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Efficient Ruthenium-Catalyzed Aerobic Oxidation of Alcohols Using a Biomimetic Coupled Catalytic System

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Efficient aerobic oxidation of alcohols was developed via a biomimetic catalytic system. The principle for this aerobic oxidation is reminiscent of biological oxidation of alcohols via the respiratory chain and involves selective electron/proton transfer. A substrate-selective catalyst (ruthenium complex **1**) dehydrogenates the alcohol, and the hydrogens abstracted are transferred to an electron-rich quinone (**4b**). The hydroquinone thus formed is continuously reoxidized by air with the aid of an oxygen-activating Co−salen type complex (**6**). Most alcohols are oxidized to ketones in high yield and selectivity within 1−2 h, and the catalytic system tolerates a wide range of O_2 concentrations without being deactivated. Compared to other ruthenium-catalyzed aerobic oxidations this new catalytic system has high turnover frequency (TOF).

Introduction

Oxidation of secondary alcohols is an important process in living organisms, in particular in animals and aerobic bacteria.[1,2] These oxidations occur under very mild reaction conditions and involve selective electron transfer processes. The dehydrogenation of the alcohol is usually carried out by NAD^+ to give the ketone and NADH + H^+. The NADH is subsequently reoxidized by molecular oxygen via the respiratory chain.[3] The latter process involves electron transfer from NADH to ubiquinone (Q) to give ubiquinol (QH_2), and the QH_2 formed carries the electrons to cytochrome c, which as its reduced form transfers them to O_2.

Because of the increased demand of environmentally benign oxidation processes in organic chemistry, especially on large-scale synthesis, there is a growing interest to mimic biological transformations. In the biomimetic approach one would employ a substrate-selective redox catalyst for the oxidation (cf. NAD^+ in biological alcohol oxidation) and then transfer the electrons of the reduced form of the redox catalyst to O_2 or H_2O_2. The latter process requires electron-transfer mediators (ETMs) between the substrate-selective redox catalyst and O_2 or H_2O_2 to proceed under mild conditions. A limited number of oxidation reactions with such coupled electron-transfer systems are known in nonbiological systems.[4−10] Our own group has recently designed and developed coupled catalytic electron-transfer systems for 1,4-oxidations of conjugated dienes,[5] allylic oxidations,[5a] oxidations of alcohols,[6] and dihydroxylations of olefins[7] where either O_2 or H_2O_2 are used as oxidant.

A number of methods for metal-catalyzed aerobic oxidations of alcohols have been developed.[6a,b,9−16] There is a demand to make these reactions more efficient, and particular emphasis has been put on facilitating electron transfer from the alcohol to molecular oxygen. We now describe an efficient aerobic biomimetic catalytic system for dehydrogenation of alcohols to ketones involving a

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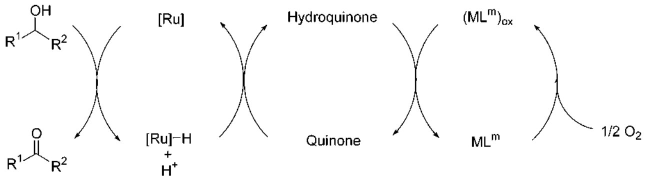
Scheme 1

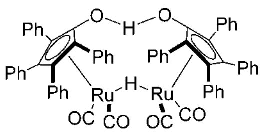


biomimetic coupled catalytic system. The design of the system was inspired by the biological oxidation of secondary alcohols. Instead of NAD^+ we are employing a ruthenium complex as the substrate-selective catalyst, the ubiquinone (Q) was replaced by another electron-rich quinone, and in place of cytochrome *c*, a metal macrocycle (ML^m) such as iron phthalocyanine or a cobalt salen complex was used for the O_2 activation.

Results and Discussion

Ruthenium complexes have been extensively studied as catalysts for aerobic oxidation of alcohols.[12] In most cases a high-valent ruthenium complex acts as the active catalyst in the reaction, and examples on the use of low-valent ruthenium complexes are rare.[6a,b,8,10] The combination of a low-valent ruthenium complex with a stabilized free radical ligand (TEMPO) was reported recently to affect aerobic oxidation of aliphatic alcohols.[10] Also, low-valent ruthenium and hydroquinone was recently used for the oxidation of primary alcohols.[8c] In our preliminary work on selective alcohol oxidation we employed a triple catalytic system with a low-valent ruthenium complex as the dehydrogenating catalyst.[6b] In our search for an efficient coupled catalytic system for biomimetic oxidation of alcohols via selective elctron transfer (cf. Scheme 1) it was of importance to choose an active substrate-selective catalyst and to find a quinone together with an appropriate oxygen-activating metal complex that both give low barriers in the electron-transfer reactions according to Scheme 1.

Choice of Substrate-Selective Catalyst. A number of ruthenium catalysts are known to be active in hydrogen transfer reactions. They have been used in asymmetric transfer hydrogenation[17] and also for racemization of alcohols in the presence of a lipase to obtain a dynamic kinetic resolution of the alcohol.[18] For the present purpose it is desirable to employ a catalyst that can readily dehydrogenate an alcohol. Preliminary DFT calculations show that electron-withdrawing ligands on the metal increases the rate of dehydrogenation, whereas electron-donating ligands depresses the rate of dehydrogenation. A few catalysts were tested and among those the Shvo catalyst **1** was found to be by far the best for promoting dehydrogenation of alcohols.



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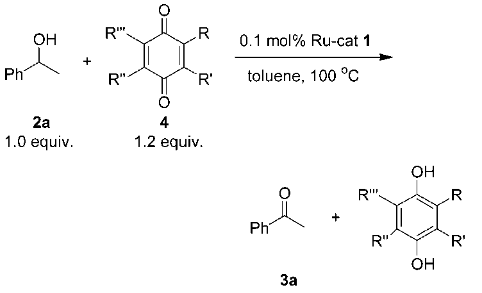
Screening of Quinones. To increase the efficiency of the reaction it was necessary to optimize the steps involving electron/proton transfer to and from the quinone, and therefore a number of quinones were screened. In a stoichiometric test reaction various quinones (**4a**) were employed as hydrogen acceptors for the ruthenium-catalyzed dehydrogenation of 1-phenylethanol (**2a**) to acetophenone (**3a**) using ruthenium catalyst **1** (eq 1).

Table 1. Oxidation of 1-Phenylethanol (2a) with Stoichiometic Amounts of Quinones[a]

entry	benzoquinone	yield (%)[b] 10 min	30 min	1 h
1	tetrafluoro-1,4-benzoquinone (**4a**)	70	89	>99
2	2,6-dimethoxy-1,4-benzoquinone (**4b**)	61	84	>99
3	2-chloro-1,4-benzoquinone (**4c**)	58	82	>99
4	2,3-dimethoxy-5-methyl-1,4-benzoquinone (**4d**)	59	80	>99
5	1,4-benzoquinone (**4e**)	55	75	91
6	2,5-di-*tert*-butyl-1,4-benzoquinone (**4f**)	34	43	78
7	2,6-di-*tert*-butyl-1,4-benzoquinone (**4g**)	36	41	71

[a] The reactions were carried out on a 0.5 mmol scale with 0.1 mol % of catalyst **1** and 1.2 equiv of the benzoquinone in 3 mL of toluene at 100 °C under argon. [b] Derminined by GC.



(1)

The results given in Table 1 show that tetrafluoro-1,4-benzoquinone (**4a**) and 2,6-dimethoxy-1,4-benzoquinone (**4b**) are the two best quinones in this stoichiometric test reaction, and they gave a turnover frequency (TOF) of 3600−4200 h^{-1} during the first 10 min. Interestingly, the 2,6-di-*tert*-butyl-1,4-benzoquinone (**4g**) employed in our preliminary study[6b] turned out to be the slowest quinone of those tested.

We have previously demonstrated that the hydroquinone can be in-situ reoxidized to the corresponding quinone by a metal macrocyclic complex/O_2, and in this way the quinone can be used in catalytic amounts. In this dynamic electron-transfer process (cf. Scheme 1) it is also important that the oxidation of the hydroquinone to quinone be fast. Now, of the two hydroquinones produced from entry 1 and 2 in Table 1, the tetrafluorohydroquinone is more difficult to reoxidize to quinone than the corresponding 2,6-dimethoxyhydroquinone. This is because of the considerably higher oxidation potential for quinone **4a** compared to the electron-rich quinone **4b**. As anticipated, the latter quinone was superior to the former in the aerobic triple catalytic system (cf. Scheme 1). Therefore, **4b** was chosen as quinone in the aerobic process.

Choice of Oxygen-Activating Catalyst. A number of metal macrocyclic complexes and related complexes are known to activate molecular oxygen. In living organisms various metal porhyrins are used for this purpose. We have previously used three different types of complexes

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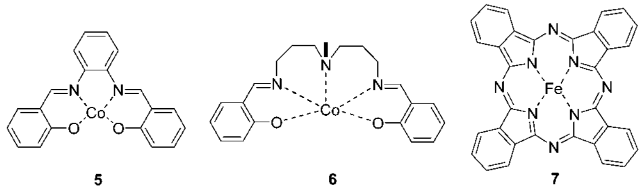


Figure 1. Oxygen-activating catalysts.

Table 2. Aerobic Oxidation of 1-Phenylethanol[a]

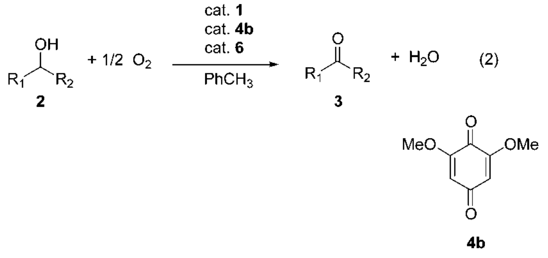
entry	solvent, temperature	ML complex	conversion (%)[b]
1	THF, 65 °C	**7**	58
2	THF, 65 °C	**6**	78
3	toluene, 100 °C	**7**	100
4	toluene, 100 °C	**6**	100[c]

[a] The reactions were carried out on a 1 mmol scale in 5 mL solvent under a balloon filled with ca. 2% oxygen in nitrogen employing 0.5 mol % of catalyst **1**, 20 mol % of **4b**, and 2 mol % of metal−ligand (ML) complex. Reaction time: 48 h. [b] Determined by GC. [c] 24 h.

for biomimetic aerobic oxidations: metal complexes of porphyrins,[5a] phthalocyanines,[5a] and salens.[5,6] Because of the tendency for oxidative degradation, porphyrins were avoided and the three complexes in Figure 1 were tested.

Attempted aerobic oxidation of 1-phenylethanol using catalyst **1**, quinone **4b**, and Co(salophen) (**5**) in toluene in the temperature range 20−100 °C was unsuccessful and gave very low conversions to ketone. We have previously shown that the addition of a fifth ligand, e.g., triphenylphosphine, improves the activity in aerobic oxidation of primary alcohols with **5** as oxygen-activating catalyst.[6a] However, in the oxidation of 1-phenylethanol poor results were still obtained on addition of triphenylphosphine. The results from the other two complexes are given in Table 2. Complex **6** seems to be slightly better than complex **7** but both complexes work well as oxygen-activating catalysts.

Biomimetic Oxidation of Alcohols. The coupled catalytic system chosen for aerobic oxidation of secondary alcohols consists of the binuclear ruthenium complex **1**[19] as the substrate-selective catalyst, quinone **4b** as electron-transfer mediator (ETM), and bis(salicylideniminato-3-propyl)methylamino−cobalt(II) **6** as the oxygen activator. These new aerobic oxidations are quite efficient and in most cases complete within 1−2 h. They can be carried out under air with only 0.5 mol % of catalyst loading and give high turnover frequency (TOF). GC analysis of the reactions showed excellent conversion of the alcohols without any observable byproduct (>99% selectivity), and the ketone products were isolated in good to high yields (eq 2).



The results of the oxidation of secondary alcohols to the corresponding ketones are summarized in Table 3. An important advantage with the present system is that the catalytic reaction tolerates a wider range of O_2 concentrations. In the preliminary study[6b] it was necessary to run the reaction at very low O_2 concentrations, in the range 1−5% O_2 in N_2. The present system tolerates much higher O_2 concentrations without being deactivated and is preferentially run under air.

When we applied our system to the oxidation of benzylic alcohols the isolated yields of ketones are good to high (Table 3, entries 1−3). These oxidation reactions were performed also at lower oxygen concentration using air:nitrogen of 1:10 (~2% O_2 in N_2, Table 2) and with different oxygen activators (such as iron(II) phthalocyanine). The conversion (monitored by GC) to the corresponding ketone was still high (>85%), but under these reaction conditions the reaction was slower.

More resistant substrates, such as cyclic aliphatic alcohols and linear aliphatic alcohols, can be oxidized with the current system in good to excellent yields (entries 4−12) and with good turnover frequencies (TOFs). Since the reaction takes 1−2 h with a substrate to catalyst (S/C) ratio of 200, the turnover frequency (TOF) is 100−200 h^{-1} (50−100 h^{-1} based on ruthenium). For example 2-octanol gave a TOF of 194 h^{-1} (97 h^{-1} based on ruthenium), which is the highest ever reported for a ruthenium-catalyzed aerobic oxidation of this substrate. As a comparison, previously reported active ruthenium systems $RuCl_2(PPh_3)_3$−TEMPO[10] and TPAP[11] (tetrapropylammonium perruthenate) gave TOFs of 14 h^{-1} and 5.5 h^{-1}, respectively, for 2-octanol in aerobic oxidation.[10]

The present catalytic system tolerates the presence of C−C double bonds, and in the oxidation of unsaturated alcohol **2g** (entry 7) no epoxidation of the alkene bond could be detected. Sterically hindered alcohols such as menthol and norborneol (entries 13−15) were also efficiently oxidized to ketones using this new ruthenium-based aerobic process.

To demonstrate the utility of this new oxidation, a scale-up for the aerobic oxidation of cyclohexanol was carried out. The oxidation was done on a 100 mmol scale (10 g scale) with a substrate/catalyst (S/C) ratio of 400 which gave a 95% isolated yield of cyclohexanone. Also, it was demonstrated that for the oxidation of cyclohexanol a substrate/catalyst (S/C) ratio of 1000 could be used to give turnover numbers (TONs) of 700 (350 based on ruthenium)(5M in toluene) and 800 (400 based on ruthenium)(neat without solvent).

Mechanistic Considerations. The ruthenium-catalyzed aerobic oxidation of alcohols with **1** as catalyst involves a highly efficient dehydrogenation step. Catalyst **1** is known to dissociate into **1a** and **1b** (Scheme 2). The former can act as a dehydrogenation species, for alcohols, and the latter can hydrogenate ketones, C−C double bonds, and other unsaturated compounds. As shown from the results in Table 1, the dehydrogenation of alcohol **2a** by **1a** has a turnover frequency of >4000 h^{-1} at 100 °C in toluene.

The principle for the biomimetic aerobic oxidation of alcohols with the coupled catalytic system is shown in Scheme 3. The dehydrogenation of the alcohol with **1a**

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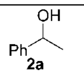
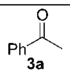
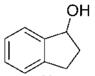
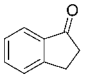
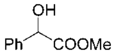
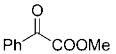
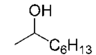
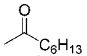
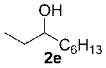
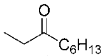
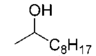
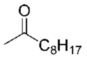
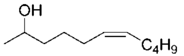
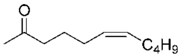
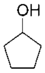
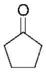
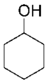
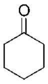
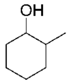
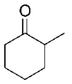
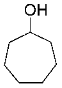
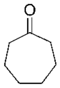
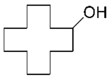
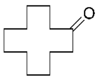
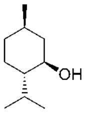
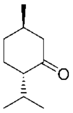
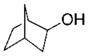
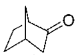
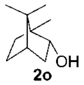
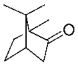
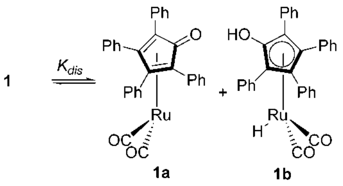
Table 3. Ruthenium-Catalyzed Aerobic Oxidation of Secondary Alcohols[a]

Entry	Substrate	Reaction Time (h)	Product	Yield[b](%)
1	 **2a**	1	 **3a**	89
2	 **2b**	2.8	 **3b**	88
3	 **2c**	2	 **3c**	81[c]
4	 **2d**	1	 **3d**	92
5	 **2e**	1	 **3e**	92
6	 **2f**	1	 **3f**	87
7	 **2g**	2.5	 **3g**	92
8	 **2h**	1	 **3h**	88
9	 **2i**	1	 **3i**	92
10	 **2j**	2	 **3j**	89
11	 **2k**	1	 **3k**	92
12	 **2l**	1.5	 **3l**	86
13	 **2m**	2	 **3m**	80
14	 **2n**	1.5	 **3n**	70[c]
15	 **2o**	2	 **3o**	73[c]

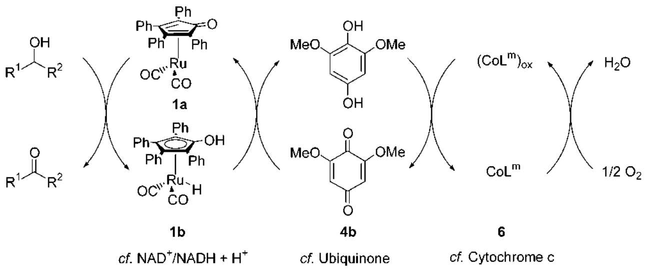
[a] Unless otherwise stated, the reactions were carried out under air on a 1 mmol scale in 1 mL of toluene at 100 °C, employing 0.5 mol % of **1**, 20 mol % of **4b**, and 2 mol % of **6**. [b] Isolated yield. [c] Employing 1 mol % of **1**.

produces ketone and **1b**. Complex **1b** can now deliver the hydrogen atoms to quinone **4b**, which regenerates **1a**, and **4b** is converted to the corresponding hydroquinone. The reoxidation of the hydroquinone to quinone **4b** is carried out by air/**6**. This aerobic oxidation of alcohol is reminiscent of biological dehydrogenations in which NAD^+/NADH−ubiquinone−cytochrome c are employed for electron transfer.

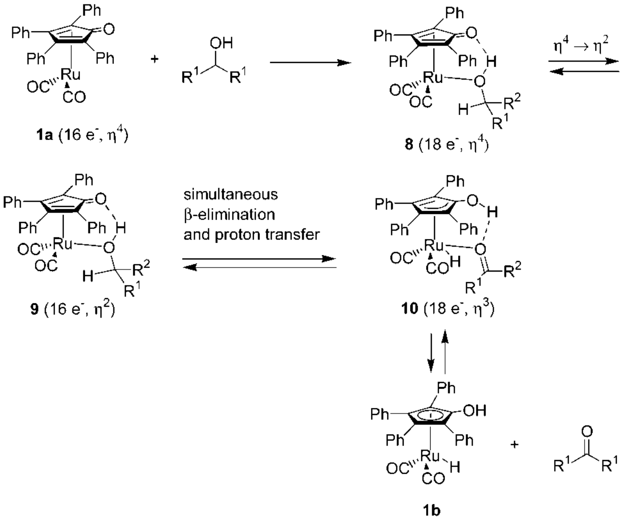
Scheme 2



Scheme 3. Biomimetic Aerobic Oxidation of Alcohols



Scheme 4



The biomimetic coupled catalytic system shown in Scheme 3 leads to a mild kinetically controlled electron transfer/H-transfer from the alcohol to molecular oxygen. The high kinetic control requires close interaction (contact) between the redox couples involved in the cascade through coordination or weak bonding. Control experiments showed that no aerobic oxidation took place according to GC within 24 h if any of the components of the catalytic system was removed.

The dehydrogenation of the alcohol by ruthenium species **1a** deserves some comments. It is likely that the alcohol coordinates to the 16-electron complex **1a** to give alcohol complex **8** (Scheme 4). The corresponding amine complexes are known to form and have been isolated and characterized.[20] Park et al.[21] has recently reported on the alcohol complex **8** from 2-propanol ($R_1 = R_2 = CH_3$).[22] A related ruthenium 2-propanol complex in which there is a hydrogen bond to an acetamido ligand was recently isolated and characterized by Yi et al.[23] Complex **8** is an 18-electron complex, which on ring slipping would give 16-electron complex **9**. Simultaneous β-elimination and proton transfer in **9** would give **10**, which would dissociate ketone and give **1b**. This mechanism is consistent with the combined isotope effect observed for the reverse reaction, addition of hydrogen to the keto function (**10** → **9**).[24] Alternatively, a direct concerted hydrogen transfer from the alcohol to **1a**, without prior coordination of the alcohol, could also occur.[24]

Conclusion

In conclusion, the present system based on ruthenium-catalyzed dehydrogenation of secondary alcohols followed by hydrogen transfer via coupled catalytic cycles is a highly efficient biomimetic process for aerobic oxidation of alcohols. The system is robust and does not undergo deactivation by air. The oxidation of benzylic as well as aliphatic alcohols can be performed with excellent yield and selectivity to give the corresponding ketones.

Experimental Section

^1H NMR spectra were recorded in $CDCl_3$ with a Varian XL-400 spectrometer using the residual peak of $CDCl_3$ (7.26 ppm for ^1H) as internal standard. Analytical gas chromatography was performed with a Varian 3400 GC with a FID detector, connected to a Varian computing integrator. A 30-m DB-17 J&M fused silica column was used. Solvents were purified by standard procedures. Ruthenium catalyst **1** was prepared according to a literature procedure.[25] Bis(salicylideniminato-3-propyl)methylamino–cobalt(II) (**6**) was purchased from Aldrich and used as received. 1-Phenylethanol and 1-cyclopentanol (Aldrich) were distilled prior to use. (*Z*)-5-Undecen-2-ol was prepared by literature method.[6d] All other reagents are commercially available and were used without further purification. Column chromatography was performed with Merck 60 silica gel and analytical TLC was performed on Merck precoated silica 60-F254 plates. Solvents for extraction and chromatography were technical grade and distilled before use. Iron(II) phthalocyanine (**7**) was activated as described in ref 5a and Co(salophen) (**5**) was prepared according to ref 5a.

All 1,4-benzoquinones are available from commercial sources, **4a**–**4f** from Aldrich and **4g** from Lancester.

Oxidation of 1-Phenylethanol with Stoichiometric Amount of Quinones. Ruthenium complex **1** (0.54 mg, 0.5 μmol, 0.1 mol %) and quinone **4b** (101 mg, 0.6 mmol, 1.2 equiv) were dissolved under argon atmosphere in 3 mL of toluene in a round-bottomed flask equipped with a condenser and a stirring bar. 1-Phenylethanol (0.5 mmol) was added, and the reaction mixture was heated to 100 °C. The reaction course was monitored by gas chromatography.

General Procedure for Ruthenium-Catalyzed Aerobic Oxidation of Secondary Alcohols. Ruthenium complex **1** (5.4 mg, 0.005 mmol, 0.5 mol %), quinone **4b** (32.8 mg, 0.2 mmol, 20 mol %), and cobalt complex **6** (8.2 mg, 0.02 mmol 2 mol %) were dissolved in 1 mL of toluene under argon atmosphere in a round-bottomed flask equipped with a condenser and a stirring bar. The appropriate alcohol (1 mmol) was added to this mixture followed by flushing with air for ca. 1 min. The final reaction mixture was heated to 100 °C with an oil bath.[26] After the appropriate reaction time, the mixture was cooled to room temperature and purified by flash

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[20] Abed, M.; Goldberg, I.; Stein, Z.; Shvo, Y. *Organometallics* **1988**, *7*, 2054.

[21] Jung, H.-M.; Shin S.-T.; Kim Y.-H.; Kim M.-J.; Park J. *Organometallics* **2001**, *20*, 3370.

[22] The correctness of the alcohol complex of ref 21 was recently investigated. It was found that the proposed complex of ref 21 was not the alcohol complex: Casey, C. P.; Bikzhanova, G. A.; Bäckvall, J. E.; Johansson, L.; Park, J.; Kim, Y. H. *Organometallics*, to be submitted.

[23] Yi, C. S.; He, Z.; Guzei, I. A. *Organometallics* **2001**, *20*, 3641.

[24] Casey, C. P.; Singer, S. W.; Powell, D. R.; Hayashi, R. K.; Kavana, M. *J. Am. Chem. Soc.* **2001**, *123*, 1090.

[25] Huerta, F. F.; Laxmi, Y. R. S.; Bäckvall, J.-E. *Org. Lett.* **2000**, *2*, 1037.

[26] Air with toluene at 100 °C produces explosive mixtures in the gas phase.

chromatography. The products were characterized by comparison with authentic samples. All the product obtained and shown in Table 1 are known compounds and were characterized by comparison with spectral data from the literature.

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Supporting Information Available: Full experimental details are available free of charge via the Internet at http://pubs.acs.org.

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