalyst on the surface of a phosphane-modified support, we studied the analogous cyclometalation reactions between **1** and the soluble OSS model $(c\text{-}C_5H_9)_7Si_8O_{12}(CH_2)_2PPh_2$, which may itself be considered as a phosphane-modified molecular section of a silica surface.[13]

Dinuclear rhodium(II) complexes $[Rh_2(\mu\text{-}\widehat{PC})_2(\mu\text{-}O_2CR)_2]$ with a head-to-tail configuration of the two bridging *ortho*-metalated phosphane ligands ($\mu\text{-}\widehat{PC}$)—as formed exclusively under the conditions employed in this study—have backbone

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chirality.[14] The introduction of an additional stereocenter arising from the replacement of a phenyl substituent on one of the *ortho*-metalated phosphane ligands in **2** thus results in the formation of diastereomeric products, denoted *endo* and *exo* in Scheme 1. The reaction between **1** and (c-$C_5H_9)_7Si_8O_{12}(CH_2)_2PPh_2$ afforded accordingly a mixture of two diastereomers of **5** in a ratio of 8.4:1, as revealed by ^{31}P NMR spectroscopy. Subsequent crystallization yielded the pure major component of the mixture, which was characterized spectroscopically and by single-crystal X-ray diffraction[15] to afford the first crystal structure of an OSS bearing a pendant transition metal complex.

The crystal structure of the major isomer of **5** (Figure 1) reveals that the OSS-substituent of the newly introduced phosphane ligand adopts a position *endo* with respect to the second *ortho*-metalated phosphane ligand of the dinuclear rhodium complex. This allows the unmetalated phenyl substituent on P1 to point towards the bridging acetate ligand on the less sterically encumbered side of the complex. This preference clearly indicates the lower steric bulk of the 1,2-ethanediyl bridge between P1 and the silsesquioxane moiety in comparison to the unmetalated phenyl substituent, since the extremely space-demanding pending silsesquioxane unit can adopt a remote position without sterically interfering with the bulky dinuclear rhodium cluster. The observed bond lengths and angles of the dinuclear rhodium cluster moiety lie within the range of the respective values in other reported structures of $[Rh_2(\mu\text{-}\widehat{PC})_2(\mu\text{-}O_2CR)_2]$ complexes.[16]

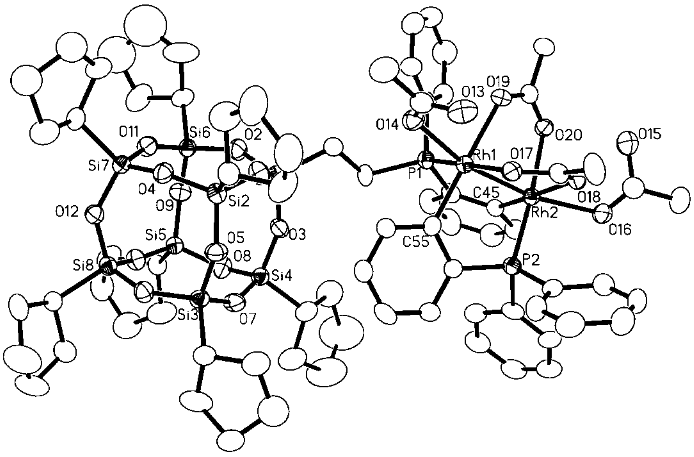

Figure 1. Molecular structure of *endo*-**5** showing the crystallographic labeling scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh1-Rh2 2.5078(6), Rh1-P1 2.2123(13), Rh2-P2 2.2125(13), Rh1-C55 2.004(4), Rh2-C45 1.992(5), Rh1-O17 2.152(3), Rh1-O19 2.187(3), Rh2-O18 2.187(3), Rh2-O20 2.151(3), Rh1-O14 2.352(3), Rh2-O16 2.346(3); Rh1-Rh2-P2 87.80(3), Rh2-Rh1-P1 87.82(3), Rh1-Rh2-C45 97.36(13), Rh2-Rh1-C55 97.29(13), Rh2-Rh1-O19 83.95(8), Rh1-Rh2-O20 86.48(8), Rh2-Rh1-017 86.36(8), P1-Rh1-C55 89.86(13), C55-Rh1-O17 91.53(15), O17-Rh1-O19 84.83(12), O19-Rh1-P1 93.91(9), P2-Rh2-C45 89.53(13), C45-Rh2-O20 91.52(15), O20-Rh2-O18 85.03(12), O18-Rh2-P2 94.10(9).

The performance of the immobilized catalysts **3** and **4** (supported on amorphous silica and MCM-41, respectively) was evaluated in repeated hydroformylation experiments employing either styrene or 1-decene as substrates (Table 1). After each catalytic run the catalysts were recovered by filtration and reused in the subsequent experiment. Contrary to the well-known sensitivity of anchored hydroformylation catalysts towards oxygen,[2b, 6c] exclusion of oxygen during this recovery procedure proved unnecessary; catalyst samples that were handled under air exhibited activities identical to those of samples that were kept under argon.

In the hydroformylation of styrene both **3** and **4** exhibited comparable activities and selectivities under identical conditions in the initial catalytic run. A decrease of the reaction rate by restricted mass transport within the mesoporous channels in the case of **4** was not observed. The chemoselectivity towards the formation of aldehyde products was nearly quantitative in all the experiments employing styrene as the substrate. No products arising from the hydrogenation of either the starting material or products were detected. The regioselectivity in favor of the branched aldehyde product is higher at 60 bar of CO/H_2 than at 30 bar under otherwise identical conditions. The observed level of activity as well as selectivity of the immobilized catalysts in the initial catalytic run is—within the margins of experimental errors—identical with that reported for their homogeneous counterpart **2**,[5] thus demonstrating the advantage of coordinative anchoring. However, the initial high level of selectivity in favor of the branched product decreased steadily in each subsequent catalytic run with both **3** and **4** and at varying pressures. The bidentate bridging coordination mode of the phenylphosphane tether could not completely suppress activity losses through catalyst leaching, as the decrease of activity in consecutive experiments indicates. Some catalyst leaching clearly took place as all filtrates exhibited a low degree of hydroformylation activity after removal of the heterogeneous

Table 1. Hydroformylation of alkenes catalyzed by immobilized dinuclear rhodium(II) complexes.[a]

Entry	Catalyst	Substrate	Run	p [bar]	Conv. [%]	Aldehyde [%][b]	Selectivity (b:n)[c]	Isoalkenes [%][b]	Alkane [%][b]
1	**3**	styrene	1	60	100	> 99	14.9	–	< 1
2	**3**	styrene	4	60	6	> 99	7.8	–	< 1
3	**4**	styrene	1	60	100	> 99	15.1	–	< 1
4	**4**	styrene	4	60	98	> 99	6.9	–	< 1
5	**4**	styrene	1	30	100	> 99	11.1	–	< 1
6	**4**	styrene	6	30	63	> 99	3.4	–	< 1
7	**2**[5]	styrene	–	30	100	–	11.5	–	–
8	**4**	1-decene	1	30	97	81	0.66	11	8
9	**4**	1-decene	4	30	34	62	0.47	14	24

[a] General reaction conditions: 0.0125 mmol of Rh^{II} complex, substrate/catalyst = 400/1, CO/H_2 = 1/1, solvent = toluene (10 mL). For styrene: T = 60 °C, t = 6 h; for decene: T = 80 °C, t = 4 h. [b] Referenced to converted alkene. [c] n = Linear aldehyde, b = branched aldehyde.

catalyst. The continuous decrease in selectivity in consecutive runs may therefore be ascribed to an increasing contribution of the highly active, but unselective, leached rhodium carbonyl species[17] to the overall conversion, corresponding to a simultaneous decrease in the concentration of the immobilized species. However, the nature of the support had a dramatic effect on the degree of leaching: while catalyst **3**, immobilized on amorphous silica, had lost almost all of its initial activity after only four catalytic runs, the respective drop in activity was less pronounced for catalyst **4**, with the catalytic complex anchored inside the mesopores of MCM-41. Furthermore, an increase in pressure from 30 to 60 bar resulted in an almost negligible drop in catalytic activity for catalyst **4** during recycling.

Catalyst **4** was also employed in the hydroformylation of 1-decene. The chemoselectivity in favor of aldehyde products exhibited by **4** is in all subsequent runs significantly lower for this olefin than for styrene hydroformylation. The fraction of the hydrogenated side-product, *n*-decane, increases steadily at the expense of hydrocarbonylated products in subsequent catalytic runs, while the amount of isomerized decene by-products is not changed significantly. Simultaneously, a steady increase in regioselectivity within the aldehyde fraction towards the linear product *n*-undecanal with each consecutive run is observed, as expressed by the rise of the linear: branched aldehyde ratio (*n*:*b*) from 1.52:1 (run 1) to 2.13:1 (run 4). The low level of regioselectivity for the linear aldehyde product in the hydroformylation of 1-decene is indicative of a reactive site with a low degree of steric encumbrance.[1]

Experimental Section

All reactions were carried out under an argon atmosphere in dry solvents using standard Schlenk techniques unless stated otherwise.

[SiO_2]-$(CH_2)_2PPh_2$: A mixture of fumed silica (5.0 g, vacuum-dried at 200 °C, 250 m^2g^{-1}, 9.75 mmol SiOH[18]), $Ph_2P(CH_2)_2SiCl_3$ (113 mg, 0.325 mmol), and pyridine (77 mg, 0.975 mmol) in toluene (30 mL) was stirred at 25 °C for 12 h. The solid was filtered, washed with methanol (250 mL) and diethyl ether (50 mL), and dried in vacuo at 80 °C; yield 5.052 g; ^{31}P CP-MAS NMR (162 MHz): $\delta = -9.95$; IR: $\tilde{\nu} = 1443\ cm^{-1}$ (P-Ph).

[MCM-41]-$(CH_2)_2PPh_2$: Siliceous MCM-41 (2.5 g, vacuum-dried at 200 °C, 1000 m^2g^{-1}, 19.5 mmol SiOH[18]) was suspended in hexane (50 mL), Me_2SiCl_2 (0.034 mL, 0.28 mmol) was added at 0 °C and the mixture was allowed to warm to ambient temperature and stirred for 1 h. The volatiles were then removed in vacuo. The solid was suspended in toluene (50 mL). $Ph_2P(CH_2)_2SiCl_3$ (695 mg, 2 mmol) was slowly added at 0 °C, and the mixture was stirred at ambient temperature for 24 h. The released HCl was then removed by heating the mixture under reflux in a stream of dry argon for 2 h. The product was collected by filtration, washed with CH_2Cl_2 (10 × 30 mL) and dried in vacuo at 80 °C; yield 3.137 g; X-ray diffraction: $2\theta_{100} = 2.275°$, $a = 44.8$ Å; ^{31}P CP-MAS NMR (162 MHz): $\delta = -9.89$; IR: $\tilde{\nu} = 1440\ cm^{-1}$ (P-Ph).

3: A mixture of **1** (35 mg, 0.046 mmol) and [SiO_2]-$(CH_2)_2PPh_2$ (1.5 g, ca. 0.1 mmol PPh_2[19]) in toluene (30 mL) was heated under reflux for 15 min. Glacial acetic acid (10 mL) was added and heating was continued for additional 1.5 h. The pink solid was collected by filtration and washed with methanol (50 mL) and diethyl ether (20 mL), and dried in vacuo; yield 1.528 g. The filtrate did not contain any residual dinuclear rhodium complex, indicating complete adsorption. ^{31}P CP-MAS NMR (162 MHz): $\delta = 18.87$ (br s, *J*(Rh,P) unresolved).

4 was prepared analogously to **3** from **1** (100 mg, 0.131 mmol) and [MCM-41]-$(CH_2)_2PPh_2$ (1.0 g, ca. 0.6 mmol PPh_2[19]); yield 1.034 g; X-ray diffraction: $2\theta_{100} = 2.265°$, $a = 45.0$ Å; ^{31}P CP-MAS NMR (162 MHz): $\delta = 18.75$ (br s, *J*(Rh,P) unresolved).

endo-**5**: A mixture of **1** (30 mg, 0.039 mmol) and $(c\text{-}C_5H_9)_7Si_8O_{12}$-$(CH_2)_2PPh_2$ (44 mg, 0.039 mmol) in toluene (20 mL) and glacial acetic acid (2 mL) was heated at 60 °C for 12 h. The solvent was removed in vacuo, and the residue was purified by chromatography on silica gel with toluene/CH_3COOH (10/1) as eluent. Collection of the first pink band and subsequent solvent removal in vacuo afforded a mixture of diastereomers of **5**. The major *endo*-component was separated by repeated chromatography on silica gel with hexane/CH_2Cl_2/CH_3COOH (70/30/2). Suitable crystals of *endo*-**5** for X-ray analysis were grown from CH_2Cl_2/hexane; yield 33 mg (48 %); ^1H NMR (400 MHz, $CDCl_3$): $\delta = -0.54$ (m, 1 H, CH_2Si), 0.42 (m, 1 H, CH_2Si), 0.85–1.02 (m, 7 H, CH, $c\text{-}C_5H_9$), 1.37–1.79 (m, 56 H, CH_2, $c\text{-}C_5H_9$), 2.06 (m, 1 H, CH_2P), 2.14 (s, 6 H, CH_3, bridging acetate), 2.20 (m, 1 H, CH_2P), 6.43 (t, ^3J(H,H) = 8.52 Hz, 1 H, aromatic CH), 6.66 (t, ^3J(H,H) = 7.49 Hz, 1 H, aromatic CH), 6.70 (t, ^3J(H,H) = 7.73 Hz, 1 H, aromatic CH), 6.76–6.87 (m, 4 H, aromatic CH), 6.96 (td, ^3J(H,H) = 7.43, 1.76 Hz, 2 H, aromatic CH), 7.08–7.18 (m, 3 H, aromatic CH), 7.25–7.35 (m, 8 H, aromatic CH), 7.51–7.59 (m, 2 H, aromatic CH), 8.16–8.22 (m, 1 H, aromatic CH); $^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta = 16.14$ (dd, ^1J(Rh,P) = 166.98, ^2J(Rh,P) 7.35 Hz, P2), 19.93 (dd, ^1J(Rh,P) = 173.14, ^2J(Rh,P) 7.95 Hz, P1); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 6.40$ (CH_2Si), 21.60 (d, CH_2P, ^1J(P,C) = 28.9 Hz), 22.26–22.70 (CH, $c\text{-}C_5H_9$), 23.46 (CH_3, bridging acetate), 27.03, 27.31, 27.41 (all CH_2, $c\text{-}C_5H_9$), 121.30 (d, *J*(C,P) = 8.8 Hz, aromatic CH), 121.85 (d, *J*(C,P) = 9.1 Hz, aromatic CH), 127.01 (d, 2 C, *J*(C,P) = 9.7 Hz, aromatic CH), 127.55 (d, 2 C, *J*(C,P) = 9.3 Hz, aromatic CH), 127.73 (d, 2 C, *J*(C,P) = 8.8 Hz, aromatic CH), 128.33, 130.27, 133.06 (all s, aromatic CH), 128.39 (d, 2 C, *J*(C,P) = 12.9 Hz, aromatic CH), 128.91 (d, 2 C, *J*(C,P) = 7.2 Hz, aromatic CH), 131.03 (d, 2 C, *J*(C,P) = 8.4 Hz, aromatic CH), 133.11 (d, 2 C, *J*(C,P) = 9.0 Hz, aromatic CH), 133.58 (d, 2 C, *J*(C,P) = 9.1 Hz, aromatic CH), 136.51 (d, *J*(C,P) = 15.8 Hz, aromatic CH), 137.91 (d, *J*(C,P) = 12.9 Hz, aromatic CH), 132.70, 133.81, 134.26, 138.21, 138.63 (all s, aromatic C), 143.95, 147.44 (all m, RhC), 179.33 (s, COO, terminal), 181.10, 181.24 (all s, COO, bridging).

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[15] Crystal data for *endo*-**5**: $C_{75}H_{104}O_{20}P_2Rh_2Si_8$, $M_w = 1818.06$, pink plate, $0.30 \times 0.18 \times 0.10$ mm, triclinic, space group $P\bar{1}$, $a = 12.003(1)$, $b = 34.795(1)$, $c = 10.306(1)$ Å, $\alpha = 91.76(1)$, $\beta = 98.82(1)$, $\gamma = 86.19(1)^\circ$, $V = 4243.0(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.423\,\mathrm{g\,cm^{-3}}$; Rigaku R-Axis IIC diffractometer, $2\theta_{max} = 50.36^\circ$, $\mathrm{Mo_{K\alpha}}$ radiation, $\lambda = 0.71073$ Å, $T = 180(2)$ K; of 24851 measured reflections, 14357 were independent and 10214 observed with $I > 2\sigma(I)$, $0 \le h \le 14$, $-41 \le k \le 41$, $-12 \le l \le 12$; $R = 0.0506$, $wR = 0.1100$, GOF = 0.993 for 967 parameters, $\Delta\rho_{max} = 0.811\,\mathrm{e\,Å^{-3}}$. The structure was solved by direct methods (SHELXS-97) and developed by least-squares refinement on $|F^2|$ (SHELXL97). All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-149158. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[19] P and Rh contents of the modified silica supports are estimates based on the assumption of complete adsorption since varying contents of physisorbed water severely affected the accuracy of elemental analysis data. Thus, an inaccuracy of ±10% has to be considered.

Ruthenium-Catalyzed Regioselective α-Alkylation of Ketones: The First Alkyl-Group Transfer from Trialkylamines to the α-C Atom of Ketones[**]

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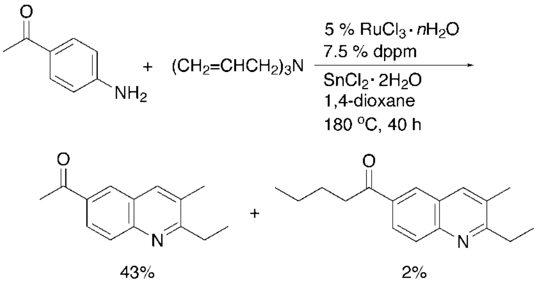
Homogeneous ruthenium-catalyzed organic reactions have been introduced for a wide variety of organic transformations and syntheses.[1] In the course of our continuing studies on transition metal-catalyzed synthesis of N-heterocyclic compounds, we recently developed and reported a ruthenium-catalyzed synthetic approach for the formation of indoles[2] and quinolines[3] by alkyl-group transfer from trialkylamines to anilines (amine-exchange reaction[4]). While studying the ruthenium-catalyzed heteroannulation between 4-aminoacetophenone and triallylamine, we found unexpectedly that careful analysis of the crude reaction mixture revealed a small amount of 1-(2-ethyl-3-methylquinolin-6-yl)pentan-1-one (2%) in addition to the expected product 1-(2-ethyl-3-methylquinolin-6-yl)ethanone [Eq. (1); dppm = bis(diphenylphosphanyl)methane].[3a] Presumably, the former quinoline was formed by alkylation of the latter.[5] These observations led us to seek a general method for the ruthenium-catalyzed α-alkylation of ketones with trialkylamines. In sharp contrast to the aforementioned amine-exchange reaction, alkyl-group transfer from trialkylamines to the α-carbon atom of ketones is unprecedented. Here we report on a general method for alkyl-group transfer from trialkylamines to the α-carbon atom of ketones in the presence of a ruthenium catalyst.



(1)

First, we examined the alkylation of acetophenone (**1a**) with tributylamine (**2a**) with various ruthenium catalyst precursors [Eq. (2)]. Typically, **1a** was treated with an

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