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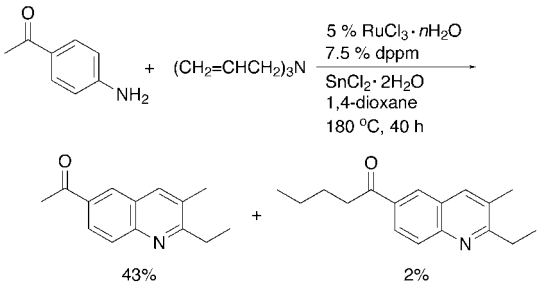
Ruthenium-Catalyzed Regioselective α-Alkylation of Ketones: The First Alkyl-Group Transfer from Trialkylamines to the α-C Atom of Ketones**

Chan Sik Cho,* Bok Tae Kim, Myung Jin Lee, Tae-Jeong Kim, and Sang Chul Shim*

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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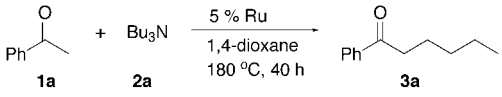


(2)

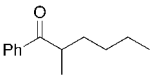
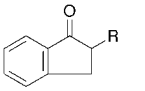
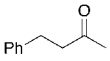
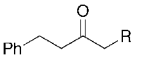
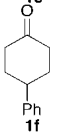
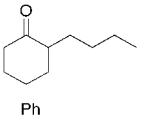
equimolar amount of **2a** in dioxane in the presence of a ruthenium catalyst precursor (5 mol%) at 180 °C for 40 h to afford 1-phenylhexan-1-one (**3a**). Table 1 shows that $RuCl_3 \cdot n H_2O/PPh_3$ and $[RuCl_2(PPh_3)_3]$ are the systems of choice for effective alkylation (entries 1 and 3). The difference between conversion and product yield could be due to reductive amination of the ketone to give a secondary amine as side product.

Table 1. Ruthenium-catalyzed α-butylation of **1a** with **2a** [Eq. (2)].[a]

Entry	Catalyst precursor	Conversion [%] of **1a**[b]	Yield [%] of **3a**[b]
1	$RuCl_3 \cdot n H_2O/3\,PPh_3$	77	70
2	$RuCl_3 \cdot n H_2O/1.5$ dppm[c]	32	19
3	$[RuCl_2(PPh_3)_3]$	90	69
4	$[RuH_2(PPh_3)_4]$	23	10
5	$[Ru_3(CO)_{12}]$	25	4
6	$[Cp^*RuCl_2(CO)]$[d]	4	3
7	$[Cp^*RuCl(CO)(PEt_3)]$[d]	1	0

[a] Reaction conditions: **1a** (1 mmol), **2a** (1 mmol), ruthenium catalyst (5 mol%), 1,4-dioxane (10 mL), 180 °C, 40 h, under Ar. [b] Determined by GLC. [c] dppm = bis(diphenylphosphanyl)methane. [d] $Cp^* = \eta^5$-C_5Me_5.

Table 2. Ruthenium-catalyzed α-alkylation of ketones **1** with trialkylamines **2**.[a]

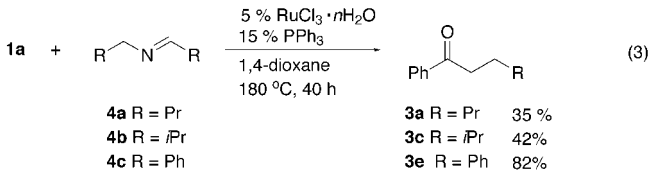
Ketone	R_3N	Product		Yield [%][b]
 **1a**	**2a** R = Bu		**3a** R = Bu	61
	2b R = hexyl		**3b** R = hexyl	73
	2c R = *i*Bu		**3c** R = *i*Bu	77
	2d R = isopentyl		**3d** R = isopentyl	67
	2e R = benzyl		**3e** R = benzyl	30
 **1b**	**2a**		**3f**	32[c]
 **1c**	**2a**		**3g** R = Bu	83
	2b		**3h** R = hexyl	89
	2c		**3i** R = *i*Bu	83
	2d		**3j** R = isopentyl	88
 **1d**	**2a**		**3k** R = Bu	70
	2b		**3l** R = hexyl	78
	2c		**3m** R = *i*Bu	75
	2d		**3n** R = isopentyl	78
 **1e**	**2a**		**3o**	81[d]
 **1f**	**2a**		**3p**	48[e,f]

[a] Reaction conditions: **1** (2 mmol), **2** (2 mmol), $RuCl_3 \cdot n H_2O$ (5 mol%), PPh_3 (15 mol%), 1,4-dioxane (10 mL), 180 °C, 40 h, under Ar. [b] Yield of isolated product. [c] Carried out in a molar ratio of **2a**:**1b** = 5:1. [d] Yield determined by GLC. [e] Mixture of diastereoisomers (1:5). [f] 2,6-Dibutyl-4-phenylcyclohexanone (isomer ratio 81:13:6) was also isolated in 13% yield.

Given these results, several ketones and amines were screened with these catalysts (Table 2). Alkyl aryl ketones **1a** and **1b** were readily alkylated with a variety of trialkylamines **2a**–**2e** to afford α-alkylated ketones **3a**–**3f** in moderate to good yields. No α,α-dialkylation was observed.[6] A fivefold excess of amine relative to the substrate was required for the reaction of **1b**, in which case the reaction became slower and the yield was lower.[7] Higher reaction rate and yield were observed with the benzo-fused cyclic ketone 1-indanone (**1c**).

To test for regioselectivity, dialkyl ketones **1d** and **1e** were employed, and alkylation took place exclusively at the less hindered methyl group.[8] The reaction of 4-phenylcyclohexanone (**1f**) with **2a** gave not only 2-butyl-4-phenylcyclohexanone (**3p**) but also a small amount of 2,6-dibutyl-4-phenylcyclohexanone (13% yield). The reaction of α,β-unsaturated ketones such as *trans*-4-phenyl-3-buten-2-one with **2a** gave no alkylated product, and the starting material was recovered.

Replacing amines with imines as alkylating agent was successful and gave the expected products [Eqs. (3) and (4)].



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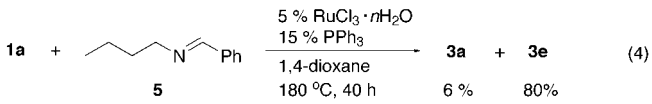

(4)

Here both yields and the type of the product depend upon the imine employed. For instance, imines **4** gave a single alkylation product, while imine **5** yielded two products (**3a** and **3e**) that resulted from the transfer of the alkyl or the alkylidene substituent on nitrogen. The formation of **3e** may be explained by the generation of (benzyl)(butyl)amine by reduction of the PhC=N bond under the reaction conditions employed. In fact, in a separate experiment the alkylation of **1a** with *N*-butylbenzylamine afforded **3a** and **3e** in 11% and 38% yields, respectively.

In summary, we have developed a novel ruthenium-catalyzed highly regioselective α-alkylation of ketones with an array of trialkylamines and imines. The present ruthenium-catalyzed alkylation is a first example of alkyl-group transfer from trialkylamines and imines to the α-carbon atom of ketones. The reaction mechanism[9, 10] and synthetic applications are currently under investigation.

Experimental Section

Typical procedure: **1a** (0.24 g, 2.0 mmol), **2a** (0.37 g, 2.0 mmol), $RuCl_3 \cdot n H_2O$ (0.026 g, 0.10 mmol), PPh_3 (0.079 g, 0.30 mmol), and dioxane (10 mL) were placed in a 50-mL autoclave and allowed to react under argon at 180 °C for 40 h. The reaction mixture was filtered through a short silica gel column ($CHCl_3$), washed with 50 mL of 5% HCl and dried over Na_2SO_4. Removal of the solvent left an oil, which was purified by column chromatography (ethyl acetate:hexane 1:15) to give 1-phenylhexan-1-one (**3a**) in 61% yield.

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[5] In a separate experiment, we confirmed that 1-(2-ethyl-3-methylquinolin-6-yl)ethanone (0.20 mmol) reacted with tripropylamine (1.0 mmol) in the presence of $RuCl_3 \cdot n H_2O$ (0.02 mmol) and PPh_3 (0.06 mmol) in dioxane (5 mL) at 180 °C for 40 h to afford 1-(2-ethyl-3-methylquinolin-6-yl)pentan-1-one in 51 % yield, and $SnCl_2 \cdot 2H_2O$ proved to be unnecessary for the alkylation.

[6] For example, ^{1}H NMR (400 MHz) analysis of the crude reaction mixture of **1a** and **2a**, after usual workup prior to separation, showed no signal for the methine proton of an α,α-dialkylated ketone.

[7] Treatment of equimolar amounts of **1b** and **2a** under the usual conditions gave 2-methyl-1-phenylhexan-1-one (**3f**) in only 5 % yield, and the yield of **3f** was not improved at much longer reaction times.

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Half-Metallocene Tantalum Complexes Bearing Methyl Methacrylate (MMA) and 1,4-Diaza-1,3-diene Ligands as MMA Polymerization Catalysts**

Yutaka Matsuo, Kazushi Mashima,* and Kazuhide Tani

Well-defined organometallic complexes were recently reported to be single-site catalysts for the polymerization of various monomers.[1] While enolate complexes of zirconium,[2–5] yttrium,[6] and samarium,[7, 8] as well as aluminum enolate complexes with Schiff base[9] or porphyrin[10] ligands, have been reported to be active initiators for the polymerization of polar olefinic monomers such as methyl acrylate (MA) and methyl methacrylate (MMA), enolate complexes of other transition metals have not been utilized. We sought a new metal enolate complex that can initiate polymerization of these polar monomers. Since Group 5 metals tolerate polar functional groups and are less oxophilic than the metals of Groups 3 and 4, we chose half-metallocene complexes of tantalum, cationic alkyl and alkylidene derivatives of which have already been applied in the living polymerization of ethylene[11] and stereoselective ring-opening metathesis polymerization of norbornene[12]. Here we report a novel tantalum initiator system and a new approach to generating catalytically active enolate species from monomer-coordinated complexes. We prepared and characterized new half-metallocene complexes of tantalum with MMA and 1,4-diaza-1,3-butadiene (DAD)[13, 14] ligands, and the tantalum – MMA complexes, upon addition of one equivalent of $AlMe_3$, were found to be catalysts for the polymerization of MMA.

Scheme 1 shows the preparation of tantalum – MMA complexes from [Cp*$TaCl_4$] (**1**; Cp* = η^5-C_5Me_5). Reduction of **1** with sodium amalgam in toluene followed by addition of MMA afforded the MMA complex [Cp*$TaCl_2$(η^4-*supine*-MMA)] (**2**), which was alternatively prepared by treatment of the dinuclear Ta^{III} complex [{Cp*$TaCl_2$}$_2$] (**3**)[15] with MMA. The structure of **2**[16] (Figure 1) is essentially the same as that of [Cp*$TaCl_2$(η^4-*supine*-MA)].[17] Reaction of **2** with one equivalent of the dilithium salt of 1,4-bis(*p*-methoxyphenyl)-1,4-diaza-1,3-butadiene (*p*-$MeOC_6H_4$-DAD) or the dilithium salt of 1,4-dicyclohexyl-1,4-diaza-1,3-butadiene (Cy-DAD) in THF afforded the half-sandwich DAD complexes of tantalum **4** and **5**, respectively. The ^{1}H NMR spectra of **4** and **5** displayed two doublets at $\delta = 6.67$ and 6.84 ($J = 3.4$ Hz) for **4**

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