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Unveiling the catalytic nature of palladium-N-heterocyclic carbene catalysts in the α-alkylation of ketones with primary alcohols†

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We report herein the synthesis of four new Pd-PEPPSI complexes with backbone-modified N-heterocyclic carbene (NHC) ligands and their application as catalysts in the α-alkylation of ketones with primary alcohols using a borrowing hydrogen process and tandem Suzuki–Miyaura coupling/α-alkylation reactions. Among the synthesized Pd-PEPPSI complexes, complex **2c** having 4-methoxyphenyl groups at the 4,5-positions and 4-methoxybenzyl substituents on the N-atoms of imidazole exhibited the highest catalytic activity in the α-alkylation of ketones with primary alcohols (18 examples) with yields reaching up to 95%. Additionally, complex **2c** was demonstrated to be an effective catalyst for the tandem Suzuki–Miyaura-coupling/α-alkylation of ketones to give biaryl ketones with high yields. The heterogeneous nature of the present catalytic system was verified by mercury poisoning and hot filtration experiments. Moreover, the formation of NHC-stabilized Pd(0) nanoparticles during the α-alkylation reactions was identified by advanced analytical techniques.

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Introduction

Over the last three decades, metal-N-heterocyclic carbene (NHC) complexes have been increasingly appreciated in homogeneous catalysis and organometallic chemistry owing to their easy preparation, enhanced stability arising from strong metal-NHC bonding, and high tunability of steric and electronic properties of the NHC ligand.[1] In particular, NHCs have emerged as excellent ancillary ligands in palladium-catalyzed cross-coupling reactions.[2] Among the NHC-Pd precatalysts for cross-coupling reactions, Organ's Pd-PEPPSI complexes (PEPPSI = pyridine-enhanced catalyst preparation, stabilization, and initiation) can be mentioned as one of the most appealing ones due to not only their high catalytic activity in these reactions but also their easy preparation and high stability towards air and moisture.[3] Such precatalysts were successfully tested in a variety of cross-coupling reactions and found to display excellent performances in the Suzuki–Miyaura,[3,4] Negishi,[4c,5] Kumada–Tamao–Corriu,[4c,6] Heck,[7] Sonogashira,[8] C–H functionalization,[9] amination,[10] and sulfination[11] reactions to construct C–C, C–N, and C–S bonds for the synthesis of more complicated molecules.

On the other hand, the transition metal (TM)-catalyzed borrowing hydrogen (BH) or the hydrogen autotransfer methodology has become a powerful and green strategy to construct a $C(sp^3)$–$C(sp^3)$ bond for the one-step synthesis of more complicated molecules.[12] The main advantage of this methodology is the utilization of readily available, sustainable, and easy-to-handle alcohols as greener alkylating agents over mutagenic alkyl halides. Additionally, this strategy offers an increased step efficiency and atom economy over the conventional methods and generates water as the sole byproduct.[12] In this context, α-alkylation of ketones with primary alcohols based on the BH strategy to prepare synthetically and biologically important long-chain or branched ketones in the presence of precious (Ru, Rh, Ir, and Pd)[13–16] and nonprecious (Mn, Fe, Co, and Ni)[17–20] TM catalysts has been reported. Among the reported catalytic systems, a number of heterogeneous[16a–h,l] and homogeneous[16i–k] Pd-catalyzed protocols have been developed for the α-alkylation of ketones with primary alcohols for the selective synthesis of α-alkylated ketones. However, the use of a stoichiometric or excess amount of a base (1–3 equiv.),[16a–d,f–h,k,l] a high catalyst loading (2–10 mol%),[16b–d,g,h,j,k] an excess amount of alkylating alcohol,[16a–g,i,j,l] or additional phosphine-based[16i–k] ligands is required for most of the

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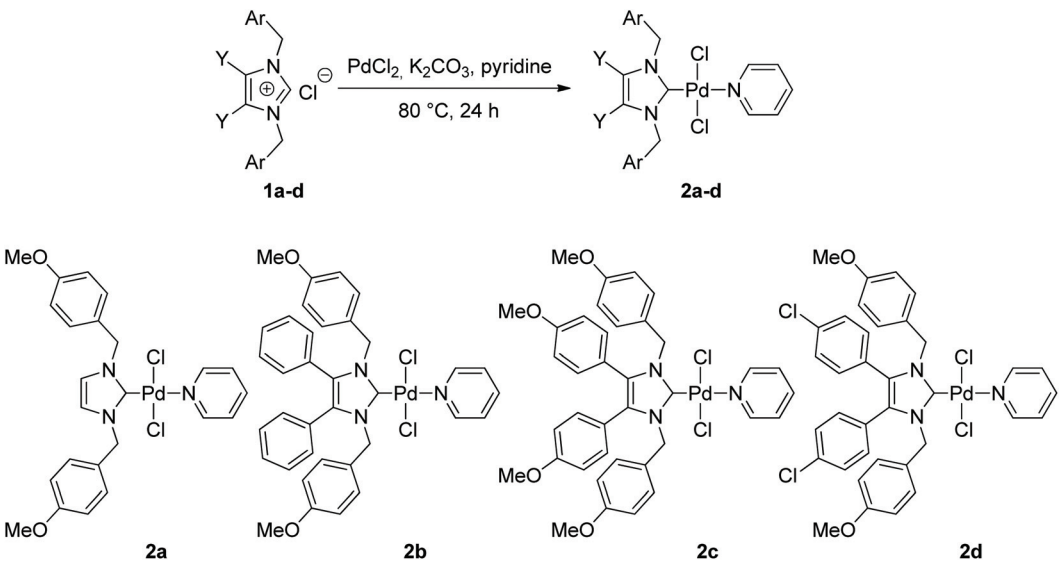
reported protocols. In this context, we have questioned whether NHC-Pd-PEPPSI type precatalysts would be useful for the chemo-selective alkylation of ketones with primary alcohols, since these precatalysts are highly active, stable, and among the easiest to synthesize in a single operationally simple step from the corresponding NHC salt, $PdCl_2$ and pyridine ligand. In a recent study, our group explored the critical role of the NHC ligand in NHC-Ir-catalyzed BH reactions and reported its superior catalytic activities for the synthesis of α-alkylated ketones,[15d] β-alkylated alcohols,[21a] quinolines,[21a] α,α-disubstituted ketones,[21b] and α-alkylated nitriles.[21c] As a continuation of our interest in the application of NHC-TM complexes in BH reactions, herein, we report the synthesis of four new NHC-Pd-PEPPSI complexes (**2a–d**) with backbone modifications on the NHC ligand and examine their catalytic activities in the α-alkylation of ketones with primary alcohols and tandem Suzuki–Miyaura coupling/α-alkylation reactions under open air conditions. To the best of our knowledge, this study represents the first example of NHC-Pd catalyzed α-alkylation of ketones with primary alcohols and also the tandem Suzuki–Miyaura coupling/α-alkylation reaction catalyzed with a monometallic TM-complex. The mechanism of the α-alkylation reaction is investigated by control experiments and kinetic studies. In addition, the catalyst material is studied by TEM, XRD, and XPS, and the nature of catalysis is examined by mercury poisoning and hot filtration experiments.

Results and discussion

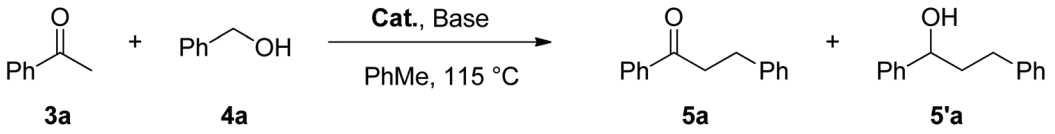
Scheme 1 outlines the route used for the synthesis of NHC-Pd-PEPPSI (**2a–d**) complexes. NHC precursors **1a–d** were synthesized according to the previously developed procedure[22] and the physical properties and spectroscopic data of the obtained compounds are in accordance with previous reports.[23] The PEPPSI type NHC-Pd (**2a–d**) complexes were synthesized by heating imidazolium salts (**1a–d**), $PdCl_2$, and K_2CO_3 in pyridine at 80 °C (Scheme 1) and obtained in 52–92% yields as air- and moisture-stable yellow solids.[3] The formation of **2a–d** was confirmed by ^1H, ^{13}C NMR spectroscopy and HRMS analyses. The characteristic downfield signals for the NC*H*N$^+$ protons of imidazolium salts **1a–d** disappeared in the ^1H NMR spectrum. Meanwhile, characteristic signals in the ^{13}C NMR resonances at δ = 151.3, 151.4, 151.2, and 151.3 ppm of Pd–$C_{carbene}$ were observed for complexes **2a–d**, respectively.

Initially, the alkylation of acetophenone (**3a**) with benzyl alcohol (**4a**) was selected as a model reaction to probe the potential of the NHC-Pd-PEPPSI complexes (**2a–d**) as catalysts. The progress of the reaction was monitored by ^1H NMR analysis of the crude reaction mixtures and the yields are based on 1,3,5-trimethoxybenzene as an internal standard (Table 1). The reaction of **3a** (1 mmol) and **4a** (1 mmol) was performed in the presence of **2a–d** (0.2 mol%) and KOH (10 mol%) in toluene (2 mL) at 115 °C (oil bath temperature) open to air for 4 h (Table 1, entries 1–4). In the presence of all catalysts tested, moderate to good yields (48–83%) of the desired product **5a** along with a 4–7% yield of the over-reduced alcohol product **5′a** were obtained (Table 1, entries 1–4). Among all catalysts tested, the highest yield of **5a** was obtained with catalyst **2c** (Table 1, entry 3). The differences in the catalytic abilities of complexes **2a–d** could be attributed to the different stabilities of the palladium precatalysts. Considering **2a–d** complexes bearing the same wingtip substituents on the N-atoms of NHC ligands, the differences in the stabilities could be attributed to the different electron densities at the palladium centers resulting from the backbone substituents of the NHC ligands. We recently evaluated the Tolman electronic parameters of the [IrCl(CO)$_2$(NHC)] complexes derived from NHC precursors **1a–**



Scheme 1 The route used for the synthesis of NHC-Pd-PEPPSI (**2a–d**) complexes.

Table 1 Optimization of the reaction conditions for the α-alkylation of acetophenone with benzyl alcohol[a]



Entry	Cat. (mol%)	Base	Time (h)	**5a** Yield (%)	**5′a** Yield (%)
1	**2a** (0.2)	KOH	4	48	4
2	**2b** (0.2)	KOH	4	74	6
3	**2c** (0.2)	KOH	4	83	7
4	**2d** (0.2)	KOH	4	75	6
5	$PdCl_2(py)_2$ (0.2)	KOH	4	31	7
6	**2c** (0.1)	KOH	6	85 (82)[b]	7
7[c]	**2c** (0.1)	KOH	6	81	8
8	**2c** (0.1)	NaOH	6	55	7
9	**2c** (0.1)	KO^{t}Bu	6	82	8
10	**2c** (0.1)	NaO^{t}Bu	6	37	4
11	**2c** (0.1)	—	6	—	—
12	—	KOH	6	24	5
13[d]	**2c** (0.1)	KOH	8	76 (71)[b]	10

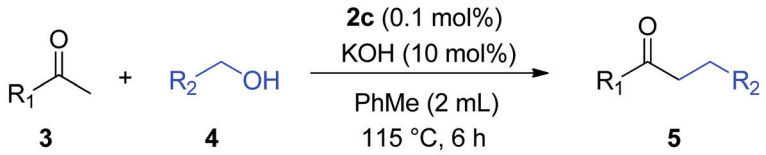
[a] Reaction conditions: **3a** (1.0 mmol), **4a** (1.0 mmol), **Cat.** (0.1–0.2 mol%), base (10 mol%), toluene (2 mL), 115 °C (oil bath temperature), open to air. Yields were determined by the ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. [b] Isolated yield. [c] Reaction was performed under an argon atmosphere. [d] Reaction was performed on a 20 mmol scale.

c and the results revealed that the NHC bearing 4-methoxyphenyl groups at the 4,5-positions of imidazole appeared as the strongest electron-donating ligand among them.[21c] However, in the presence of $PdCl_2(py)_2$ as the catalyst, only 31% conversion to the desired product was observed, which indicates the critical role of the NHC ligand (Table 1, entry 5). Consequently, we choose complex **2c** as the catalyst for further studies. Decreasing the catalyst loading to 0.1 mol% resulted in a 85% NMR yield within 6 h where **5a** was isolated in 82% yield (Table 1, entry 6). It should be noted that using an inert atmosphere seemed to be unnecessary (Table 1, entry 7). The influence of the base was then evaluated. Replacing KOH with NaOH, KO^{t}Bu, or NaO^{t}Bu did not improve the yields (Table 1, entries 8–10), but no product formation was observed in the absence of a base (Table 1, entry 11). On the other hand, the reaction resulted in only a 24% yield in the absence of a palladium catalyst (Table 1, entry 12). As a result, the optimized reaction conditions for the presented protocol were identified as the following: **2c** (0.1 mol%) and KOH (10 mol%) as the base at 115 °C open to air for 6 h (Table 1, entry 6). Finally, in order to make this process practically viable, we examined a 20 mmol scale reaction where **5a** was isolated in 71% yield (2.96 g) in 8 h (Table 1, entry 13).

With the optimized reaction conditions in hand, the substrate scope and the limitations of the α-alkylation of ketones (**3**) with primary alcohols (**4**) were studied over different ketone and primary alcohol derivatives (Table 1, entry 6), and the results are summarized in Table 2. Firstly, the substrate scope was examined by using acetophenone as ketone and varying the primary alcohols. The reaction of acetophenone with a range of *para*-substituted benzyl alcohols having electron-donating –OMe, –Me, or –^{i}Pr groups and electron-withdrawing $-CF_3$ groups afforded the desired ketone products (**5b–e**) in good to excellent isolated yields (80–95%). Furthermore, the reaction of acetophenone with ferrocenemethanol and 2-methoxybenzyl alcohol afforded the desired products **5h** and **5i** in 92% and 63% isolated yields, respectively. In the case of 1-naphthalenemethanol and 1-octanol, the amount of catalyst was increased to 0.2 mol% and 0.5 mol%, respectively, to obtain related products **5j** and **5k** in moderate yields. Next, the scope of the reaction was examined with respect to ketones. The reaction of benzyl alcohol with aryl methyl ketones having 4-OMe, 4-Me, or 4-CF_3 substitution on the aryl ring, and also with 1-acetylnaphthalene and acetylferrocene all resulted in high yields (69–95%) to give a series of α-alkylated ketones (**5l–n**, **5p**, and **5q**). Finally, the reaction of α-tetralone, a cyclic ketone, with benzyl alcohol afforded product **5r** in 55% yield in the presence of 0.5 mol% catalyst.

However, some limitations of the present catalytic system arise when substrates with –Cl or –Br substitution on the aryl ring are tested. The current catalytic protocol produced the desired α-alkylated ketones **5f** and **5g** in less than 10% yield and the remaining starting materials were recovered when acetophenone reacted with 4-chlorobenzyl alcohol or 2-bromobenzyl alcohol under the optimized reaction conditions. A similar result was observed for the reaction of 4′-chloroacetophenone with benzyl alcohol where the corresponding product **5o** was detected only in 3% yield by ^{1}H NMR analysis of the crude reaction mixture. Increasing the catalyst loading to 1 mol% for these substrates did not improve the yields of the desired α-alkylated ketone products **5f**, **5g**, and **5o**. However, these limitations cannot be explained with the apparent low tolerance of substrates substituted with electron-withdrawing groups on the aryl ring since $-CF_3$ substituted products **5e** and **5n** were obtained in high yields under similar conditions. This is most likely due to the rapid oxidative addition of aryl

Table 2 Scope and the limitations of the α-alkylation of ketones with primary alcohols



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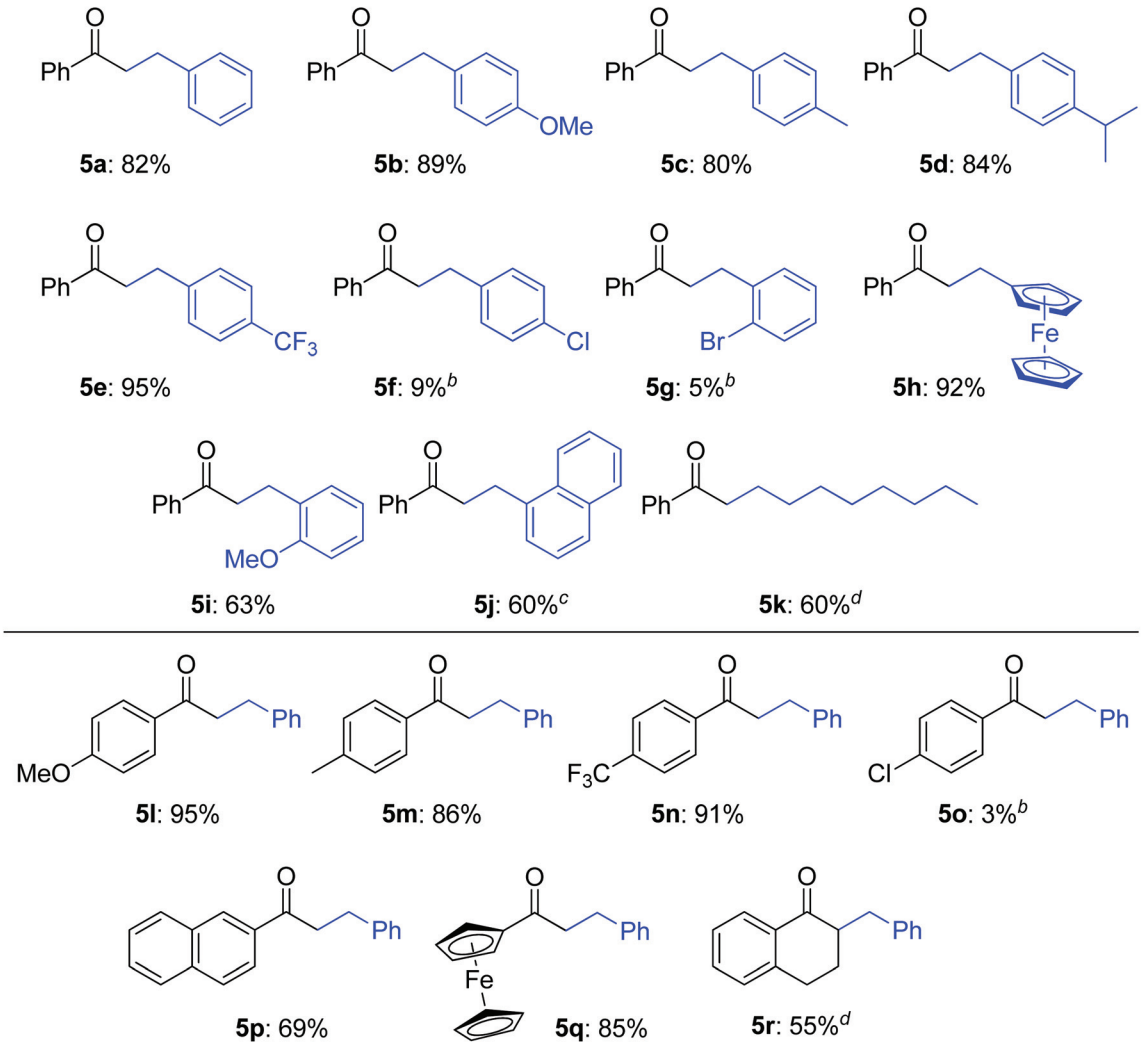


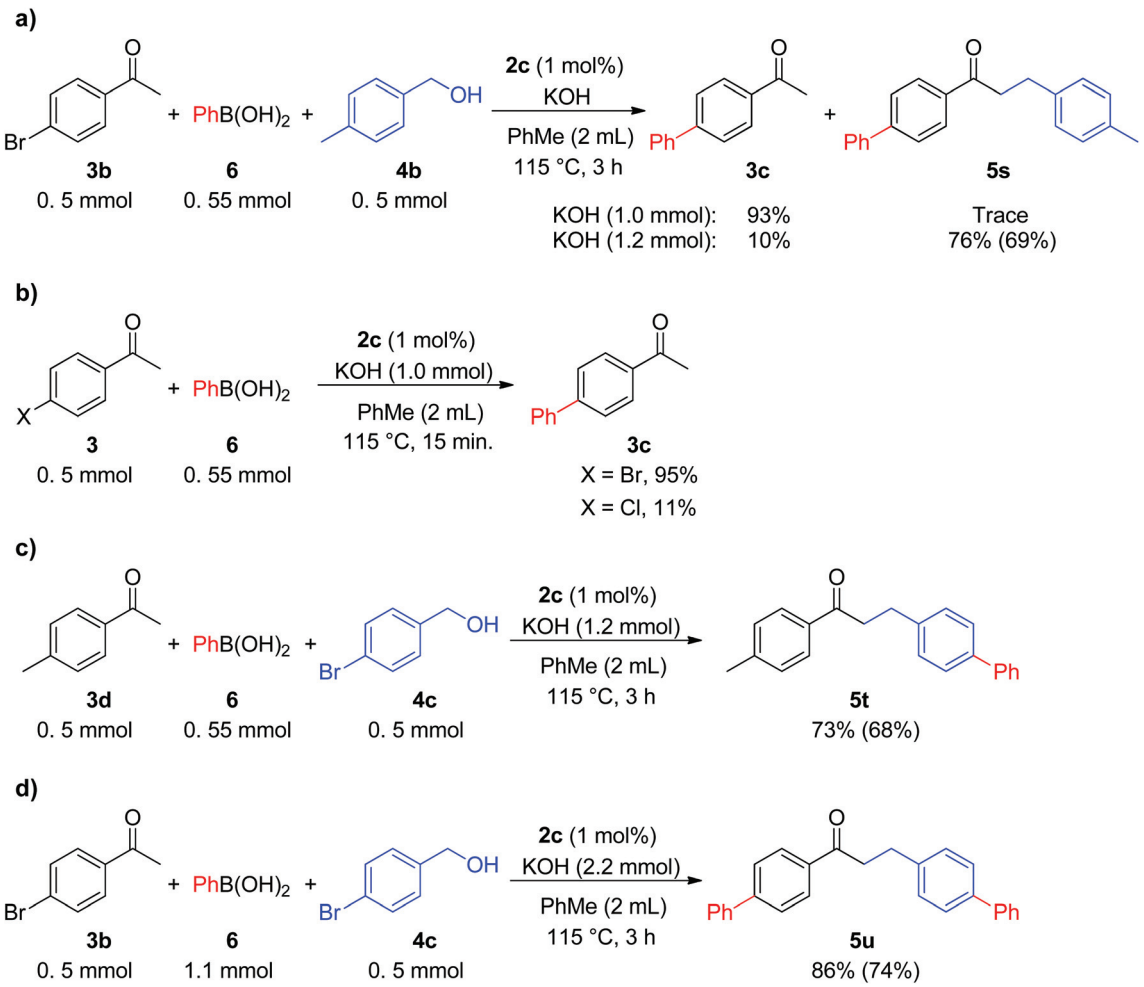
Reaction conditions: **3** (1.0 mmol), **4** (1.0 mmol), **2c** (0.1 mol%), KOH (10 mol%), toluene (2 mL), 115 °C (oil bath temperature), open to air. Reported yields correspond to isolated pure compounds. [a] Determined by ^{1}H NMR analysis. [b] **2c** (0.2 mol%), isolated yield. [c] **2c** (0.5 mol%), isolated yield.

halides to the Pd(0) center under basic conditions, the first step of the Pd-catalyzed cross-coupling reactions such as Suzuki–Miyaura,[3,4] and the poisoning of the Pd catalyst for the α-alkylation reaction.

On the basis of the above-mentioned findings and the fact that NHC-Pd-PEPPSI type complexes can effectively catalyze the Suzuki–Miyaura reactions,[3,4] we were interested to see whether catalyst **2c** could effectively catalyze a tandem reaction involving the Suzuki–Miyaura C(sp^2)–C(sp^2) coupling and α-alkylation C(sp^3)–C(sp^3) coupling. Such reactions were previously accomplished by the reaction of 4′-bromoacetophenone, phenylboronic acid, an excess amount of primary alcohol and Cs_2CO_3 (3 equiv.) in the presence of triazolyl-diylidene bridged heterobimetallic Pd(II)/Ir(III),[24a] or heterobimetallic Pd(II)/Ir(III) and Pd(II)/Rh(III) NHC complexes.[24b] In these studies, the presence of the two different metals allows a tandem process by combined reactions that are typically catalyzed by Pd (Suzuki–Miyaura) and Ir or Rh (α-alkylation). Considering the laborious steps in the preparation of these heterobimetallic complexes, using easily prepared NHC-Pd-

PEPPSI complexes would be highly beneficial for this tandem transformation. The initial reaction was performed using 4′-bromoacetophenone (**3b**; 0.5 mmol), phenylboronic acid (**6**; 0.55 mmol), 4-methylbenzyl alcohol (**4b**; 0.5 mmol), and KOH (2 equiv.; 1 mmol) in the presence of **2c** (1 mol%) as the catalyst at 115 °C in open air for 3 h (Scheme 2a). The reaction resulted in a complete conversion of **3b** into 4-acetylbiphenyl (**3c**) together with the unreacted primary alcohol **4b** where only a trace amount of α-alkylated biphenyl ketone (**5s**) was detected (Scheme 2a). Increasing the amount of KOH to 1.2 mmol resulted in a better outcome and in this case α-alkylated biphenyl ketone **5s** was isolated in 69% yield (Scheme 2a). The requirement of more than 2 equiv. of KOH for this tandem process can be rationalized by taking into account that the Pd-catalyzed Suzuki–Miyaura reaction usually requires 2 equiv. of a base and is faster than the α-alkylation reaction. To prove the rapid formation of 4-acetylbiphenyl (**3c**), 4′-bromoacetophenone (**3b**) was reacted with phenylboronic acid (**6**) under the conditions given in Scheme 2b, and the desired product was obtained in 95% yield within just 15 min. The reaction of less reactive 4′-chloroacetophenone with phenylboronic acid resulted in only 11% yield of **3c** under the same conditions (Scheme 2b). We were pleased that the reaction of 4′-methylacetophenone (**3d**), phenylboronic acid (**6**), and 4-bromobenzyl alcohol (**4c**) also furnished the corresponding tandem coupling product **5t** in good yield (Scheme 2c). Finally, the reaction of two different aryl bromides having a ketone or a primary alcohol function, **3b** and **4c**, with phenylboronic acid (**6**; 2.2 equiv.) afforded the desired α-alkylated ketone **5u**, bearing biphenyl handles, in 74% isolated yield, indicating the generality of the developed tandem coupling method (Scheme 2d).

Next, we performed a series of experiments to get further insights into the mechanism of the Pd-catalyzed α-alkylation of ketones with primary alcohols. It should be mentioned that black precipitates were formed at the bottom of the reaction tube at the end of all the α-alkylation reactions, regardless of the reaction conditions or the type of catalyst used. Therefore, we characterized the black precipitates that were obtained from the reaction of acetophenone with benzyl alcohol in the



Scheme 2 Tandem Suzuki–Miyaura coupling/α-alkylation reactions catalyzed by **2c**. Yields were determined by ^{1}H NMR analyses of the crude reaction mixtures using 1,3,5-trimethoxybenzene as the internal standard (isolated yields in parentheses).

presence of complex **2c** under the optimized conditions (Table 1, entry 6) by transmission electron microscopy (TEM), scanning TEM (STEM) associated electron dispersive X-ray (EDX), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and UV-vis spectroscopy analyses. The TEM images given in Fig. 1a and b show that the well-dispersed Pd nanoparticles with an average particle size of 3.1 ± 0.6 nm were formed over a cloudy substrate after the catalytic reactions. To identify the integrity of the cloudy substrate and get more insights into the structure of the black precipitates, STEM-HAADF associated EDX elemental mapping analyses were conducted on the sample. As seen from the elemental mapping images shown in Fig. S1 (see the ESI†), the Pd atoms are well-dispersed over a substrate composed of N atoms, which is most probably attributed to the NHC and pyridine ligands dissociated into the reaction solution from the dissociation of the Pd(II)-PEPPSI complexes. In this regard, it can be concluded that the black precipitates that are formed during the catalytic reactions are the stabilized Pd nanoparticles.[25]

To further support the formation of Pd nanoparticles, the crystal structure of the black precipitates formed from complex **2c** was analyzed by powder XRD. The XRD pattern of the black precipitates showed four peaks at 2θ = 39.7°, 45.2°, 61.4° and 81.7° (Fig. 2), which are readily assigned to the (111), (200), (220), and (311) planes of face centered cubic (fcc) metallic palladium.[26] The broad peak observed at 2θ = 30° is most probably attributed to the amorphous NHC ligand that is a cloudy substrate seen in the TEM images.

On the other hand, the progress of the reaction of complex **2c** (0.001 mmol) with KOH (0.1 mmol) in PhMe (2 mL) at 115 °C over different reaction times was monitored by using a UV-Vis absorption spectrophotometer and the recorded spectra are depicted in Fig. 3. The intensity of the absorption band of complex **2c** at 284 nm was decreased during the course of the reaction and a new absorption continuum appeared in the wavelength range of 360–300 nm, indicating

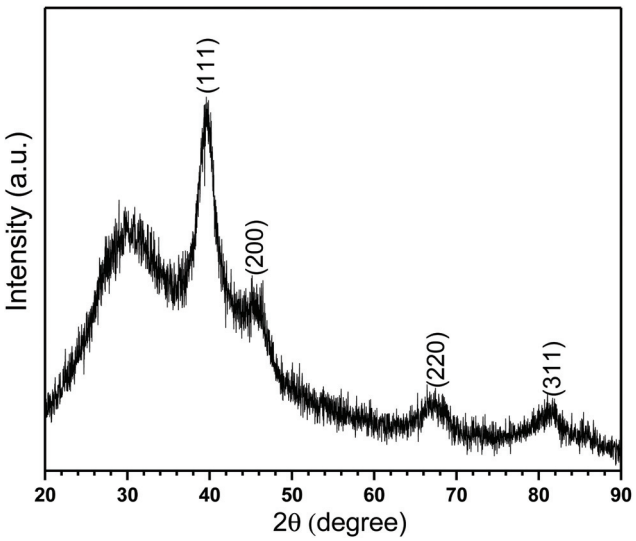


Fig. 2 XRD pattern of the Pd nanoparticles formed from complex **2c** under the optimum reaction conditions.

that the concentration of **2c** is decreased due to the dissociation of complex **2c** in the solution and the formation of NHC-stabilized Pd nanoparticles.

Finally, XPS analysis was conducted on the black precipitates to get more insights into the chemical state of the surface atoms, especially Pd and N. There are two sets of asymmetric peaks observable at binding energies (BEs) of 333.6/338.8 eV and 335.6/340.8 eV in the XPS spectrum of the Pd 3d core-level (Fig. 4a), which are readily assigned to $3d_{5/2}/3d_{3/2}$ core-levels, respectively.[27] Considering the asymmetric shape of the peaks and the spin–orbit component (Δ) of 5.2 eV, these sets are attributed to the Pd(0) atoms with different electron density environments, most probably the ones in the NHC- or pyridine-stabilized Pd NPs.[28] The N 1s XPS spectrum (Fig. 4b) also indicates the presence of two types of nitrogen atoms in the black precipitates surrounded by different chemical environ-

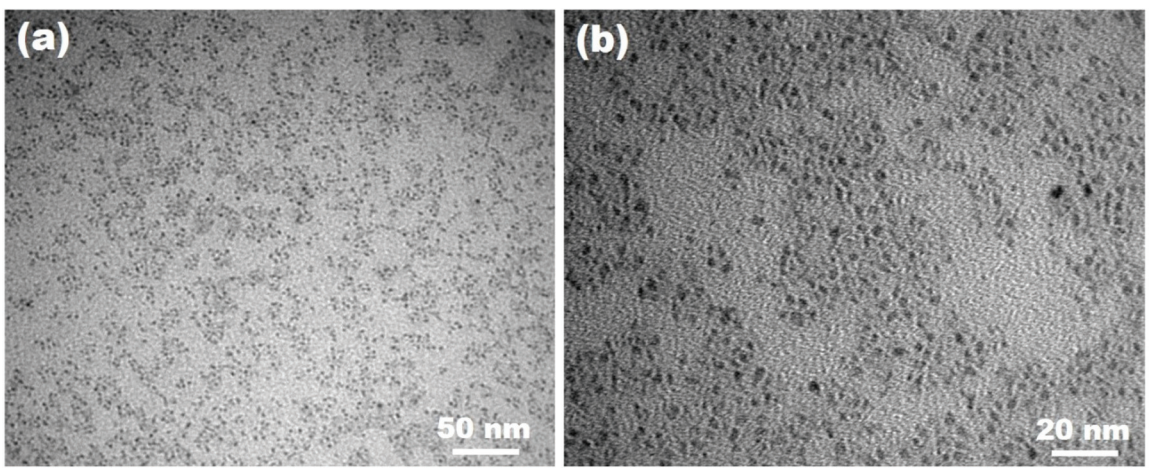


Fig. 1 (a and b) TEM images of Pd nanoparticles formed from complex **2c** under the optimum reaction conditions.

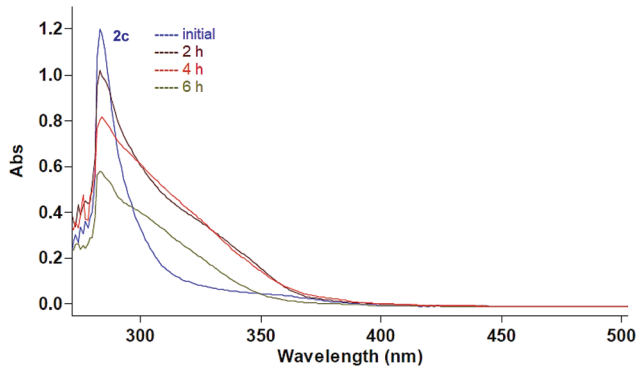


Fig. 3 UV-vis spectra of complex **2c** before (the blue line) and after the reaction with KOH.

ments, which are attributed to the pyridine and NHC ligands at BEs of 397.5 and 394.5 eV, respectively.[28a–c]

To understand whether the reaction was homogeneously or heterogeneously catalyzed and to get more insights into the catalytically active palladium species, mercury poisoning and hot filtration experiments were performed (Scheme 3). When 50 μL of Hg was added initially into the reaction mixture under the optimum conditions (Table 1, entry 6), only a 13% product formation was observed after 6 h (Scheme 3a). This 13% product formation can be attributed to the catalytic activity of KOH itself. The significant decrease in the catalytic activity (Scheme 3a compared to Table 1, entry 6) and the inhibition of the α-alkylation reaction due to the deactivation of Pd nanoparticles indicate the heterogeneous nature of the present catalytic system. To support this observation, a hot filtration

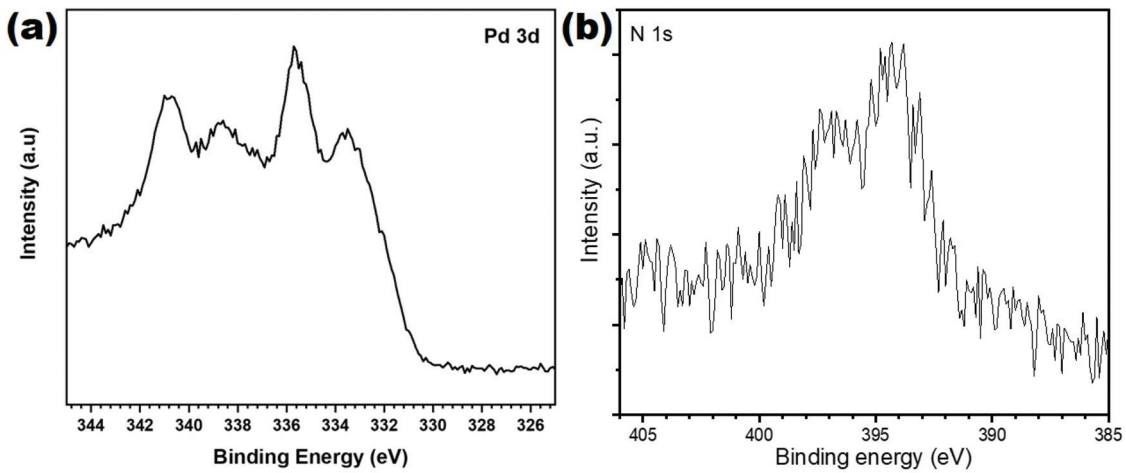
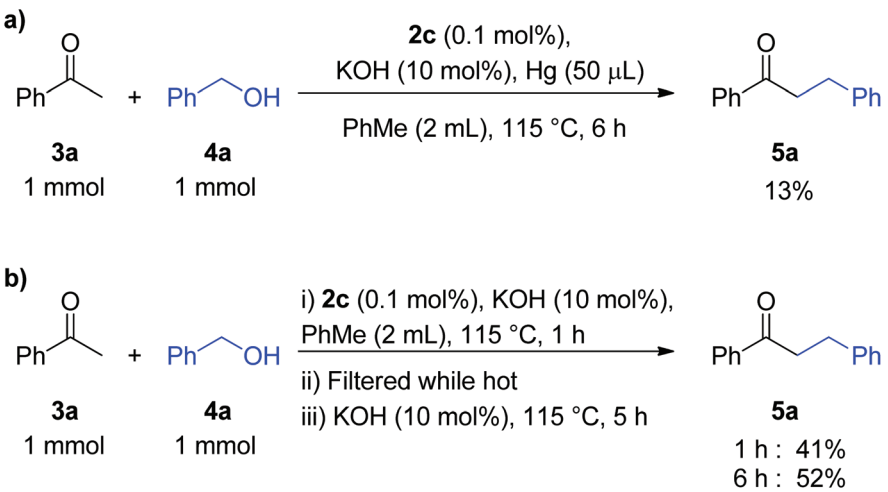


Fig. 4 XPS spectra (a) Pd 3d, (b) N 1s core-levels of the Pd nanoparticles formed from complex **2c** under the optimum reaction conditions.



Scheme 3 Mercury poisoning (a) and hot filtration (b) tests for α-alkylation of acetophenone with benzyl alcohol catalyzed by **2c**. Yields were determined by ^{1}H NMR analyses of the crude reaction mixtures using 1,3,5-trimethoxybenzene as the internal standard.

experiment was also performed. The reaction was carried out under the optimized conditions, and after 1 h (41% formation of **5a**), the reaction mixture was filtered off through a pad of Celite® while hot. Then, KOH (10 mol%) was added to the reaction mixture and the reaction was further continued for 5 h (Scheme 3b). After this period, only an 11% increase was observed in the product yield (52%), most probably due to the catalytic activity of KOH itself. The outcomes of the hot filtration experiment also confirm that the active species involved in the α-alkylation reaction are Pd nanoparticles.

Next, we studied the time-dependent progress of the reaction of model substrates **3a** and **4a** under the conditions given in Table 1, entry 6 by performing individual experiments over different reaction times (Fig. 5). Control experiments were also carried out to support the observations obtained from the progress of the reaction (Scheme 4). Monitoring the time-dependent reaction profile revealed the complete conversion of the substrates into the desired product **5a** (83%) and over-reduced alcohol product **5′a** (8%) in 6 h (Fig. 1). The accumulation of the intermediate chalcone (**7**) was very low (less than 4%) during the whole course of the reaction, which suggests that the reduction of **7** was very fast. The reduction of intermediate **7** with benzyl alcohol as a hydrogen source afforded the desired product **5a** in 89% conversion only in 1 h (Scheme 4a). In addition, the formation of 1,3,5-triphenylpentane-1,5-dione (**8**), resulting from the 1,4-addition of acetophenone to chalcone, was observed in the early stages of the reaction (~10% in 30 min). The 1,4-addition product (**8**) was consumed during the course of the reaction, suggesting the reversibility of this step. Similarly, the formation of 1-phenylethanol (**3′a**), the product of acetophenone reduction, was also observed in the initial stages of the reaction. Then **3′a** was gradually consumed during the progress of the reaction. The slow dehydrogenation of intermediate secondary alcohols was also confirmed by independent control experiments where the secondary alcohols **5′a** and **3′e** were dehydrogenated to corresponding ketones **5a** (23%) and **3e** (44%) (Scheme 4b and c). Finally, the dehydrogenation of 4-methoxybenzyl alcohol (**4b**) was carried out in a sealed reaction tube for 6 h, resulting in the formation of 4-methoxybenzaldehyde (**9**) in 42% yield and the presence of H_2 in the gas phase of the reaction was detected by GC analysis (Fig. S2, see the ESI†) (Scheme 4d).

On the basis of the above-mentioned experimental findings, a plausible mechanism for the Pd-catalyzed α-alkylation of

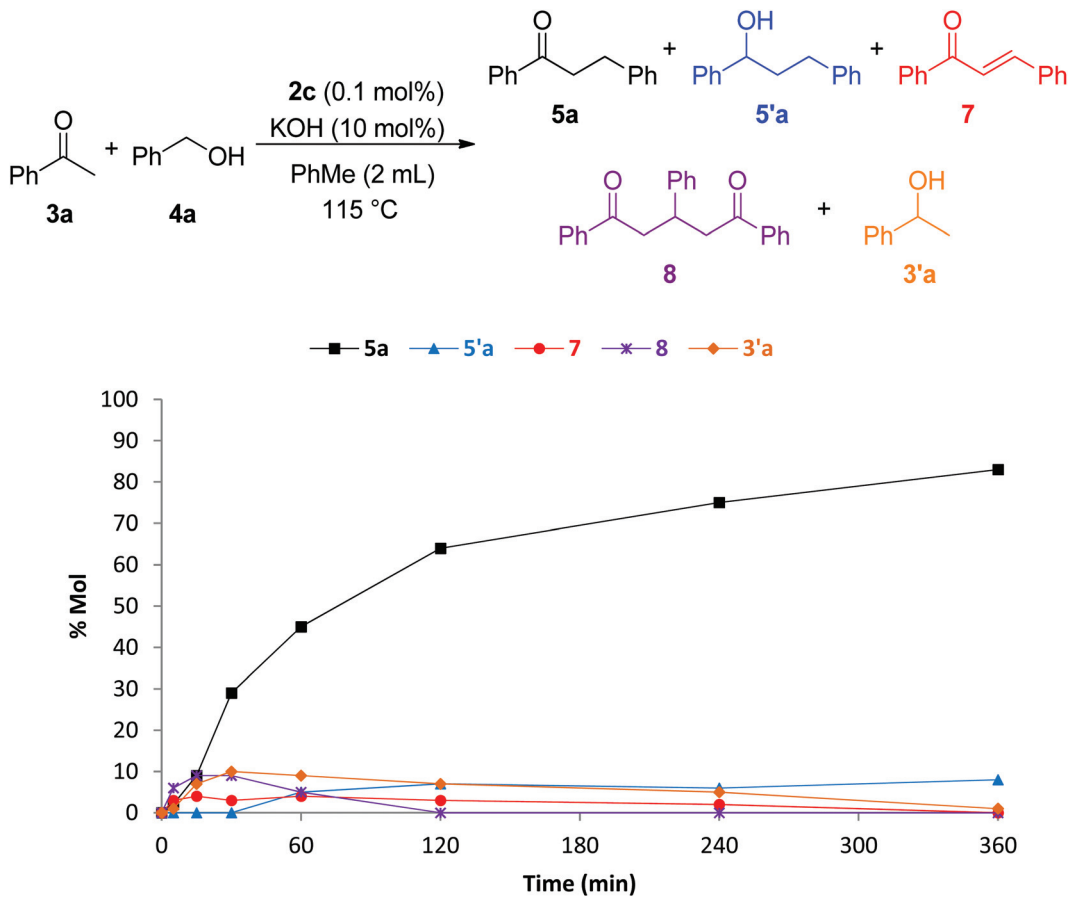
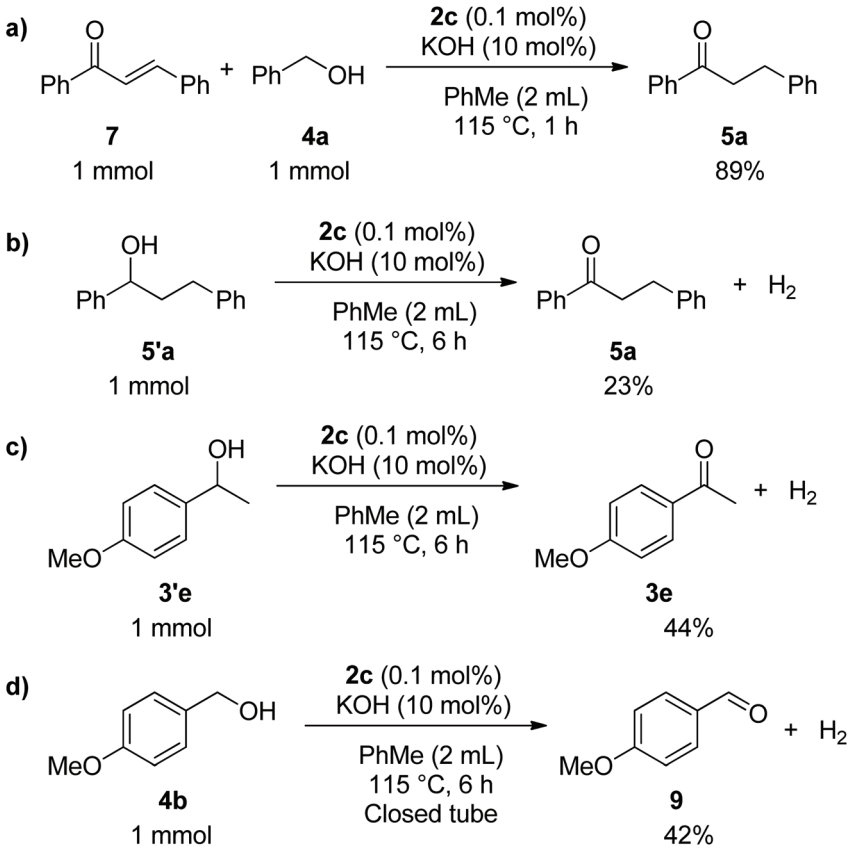
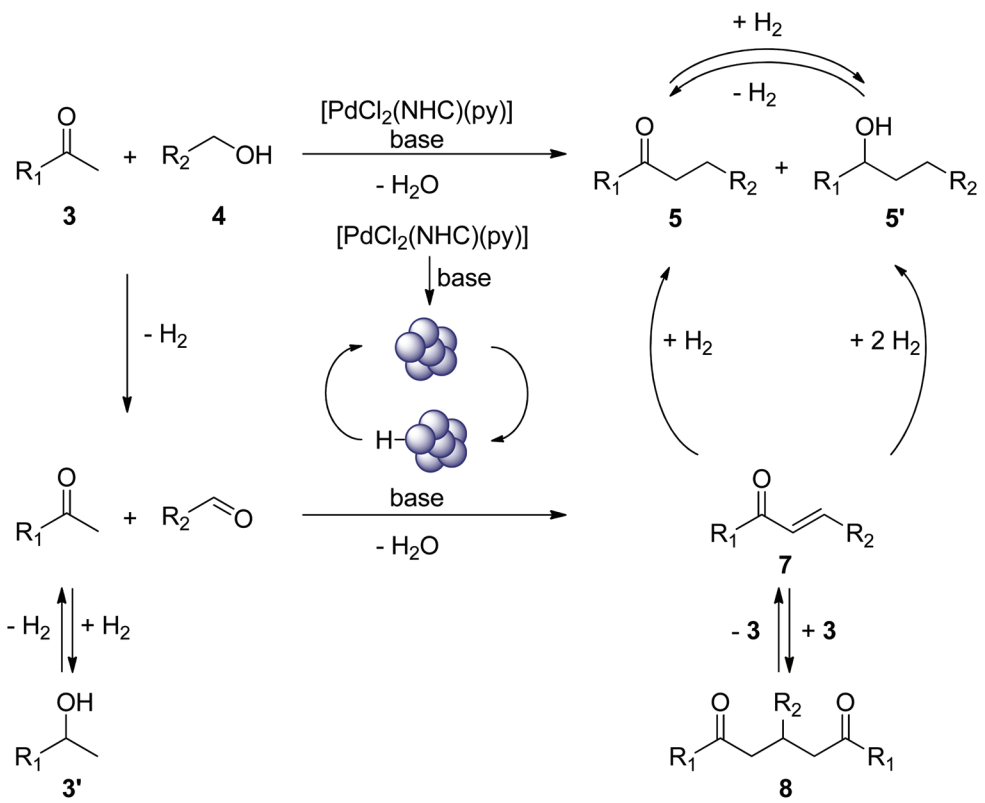


Fig. 5 Time course of the reaction. Reaction conditions: **3a** (1 mmol), **4a** (1 mmol), **2c** (0.1 mol%), KOH (10 mol%), toluene (2 mL), 115 °C (oil bath temperature), open to air. %Mol values were determined by ^{1}H NMR analyses of the independent reaction mixtures using 1,3,5-trimethoxybenzene as the internal standard.



Scheme 4 Control experiments. Conversions were determined by ^{1}H NMR analyses of the crude reaction mixtures.



Scheme 5 Proposed mechanism for the Pd-catalyzed α-alkylation of ketones with primary alcohols.

ketones with primary alcohols can be proposed as shown in Scheme 5. The mechanism involves the formation of NHC-stabilized Pd NPs under basic reaction conditions. Then, the dehydrogenation of primary alcohol into an aldehyde may generate transient Pd–H species. Next, the condensation of the ketone and aldehyde gives the intermediate enone (7). Here, the reversible 1,4-addition of ketone on 7 may take place. Finally, 7 is hydrogenated to afford **5** as the major product accompanied by over-reduced alcohol product **5′**.

Conclusions

In summary, we reported for the first time the use of $[PdCl_2(NHC)(py)]$ complexes as catalyst precursors to promote the α-alkylation of ketones with primary alcohols under borrowing hydrogen conditions. The variation of the nature of the NHC ligand framework seemed to play an important role in catalyst efficiency and complex **2c** having 4-methoxyphenyl groups at the 4,5-positions and 4-methoxybenzyl substituents on the N-atoms of imidazole exhibited the highest activity in this transformation. As a result of mechanistic studies, the active species involved in the present α-alkylation reaction were mainly Pd NPs formed from the NHC-Pd-PEPPSI complexes. Importantly, this catalytic system also allowed the synthesis of biaryl ketones by tandem Suzuki–Miyaura-coupling/α-alkylation reactions. Currently, our studies are focused on the development of efficient catalysts and their application in these tandem reactions. Considering that NHC-Pd-PEPPSI complexes have found widespread applications in catalysis chemistry, the results described in this study could be of great importance for further studies.

Experimental

General information

Unless otherwise noted, all reagents and solvents were obtained commercially and used without further purification. NHC precursors **1a–d** were synthesized according to the previously developed procedure[22] and the physical properties and spectroscopic data of the obtained compounds are in accordance with previous reports.[23] The NMR spectra were recorded on a Varian AS 400 Mercury NMR spectrometer at 298 K. Chemical shifts are reported in units of parts per million (ppm) relative to tetramethyl silane (δ = 0 ppm) and $CDCl_3$ (δ = 7.26 ppm for ^{1}H and δ = 77.0 ppm for ^{13}C NMR). Melting points were measured on a Gallenkamp electrothermal melting-point apparatus without correction. High-resolution mass spectra (HRMS) were recorded on an Agilent 6530 Accurate-Mass Q-TOF mass spectrometer at the East Anatolia High Technology Application and Research Center, Atatürk University. GC analysis for the H_2 evolution experiment was performed on an Agilent 7890A GC instrument, and gas products were identified according to the standard gas mixture (Agilent P/N 5190-0519). The UV spectra were recorded on an Agilent Cary 60 UV-Vis spectrophotometer. Transmission electron microscopy (TEM) images were obtained using a Hitachi HT7800 equipped with a scanning TEM and the associated EDX analyzer working in a high-resolution (HR) mode at 120 kV. The crystal structure of the materials was investigated with a Bruker D8 Advance X-Ray diffractometer using Cu Kα radiation (1.54 Å). The chemical states and surface compositions of the photocatalysts were identified by X-ray photoelectron spectroscopy (XPS, Thermo K-Alpha).

General procedure for the synthesis of NHC-Pd-PEPPSI complexes (2a–d)

A mixture of imidazolium salt (**1a–d**) (0.5 mmol), $PdCl_2$ (0.5 mmol), and K_2CO_3 (2.5 mmol) was suspended in pyridine (3 mL) and stirred at 80 °C for 24 h open to air. The excess of pyridine was removed under vacuum. The reaction mixture was then diluted with dichloromethane, and filtered through a short pad of Celite. The remaining solid was washed twice with dichloromethane and the solvent of the filtrate was evaporated. The pure complexes were isolated as yellow solids by column chromatography on silica gel using dichloromethane/methanol (95/5).

2a. Yield: 230 mg (%82). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): δ = 9.02 (d, J = 6.8 Hz, 2H), 7.76 (t, J = 7.8 Hz, 1H), 7.46 (d, J = 7.6 Hz, 4H), 7.34 (t, J = 6,2 Hz, 2H), 6.90 (d, J = 7.2 Hz, 4H), 6.65 (d, J = 1.6 Hz, 2H), 5.79 (s, 4H), 3.78 (s, 6H). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 25 °C, ppm): δ = 159.7, 151.3, 149.0, 138.0, 130.4, 127.4, 124.4, 121.4, 114.3, 55.3, 54.2. HRMS (ESI) m/z: $[M - Cl]^+$ calcd for $C_{24}H_{25}ClN_3O_2Pd$ 528.0670; found 528.0679.

2b. Yield: 310 mg (%78). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): δ = 8.92 (d, J = 5.2 Hz, 2H), 7.74 (t, J = 7.6 Hz, 1H), 7.32 (t, J = 7.2 Hz, 2H) 7.22 (t, J = 7,4 Hz, 6H), 7.15 (t, J = 7,6 Hz, 4H), 6.94 (d, J = 7.2 Hz, 4H), 6.74 (d, J = 8.4 Hz, 4H), 5.82 (s, 4H), 3.75 (s, 6H). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 25 °C, ppm): δ = 159.0, 151.4, 149.3, 137.9, 133.4, 130.8, 129.6, 128.8, 128.6, 128.2, 127.8, 124.4, 113.7, 55.2, 52.4. HRMS (ESI) m/z: $[M - Cl]^+$ calcd for $C_{36}H_{33}ClN_3O_2Pd$ 680.1296; found 680.1361.

2c. Yield: 360 mg (%92). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): δ = 8.89 (d, J = 5.2 Hz, 2H), 7.72 (t, J = 7.6 Hz, 1H), 7.32–7.27 (m, 6H), 6.84 (d, J = 8.8 Hz, 4H), 6.77 (d, J = 8.8 Hz, 4H), 6.67 (d, J = 9.2 Hz, 4H), 5.77 (s, 4H), 3.76 (s, 6H), 3.73 (s, 6H). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 25 °C, ppm): δ = 159.7, 158.9, 151.2, 148.3, 137.9, 133.1, 132.0, 129.5, 128.7, 124.3, 119.9, 113.6, 55.1, 52.1. HRMS (ESI) m/z: $[M - Cl]^+$ calcd for $C_{38}H_{37}ClN_3O_4Pd$ (96.8%) 742.1512; found 742.1523.

2d. Yield: 203 mg (%52). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): δ = 8.91 (d, J = 4.8 Hz, 2H), 7.73 (t, J = 7.8 Hz, 1H), 7.31 (t, J = 7.0 Hz, 2H), 7.23 (d, J = 8.8 Hz, 4H), 7.13 (d, J = 8.8 Hz, 4H), 6.82 (d, J = 8.8 Hz, 4H), 6.76 (d, J = 8.4 Hz, 4H), 5.83 (s, 4H), 3.75 (s, 6H). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 25 °C, ppm): δ = 159.2, 151.3, 138.0, 135.3, 132.5, 131.9, 129.5, 128.6, 128.1, 126.0, 124.4, 113.8, 55.2, 52.7. HRMS (ESI) m/z: $[M - Cl]^+$ calcd for $C_{36}H_{31}Cl_3N_3O_2Pd$ (96.8%) 750.0521; found 750.0562.

General procedure for the α-alkylation of ketones with primary alcohols

To a 10 mL reaction tube with a condenser, ketone (1.0 mmol), primary alcohol (1.0 mmol), base (0.1 mmol; 10 mol%), and a solution of the palladium complex (0.1–0.5 mol%) in toluene (2.0 mL) were added under open air conditions. The reaction mixture was vigorously stirred under reflux in a preheated oil bath at 115 °C for 4–6 h. Thereafter, the reaction mixture was cooled to ambient temperature. For the optimization studies 1,3,5-trimethoxybenzene was added into the reaction mixture as an internal standard, and the yields were calculated through ^{1}H NMR analysis. For the substrate scope experiments, the reaction mixture was diluted with 5 mL of dichloromethane. After filtration, the solvent was evaporated, and the crude product was purified by column chromatography on silica gel using a hexane/ethyl acetate (9/1) mixture as an eluent to afford the desired product.

General procedure for the tandem Suzuki–Miyaura coupling/α-alkylation reactions

To a 10 mL reaction tube with a condenser, ketone (0.5 mmol), primary alcohol (0.5 mmol), phenylboronic acid (0.55 or 1.1 mmol), base (1.2 or 2.2 mmol), and a solution of the palladium complex (0.005 mmol; 1 mol%) in toluene (2.0 mL) were added under open air conditions. The reaction mixture was vigorously stirred under reflux in a preheated oil bath at 115 °C for 3 h. Thereafter, the reaction mixture was cooled to ambient temperature and diluted with 5 mL of dichloromethane. After filtration, the solvent was evaporated, and the crude product was purified by column chromatography on silica gel using a hexane/ethyl acetate (9/1) mixture as an eluent to afford the desired product.

Procedure for the time profile of the α-alkylation reaction

Seven identical reactions were performed in different reaction tubes for specified times (5, 15, 30, 60, 120, 240, and 360 min). To a 10 mL reaction tube with a condenser, acetophenone (1.0 mmol), benzyl alcohol (1.0 mmol), KOH (0.1 mmol; 10 mol%), and a solution of **2c** (0.1 mol%) in toluene (2.0 mL) were added under open air conditions. The reaction mixture was vigorously stirred under reflux in a preheated oil bath at 115 °C for a specified time. After completion of the reactions, yields were determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

Mercury poisoning experiments

To a 10 mL reaction tube with a condenser, acetophenone (1.0 mmol), benzyl alcohol (1.0 mmol), KOH (0.1 mmol; 10 mol%), mercury (50 μL), and a solution of **2c** (0.1 mol%) in toluene (2.0 mL) were added under open air conditions. The reaction mixture was vigorously stirred under reflux in a preheated oil bath at 115 °C for 6 h. Thereafter, the reaction mixture was cooled to ambient temperature. The yield was determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

Hot filtration experiments

To a 10 mL reaction tube with a condenser, acetophenone (1.0 mmol), benzyl alcohol (1.0 mmol), KOH (0.1 mmol; 10 mol%), and a solution of **2c** (0.1 mol%) in toluene (2.0 mL) were added under open air conditions. The reaction mixture was vigorously stirred under reflux in a preheated oil bath at 115 °C for 1 h. Thereafter, the reaction mixture was filtered while hot into a new reaction tube, which contained KOH (0.1 mmol; 10 mol%). The reaction mixture was vigorously stirred under reflux in a preheated oil bath at 115 °C for an additional 5 h. After completion of the reaction, the yield was determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

Conflicts of interest

There are no conflicts to declare.

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