

Silica-Supported Molybdenum Alkylidyne *N*-Heterocyclic Carbene Catalysts: Relevance of Site Isolation to Catalytic Performance

Philipp M. Hauser¹, Michael Hunger², Michael R. Buchmeiser^{*1}

¹Institute of Polymer Chemistry, ²Institute of Chemical Technology, University of Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany

*corresponding author: michael.buchmeiser@ipoc.uni-stuttgart.de

Abstract

The immobilization molybdenum alkylidyne [(p-OMeof the complex $C_6H_4C \equiv MO(OCMe(CF_3)_2)_3 \cdot DME$ (DME = 1,2-dimethoxyethane) on silica using a silicasupported N-heterocyclic carbene (NHC), i.e. 1,3-di(*i*-propyl)imidazol-2-ylidene, is reported. Two different types of silica, that is silica 60 and partially dehydroxylated silica 60 obtained via heating to 650°C (SiO₂₋₆₅₀) were used. In both cases, excess silanol groups were end capped with trimethylsilyl chloride. Immobilization of both the NHC precursor and the metal alkylidyne was followed by ¹⁹F magic angle spinning (MAS) and ¹³C cross polarization magic angle spinning (CPMAS) NMR and inductively-coupled optical emission spectroscopy (ICP-OES). The metal alkylidyne supported on both types of silica was active in alkyne metathesis and showed activity for a series of functional 2-alkynes. Most important, the metal alkylidyne supported on SiO₂₋₆₅₀ displayed a substantially higher alkyne metathesis activity than the homogeneous analog or the one supported on regular silica, which is attributed to a site isolation effect and, as a result, reduced bimolecular decomposition.

Introduction

Alkyne metathesis catalyzed by well-defined metal alkylidynes was first reported by Schrock et al.^[1] Seminal work by this group^[1a, 2] and by Fürstner,^[3] Nuckolls,^[4] Veige,^[5] Tamm,^[6] Fischer,^[4, 7] Zhang^[8] and Moore^[9] contributed to the armor of catalysts and protocols relevant to alkyne metathesis. Inspired by the high activity of Mo- and W-imido/oxo alkylidene NHC complexes,^[10] we recently reported on a new class of formally 14-electron (not counting the lone pairs of oxygen) metal alkylidynes bearing *N*-heterocyclic carbenes (NHCs) and their catalytic activity in some 2-alkyne benchmark reactions^[11] In case NHCs such as 1,3-di(*i*-propyl)imidazol-2-ylidenen (**IPr**) with a low Tolmann electronic parameter^[12] and sufficiently high *pK*_a value, respectively, are used, the corresponding metal alkylidyne complexes bear the NHC throughout the catalytic cycle. Based on the set of existing data, a cationic metal alkylidene NHC intermediate has been proposed,^[11] yet was not unambiguously proved so far. In view of the high stability of metal alkylidynes that bear the **IPr**-ligand,^[11] we immobilized the corresponding metal alkylidyne on two types of silica to (i) proof the integrity of the complex under catalytic conditions and (ii) to study the influence of site isolation on catalytic performance. Here we present our results.

Results and Discussion

Synthesis of silica-supported Mo-alkylidyne NHC complexes cat-1 and cat-2

Immobilization of **IPr** on silica was accomplished using the synthetic protocol outlined in Scheme 1. Starting from 4-hydroxymethylimidazole, the corresponding *t*-butyldimethylsilyl-protected compound **1** was prepared and bisalkylated at the 1- and 3-postion, respectively, using *i*-propyl iodide to yield **2**. Compound **2** was converted into the corresponding tetrafluoroborate salt **3** via reaction with NaBF₄. Reaction of **3** with dry silica at 130°C in 1,2-dichloroethane yielded the corresponding silica-supported imidazolium salts **4** and **5**. *t*-Butyldimethylsilanol was detected by GC-MS, confirming immobilization via a newly formed C-O-Si bond. Notably, two types of silica were employed, (i) dry silica 60 and (ii) partially dehydroxylated silica prepared via heating silica 60 to 650°C under vacuum, referred to as SiO₂₋₆₅₀. The two silica materials had the same specific surface area (~ 565 m²/g) and average pore diameter (6.2 nm) but differed in the number of surface-silanol groups

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(2.1 mmol SiOH/g for silica 60 and ~ 0.3 mmol SiOH/g for the partly dehydroxilated SiO₂₋₆₅₀). Reactions were also followed by ¹H MAS NMR and ¹³C CPMAS NMR (Figures S6, S7, S.I.) and unambiguously confirmed immobilization of the precursor. Thus, the imidazolium moleties were observed at δ = 119.5 and 133.8 ppm in the ¹³C CPMAS NMR spectrum and at δ = 7.21 ppm in the ¹H MAS NMR spectrum. The ¹³C CPMAS NMR signal at δ = 53.6 ppm can be assigned to the CH₂-O-silica group. Accordingly, a ¹H MAS NMR signal at δ = 4.65 ppm was found. The CH(CH₃)-groups were found at δ = 22 ppm in the ¹³C CPMAS NMR spectrum and at δ = 0.7 ppm in the ¹H MAS NMR spectrum. The ¹³C CPMAS NMR signal at δ = -7.6 ppm was assigned to CH₃-Si groups, resulting from the reaction of intermediary formed t-butyldimethylsilanol with the silica surface. Next, with both silica materials, excess silanol groups were end capped with a large excess of trimethylsilyl chloride. Reaction with lithium hexamethyldisilazide (LiHDMS) followed by the reaction with [(p-OMe- $C_6H_4C=MO(OCMe(CF_3)_2)_3 DME$ resulted in the formation of cat-1 (on silica 60) and cat-2 (on SiO₂₋₆₅₀). ¹⁹F MAS NMR (Figures S8, S9, S.I.) confirmed the formation of the catalysts. While with **cat-1** some remaining imidazolium BF₄-salt could be detected at $\delta = -148$ ppm along with the signals for the supported catalyst around $\delta = -80$ ppm, conversion to the immobilized catalyst proceeded clearly for cat-2 using dehydroxylated silica. Thus, after deconvolution, two ¹⁹F MAS NMR signals at $\delta = -78.0$ and -81.7 ppm, ratio 1:2, were observed (Figure S10, S.I.). Both the shifts and the relative intensity ratios are in line with those of the homogeneous analog, $[(p-OMe-C_6H_4C=)Mo(OCMe(CF_3)_2)_3(IPr)]$, for which the alkoxides (in C₆D₆) are observed at $\delta = -76.15$ (m, 6F), -76.32 (m, 6F), -76.87 (s, 6F).^[11] Together with molybdenum contents of 0.17 and 0.08 mmol Mo/g_{silica} for cat-1 and cat-2, determined by treatment of the immobilized catalysts with aqua regia and followed by analysis by ICP-OES, respectively, this strongly points towards immobilization of the metal alkylidyne via the NHC. Notably, both cat-1 and cat-2 differ from the systems recently reported by Coperét and Tamm et al.,^[6g] in which one fluorinated alcohol was replaced by a

surface-silanolate, and from the system described by Moore et al., in which one amide was replaced by a surface-silanolate.^[9g]



Scheme 1. Synthetic route for the synthesis of silica-supported Mo-alkylidyne NHC complexes **cat-1** and **cat-2**. TBDMSO = *t*butyldimethylsilyloxy, TMS = trimethylsilyl, HMDS = hexamethyldisilazide.

Alkyne metathesis reactions

A set of benchmark reactions was chosen to identify potential differences between the two supported Mo-alkylidyne NHC catalysts **cat-1** and **cat-2** and the homogeneous analog, [(p-OMe-C₆H₄C=)Mo(OCMe(CF₃)₂)₃(IPr)]. Table 1 summarizes the results obtained; Figure 1 shows the structures of the substrates **S1** – **S7** and the corresponding products **P1** – **P7**.

Table 1. Productivity (TON) in alkyne metathesis reactions using catalysts [(p-OMe- $C_6H_4C=$)Mo(OCMe(CF₃)₂)₃(IPr)], cat-1 and cat-2. (substrate:catalyst = 1000:1).Reaction conditions: toluene, room temperature, 4 h.

catalyst	S1	S2	S 3	S4	S5	S 6	S7
[(p-OMe-C ₆ H ₄ C≡)Mo(OCMe(CF ₃) ₂) ₃ (IPr)]	990	990	790	670	0	380	160

99	99	79	67	0	38	16
990	990	230	440	0	-	-
99	99	23	44	0	-	-
990	990	990	960	260	970	800
99	99	99	96	26	97	80
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Figure 1. Structures of substrates **S1** – **S7** and the corresponding products **P1** – **P7** formed along with 2-butyne.

While **cat-1** is outrivaled by the homogeneous analog, **cat-2** shows substantially higher productivities, expressed in turnover numbers, TONs, for all substrates used. Compared to the TONs for both the homogeneous, NHC free catalyst [MesC=Mo(OCMe(CF₃)₂)₃] (TON = 185,000) and the corresponding supported catalyst [(=SiO)Mo(=CMes)(OCMe(CF₃)₂)₂] (TON = 54000),^[6g] both the supported and homogeneous Mo-alkylidyne NHC catalysts show lower productivities, yet the supported Mo-alkylidyne NHC catalyst showed higher TONs compared to the homogeneous analog. Interestingly, also substrates that are either poorly converted (S3, S4) or not converted at all (S5, a nitrile-containing 2-alkyne) by both [(*p*-OMe-C₆H₄C=)Mo(OCMe(CF₃)₂)₃(IPr)] and **cat-1** undergo alkyne metathesis with the same catalyst supported on partially dehydroxylated silica. To confirm that the products P1 – P7 were the sole products to be generated, metathesis reactions were conducted in deuterated benzene

(for further information, see S.I.). No other products could be detected, neither by NMR nor by GC-MS. In view of the lower catalyst loading in **cat-2**, which is approximately half the one in **cat-1**, site isolation of the catalytic centers must occur and is made responsible for the higher productivity observed for **cat-2**. In fact, similar effects have been proposed earlier.^[13] The data presented here also proof the integrity of the complex under catalytic conditions. Implications of the results presented here on the stability of the proposed intermediary cationic Mo-alkylidynes are under investigations. To further compare the activities of the different catalysts, the conversion of substrate **S3** was measured over time for catalysts **cat-2** and the homogeneous analog. Figure 2 shows that after 30 minutes **cat-2** already reaches 90 % conversion as compared to 40 % for the homogeneous catalyst.





 $C_6H_4C=$)Mo(OCMe(CF₃)₂)₃(IPr)] and cat-2 (substrate : catalyst = 1000 : 1, room temperature,

toluene, internal standard for GC-MS: t-butylbenzene).

On a final note, molybdenum leaching was below the limit of detection of ICP-OES (< 2 ppm). This supports the initial assumption that the corresponding Mo-alkylidyne NHC complex remains fully integer throughout the catalytic cycle and no dissociation of the NHC occurs.

Conclusions

The first silica-supported Mo-alkylidyne NHC complexes have been prepared. Using partially dehydroxylated silica, catalyst loadings are lower by approximately a factor of two compared to regular silica. The resulting site isolation effectively prevents bimolecular catalyst decomposition, which could be responsible for the higher productivities and higher functional group tolerance of catalysts supported on partially dehydroxylated silica. Both catalytic activities and the low metal leaching strongly suggest a high structural integrity of the supported catalyst.

Experimental

All reactions were performed under the exclusion of air and moisture by standard Schlenk techniques unless otherwise noted. Reactions involving metal complexes were performed in a nitrogen-filled glove box (MBraun Labmaster 130). Glassware was either stored at 120°C over night and cooled in an evacuated antechamber or dried at 500°C under high vacuum (0.01 mbar). CH₂Cl₂, diethyl ether, toluene and pentane were dried by using an MBraun SPS-800 solvent purification system with alumina drying columns and stored over 4 Å Linde type molecular sieves. THF was distilled from Na prior to use and stored over 4 Å Linde type molecular sieves and Selexsorb®. Deuterated solvents were filtered over activated alumina and stored over 4 Å Linde type molecular sieves inside the glove box. All liquid substrates were dried by stirring over CaH₂ for several hours and subsequent distillation followed by filtration over activated alumina. Substrates were degassed by several freeze-pump-thaw Å cycles stored activated 4 molecular sieves. and over [(p-OMe- $C_6H_4C=MO(OCMe(CF_3)_2)_3(IPr)$] was prepared according to the literature.^[11] Silica 60 M (Machery-Nagel, particle diameter 0.04-0.063 mm, pore diameter ~ 6.2 nm, specific surface area ~ 565 m²/g, 2.1 mmol SiOH/g) was used. Silica 650 prepared therefrom had the same

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particle diameter, average pore diameter and specific surface area, but ca. 0.3 mmol SiOH/g. For the synthesis of substrates S1 - S7 refer to refs.^[6d, 11, 14]

¹H and ¹³C NMR spectra were recorded on a Bruker Avance III 400 spectrometer at 400 and 100 MHz, respectively. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance resulting from residual solvent protons (CDCl₃: 7.26 ppm, C₆D₆ 7.16 ppm, CD_2Cl_2 5.13 ppm) as reference. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept = septet, br = broad, m = multiplet), integration and coupling constants (Hz). GC-MS-data were obtained on an Agilent Technologies 5975C inert MSD with triple-axis detector, a 7693 autosampler, and a 7890A GC system equipped with a SPB-5 fused silica column (34.13 m×0.25 mm×0.25 µm film thickness). The injection temperature was set to 150°C. The column temperature ramped from 45 to 250°C within 8 min, and was then held for further 5 min. The column flow was 1.05 mL min⁻¹. Elemental analyses were carried out at the Institute of Inorganic Chemistry, University of Stuttgart, Germany. ¹H MAS NMR, ¹³C CPMAS NMR, and ¹⁹F MAS NMR spectra were recorded on a Bruker Avance III 400 WB spectrometer at the Institute of Chemical Technology, University of Stuttgart, Germany, under in situ conditions. A 4 mm ZrO₂ rotor with a gas-tight delrin cap and a sample spinning rate of 8 kHz were used. ICP-OES data were recorded on a Spectro Acros 160 CCD, equipped with a Cetac ASX-260 Autosampler. Analysis of the samples was carried out with the Software Smart Analyzer *Vision 4.02.0834*. For calibration, Mo-containing standard solutions (5% HNO₃, Chem-Lab, Zedelgem, Belgium) containing 0.00, 0.10, 1.00, and 5.00 mg kg⁻¹ of Mo were used. Mo was measured at λ = 202.095 nm, the background was measured at λ = 430.01 nm. The detection range was 0.00205-6 mg L⁻¹. The standard deviation was 0.0636 mg L⁻¹. The surface area and the pore size were calculated from N2 adsorption / desorption measurements at -196°C using an Autosorb-1 Surface Area and Pore Size Analyzer (Quantachrome Instruments, Boynton Beach, Fl., USA) with the corresponding AS1 win version 1.51 software. To remove adsorbed material from the surface, samples were first heated in vacuo for several hours.

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4-(((t-Butyldimethylsilyl)oxy)methyl)-1H-imidazole (4.00 g, 18.9 mmol) was dissolved in tetrahydrofuran (200 mL) and cooled to -30°C. To this solution NaH (0.68 g, 28.4 mmol) was added in small portions and the mixture was stirred for 3 h at room temperature. Next, the reaction mixture was filtered through a pad of celite and 2-iodopropane (8.00 mL, 80.0 mmol) was added to the filtrate and the mixture was refluxed for 80 h. All volatiles were removed under reduced pressure, the residue was dissolved in chloroform (200 mL) and filtered through a pad of celite. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica G60 using CHCl₃:CH₃OH=95:5 as mobile phase to yield the product as a white solid (1.48 g, 2.7 mmol, 14%): ¹H NMR (400 MHz, CDCl₃) δ = 10.30 (d, ⁴*J*_{H-H} = 1.7 Hz, NC*H*N, 1H), 7.43 (d, ⁴*J*_{H-H} = 1.6 Hz, NC*H*C, 1H), 5.06 (sept, ³*J*_{H-H} = 6.7 Hz, ^{*i*}Pr, 1H), 4.78 – 4.60 (m, CH₂, ^{*i*}Pr, 3H), 1.69 (d, ³*J*_{H-H} = 6.8 Hz, ^{*i*}Pr, 6H), 1.60 (d, ${}^{3}J_{H-H}$ = 6.7 Hz, i Pr, 6H), 0.86 (s, t Bu, 9H), 0.10 (s, Me, 6H) ppm; 13 C NMR (101 MHz, CDCl₃) δ = 135.2 (C_{Imidazolium}), 133.3 (C_{Imidazolium}), 117.4 (C_{Imidazolium}), 54.8 (ⁱPr), 53.4 (ⁱPr), 51.8 (Me), 25.7 (^tBu), 23.6 (ⁱPr), 23.3 (ⁱPr), 18.2 (^tBu), -5.3 (Me) ppm; Anal. calcd. (%) for C₁₆H₃₃IN₂OSi: C, 45.28; H, 7.84; N, 6.60; found: C, 45.07; H 8.01; N, 6.70. 4-(((t-Butyldimethylsilyl)oxy)methyl)-1,3-di(i-propyl)-1H-imidazolium tetrafluoroborate

4-(((t-Butyldimethylsilyl)oxy)methyl)-1,3-di(i-propyl)-1H-imidazolium

(3). 2 (1.10 g, 2.59 mmol) was dissolved in CH_2Cl_2 (50 mL) and stirred with a solution of sodium tetrafluoroborate (0.34 g, 3.11 mmol) in demineralized water (20 mL) at room temperature for 18 h. The organic layer was separated, dried over sodium sulfate and all volatiles were removed under reduced pressure to yield the product as a white solid (0.74 g, 1.93 mmol, 75%): ¹**H NMR** (400 MHz, CDCl₃) δ = 9.51 (d, ⁴*J*_{H-H} = 1.7 Hz, NC*H*N, 1H), 7.39 (d, ⁴*J*_{H-H} = 1.6 Hz, NC*H*C, 1H), 4.87 (sept, ³*J*_{H-H} = 6.7 Hz, ^{*i*}Pr, 1H), 4.75 – 4.62 (m, C*H*₂, ^{*i*}Pr, 3H), 1.64 (d, ${}^{3}J_{H-H}$ = 6.8 Hz, i Pr, 6H), 1.57 (d, ${}^{3}J_{H-H}$ = 6.7 Hz, i Pr, 6H), 0.87 (s, Me, 9H), 0.10 (s, i Bu, 6H) ppm; ¹⁹**F NMR** (376 MHz, CDCl₃) $\delta = -151.06$, -151.12 ppm; ¹³**C NMR** (101 MHz, CDCl₃) δ = 134.3 (C_{Imidzolium}), 133.6 (C_{Imidzolium}), 117.5 (C_{Imidzolium}), 54.7 (ⁱPr), 53.5 (ⁱPr), 51.7

(CH₂), 25.8 (^tBu), 23.2 (^tPr), 23.1 (^tPr), 18.2 (^tBu), −5.4 ppm (Me). **HRMS (ESI)** *m*/*z* calcd. for C₁₆H₃₃N₂OSi⁺: 297.2358; found: 297.2358.

Immobilization of 3 on silica and endcapping (4): Silica (200 mg, 2.1 mmol SiOH/g) and 4-(((*t*-butyldimethylsilyl)oxy)methyl)-1,3-di(*i*-propyl)-1*H*-imidazolium tetrafluoroborate (240 mg, 0.62 mmol) were suspended in 1,2-dichloroethane (25 mL) and stirred for 18 h at 130°C. After cooling the reaction mixture to room temperature, the silica was filtered off, washed several times with methylene chloride and diethyl ether and dried *in vacuo*. Next, $(CH_3)_3SiCl$ (1.5 mL, 11.8 mmol) was added to a suspension of this material (200 mg) in CH_2Cl_2 and the mixture was stirred for 18 h at room temperature. Then the silica was filtered off, washed with methylene chloride and diethyl ether and dried *in vacuo*.

Immobilization of 3 on partly dehydroxylized silica and endcapping (5): Silica₆₅₀, (1.13 g, partly dehydroxylized *in vacuo* for 5 h at 500°C and another 10 h at 650°C, 0.3 mmol SiOH/g) and 4-(((*t*-butyldimethylsilyl)oxy)methyl)-1,3-di(*i*-propyl)-1*H*-imidazolium tetrafluoroborate (100 mg, 0.26 mmol) were suspended in 1,2-dichloroethane (30 mL) and stirred for 18 h at 130°C. The surface-modified silica was filtered off, washed several times with methylene chloride and diethyl ether and dried *in vacuo*. To a suspension of this material (200 mg) in CH₂Cl₂ (20 mL) was added (CH₃)₃SiCl (1.5 mL, 11.8 mmol) and the mixture was stirred for 18 h at room temperature. Then the silica was filtered off, washed with methylene chloride and diethyl ether and dried *in vacuo*.

Deprotonation of immobilized imidazolium salt (6): A solution of lithium hexamethyldisilazide (104 mg, 0.62 mmol) in tetrahydrofuran (20 mL) was added slowly to a suspension of **4** (200 mg) in the same solvent and stirred for 2 h at room temperature. The silica was filtered off, washed with dry dimethylsulfoxide and diethyl ether and dried *in vacuo*. Deprotonation of **5** was carried out in an analogous manner to yield **7**.

Immobilization of [(*p*-OMe-C₆H₄C=)Mo(OCMe(CF₃)₂)₃·DME] (cat-1): 6 was suspended in toluene (10 mL) and a solution of [(*p*-OMe-C₆H₄C=)Mo(OCMe(CF₃)₂)₃·DME] (340 mg,

0.40 mmol) in toluene (8 mL) was added. The reaction mixture was stirred for 18 h at room temperature. The silica was filtered off, washed with toluene and diethyl ether and dried *in vacuo*. Immobilization of $[Mo(CC_6H_4OMe)(OC(CF_3)_2Me)_3(DME)]$ via **7** to yield **cat-2** was carried out in an analogous manner.

Determination of the molybdenum content by ICP-OES: A known amount of **cat-1** (8.5 mg) was dissolved in *aqua regia* (5 mL) by heating in a microwave oven for 1 h at 160°C. After cooling to room temperature, the mixture was diluted with demineralized water to 25 mL and filtered through a CHROMAFIL Xtra syringe filter (RC 0.20). The molybdenum content of the sample was determined by ICP-OES to be 5.6 mg/L, which corresponds to 1.64 wt.-% molybdenum or 0.17 mmol catalyst/g_{silica}. Determination of the molybdenum content of **cat-2**/g_{silica}.

Representative procedure for the determination of the molybdenum content of the metathesis products by ICP-OES: Cat-2 (20.9 mg, $1.7 \cdot 10^{-3}$ mmol) and 300 mg ground 5 Å molecular sieves were suspended in toluene. A solution of 1-phenyl-1-propyne (21.1 mg, 0.17 mmol) was added and the mixture was stirred for 4 h at room temperature. Then the mixture was filtered and all volatiles of the filtrate were removed under reduced pressure. Aqua regia (5 mL) was added to the residue and the mixture was diluted to 25 mL with demineralized water and filtered through a CHROMAFIL Xtra syringe filter (RC 0.20). No molybdenum was detected by ICP-OES. The limit of detection was 0.95 μ g·L⁻¹; accordingly, catalyst bleeding was < 0.15% (< 1.5 ppm Mo in the metathesis product).

General procedure for alkyne metathesis reactions: The substrate (20-40 mg) was dissolved in toluene (3 mL), 0.1 mL *t*-butylbenzene and 300 mg ground 5 Å molecular sieve were added. Then a solution of the respective catalyst in toluene was added and the reaction mixture was stirred for 4 h. Conversion was determined by GC-MS referring to *t*-butylbenzene as internal standard.

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General procedure for alkyne metathesis reactions with immobilized catalysts: The immobilized catalyst (for cat-2 and S1: 3.3 mg, $2.6 \cdot 10^{-4} \text{ mmol}$) and 300 mg ground 5 Å molecular sieves were suspended in toluene (1 mL). A solution of the respective substrate (for cat-2 and S1: 30.6 mg, 0.26 mmol) and 0.1 mL *t*-butylbenzene in toluene (2 mL) was added and the mixture was stirred for 4 h at room temperature. Conversion was determined by GC-MS referring to *t*-butylbenzene as internal standard.

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TOC Graphics



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