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C–C coupling formation using nitron complexes†

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A series of Ru^{II} (**1**), Rh^{III} (**2**), Ir^{III} (**3**, **4**), Ir^{I} (**5**) and Pd^{II} (**6–9**) complexes of the 'instant carbene' nitron were prepared and characterized by ^{1}H- and ^{13}C-NMR, FT-IR and elemental analysis. The molecular structures of complexes **1–4** and **6** were determined by X-ray diffraction studies. The catalytic activity of the complexes (**1–9**) was evaluated in alpha(α)-alkylation reactions of ketones with alcohol *via* the borrowing hydrogen strategy under mild conditions. These complexes were able to perform this catalytic transformation in a short time with low catalyst and base amounts under an air atmosphere. Also, the Pd^{II}–nitron complexes (**6–9**) were applied in the Suzuki–Miyaura C–C coupling reaction and these complexes successfully initiated this reaction in a short time (30 minutes) using the H_2O/2-propanol (1.5 : 0.5) solvent system. The DFT calculations revealed that the $Pd^{0/II/0}$ pathway was more preferable for the mechanism.

Introduction

N-Heterocyclic carbenes (NHCs) were first introduced by Öfele half a century ago.[1] The first stable NHC was isolated and characterized by Arduengo *et al.*[2] Many of the structural modifications undertaken focused on the σ-donation and π-accepting properties of NHCs,[3] which were achieved through the modification of either the groups attached to the nitrogen atoms or the backbone structure of the imidazole ring. The latter approach includes changing the ring size and the backbone topology by attaching functional groups or heteroatoms to the backbone. NHCs derived from five-membered heterocycles with different numbers of nitrogen atoms ranging from two to four lead formally either to normal N-heterocyclic or mesoionic carbenes with, in some cases, the same skeletal structure. 1,2,4-Triazol-5-ylidine (**A**) from the NHC family is the result of a replacement of a nitrogen atom with CH at positions 4 or 5 of the imidazole ring (Fig. 1). They were found by Enders *et al.* in 1995 and called the 'Enders carbene'.[4,5] They are rather unexplored although they might lead to interesting systems because of their weak σ-donating and strong π-accepting properties as compared to the most studied classic NHC moiety.[6]

Nitron (**B**) of the 1,2,4-triazol-5-ylidine derivative was first presented as Busch's analytical reagent and utilized in gravimetric anion analysis in 1905.[7] Later, Kriven'ko and Morozova proposed a different synthesis method for nitron and obtained good yields.[8] Baker *et al.* suggested that nitron (**B′**) was a mesoionic carbene.[9] Due to the tautomerization of its structure, nitron can easily bond with the metal from the unpaired pairs of electrons on carbon in solution and does not require any base for this process. Therefore, it is also known as "instant carbene". In 2012, Siemeling *et al.* synthesized Rh^{I} complexes bearing nitron and demonstrated that they structurally and electronically resembled the typical Enders carbene according to the results of the Tolman electronic parameter (TEP).[10] The authors also prepared $RuCl(nitron)(PPh_3)_2$ complexes containing nitron under anaerobic conditions.[11] Recently, in another study, coinage metal complexes of nitron were developed, such as Cu, Ag, and Au. Different copper-halides and copper-dimer complexes were obtained from nitron.[12] This material is commercially available and can also be used as a ditopic ligand due to its structure containing an anilite group providing electrons.[13] Transition metal complexes of 1,2,4-triazol-5-ylidine have recently been used for determining catalytic activity in many organic reactions.[14] However, there are no catalytic applications of nitron metal complexes in the literature.

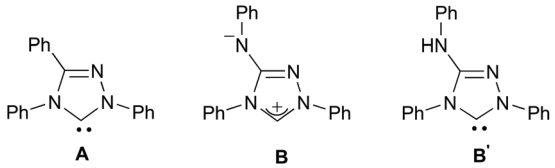

Fig. 1 Enders carbene and resonance of the nitron compound.

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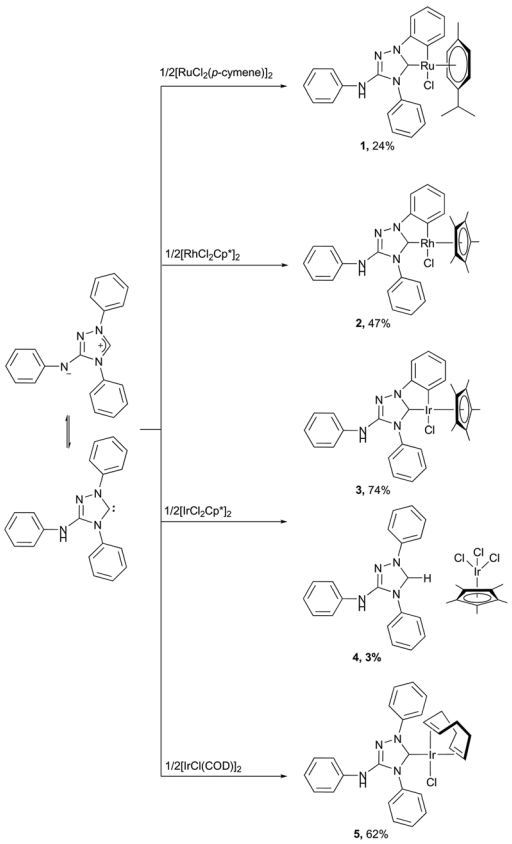
C–C bond forming reactions are highly demanded in chemical synthesis.[15g] Cross-coupling is an important way for synthetic chemists to prepare specific organic compounds such as natural products, industrial materials and drugs.[15a–i] The Suzuki–Miyaura and α-alkylation of ketones are two of the most important C–C bond forming reactions in organic synthesis. Herrmann pioneered the use of Pd^{II}–NHC complexes in cross-coupling reactions[15j,k] and this interest has increased over the past decade.[15l,m] The α-alkylation of ketones with alcohol is very useful in the preparation of biologically and synthetically organic compounds through the borrowing hydrogen strategy. However, conventional methods have major disadvantages; *e.g.*, the use of toxic and contaminant alkyl halides, the formation of salt as waste, low atom economy or efficiency, and the need to use an excessive amount of a strong base. The α-alkylation reaction of ketones with alcohol eliminates these undesirable effects, offering benefits, such as green chemistry, high atom economy, and water formation as a by-product.[15h] Transition metal complexes such as Ru, Rh, Ir and other metals have been used as catalysts for this reaction.[16]

In this study, to develop an effective strategy for forming C–C bonds, we prepared a series of ruthenium (**1**), rhodium (**2**), iridium (**3–5**), and palladium (**6–9**) complexes of nitron. We investigated the catalytic properties of these complexes in the α-alkylation of ketones with alcohol and Suzuki–Miyaura C–C cross-coupling reactions. We present a highly selective and effective α-alkylation of ketones with alcohol and Suzuki–Miyaura C–C cross-coupling reaction catalyzed by nitron complexes.



Scheme 1 Synthetic pathway for the related compounds (**1–5**).

Results and discussion

Synthesis and characterization of complexes

As seen in Scheme 1, the nitron complexes (**1–5**) were prepared using the corresponding starting materials $[RuCl_2(p\text{-cymene})]_2$, $[RhCl_2(Cp^*)]_2$, $[IrCl_2(Cp^*)]_2$ or $[IrCl(cod)]_2$ with nitron in CH_2Cl_2 at room temperature. The piano-stool complexes (**1–3**) were air- and moisture-stable orange solids containing the chelating NHC ligand formed by nitron through the *ortho*-metalation of the 1-phenyl substituent. The related *ortho*-metallated NHC complexes with $M–C_{aryl}$ are well known in the literature.[17] Surprisingly, we observed the formation of **4** as a by-product in a very low amount in the solution during the synthesis of **3**. These complexes **1–5** have good solubility in DCM, alcohols, and DMSO. The complexes **1–5** were characterized by ^{1}H-, ^{13}C-NMR spectroscopy and elemental analysis. In the ^{1}H-NMR spectra of complexes **1**, **2**, **3**, and **5**, the Ph–NH proton in the backbone of nitron has been observed at δ 6.14, 6.41, 6.20, and 6.04 ppm, respectively. This indicated a slight shift to a lower location compared to the signal in nitron (δ 10.22 ppm). The Ph–NH proton was located at δ 11.85 ppm in the ^{1}H-NMR of complex **4**. Complex **1** was detected to have four doublets for the aromatic protons of *p*-cymene, and the Cp* methyl protons for complexes **2** and **3** were detected as a singlet. In the ^{13}C-NMR spectra, the characteristic C_{NHC} resonance of the complexes was observed at δ 188.3 (**1**), 182.0 (**2**), 199.1 (**3**), and 181.3 (**5**) ppm.

The molecular structures of the complexes (**1–4**) were determined by single-crystal X-ray diffraction. An intermolecular π···π contact occurred between the triazole and phenyl rings of neighbouring molecules. The distance between the ring centroids was 3.403 Å. The combination of these interactions produced a 2D network. The crystallographic analyses revealed that complexes **2** and **3** were very similar. The asymmetric units of complexes **2** and **3** contained three crystallographically independent molecules, while the asymmetric unit of complexes **1** and **4** contained one molecule. In complex **2**, the bond distances of Rh–C were 1.993(10) and 2.052(12) Å in Rh1, 2.052(12) and 2.046(10) Å in Rh2, and 2.015(10) and 2.054(11) Å in Rh3, while those of Ir–C in complex **3** were 1.989(12) and 2.063(12) Å in Ir1, 2.036(11) and 2.047(14) Å in Ir2, and 2.052 (13) and 2.005(13) Å in Ir3. The Ru–Cl bond length was 2.396 (3) Å in Rh1, 2.408(3) Å in Rh2, and 2.411(3) Å in Rh3, while the bond length Ir–Cl was 2.403(4) Å in Ir1, 2.411(3) Å in Ir2, and 2.407(3) Å in Ir3. In complex **1**, the bond distances of Ru–C were 2.003(6) and 2.085(6) Å, while the bond distance of Ru–Cl was 2.4277(17) Å. In complex **4**, the bond distances of Ir–Cl were 2.400(2), 2.413(2), and 2.433(2) Å (Fig. 2 and 3).

The synthesis pathways of the Pd^{II} complexes (**6–9**) are shown in Scheme 2. Complex **6** was prepared through the reaction of nitron with $[Pd(Py)_2Br_2]$. The reaction of complex **6** with

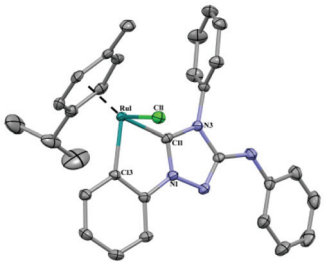


Fig. 2 The molecular structure of complex **1**.

triphenylphosphine resulted in complex **7**. The reaction of nitron with $PdBr_2(MeCN)_2$ produced complex **8** with a yield of 24%. Complex **9** was prepared by the reaction of $PdBr_2$ in the presence of NaBr in DMSO. These complexes were obtained as air- and moisture-stable yellow solids and were fully characterized by ^{1}H- and ^{13}C-NMR. The solubility of complexes (**6–9**) was good in apolar and polar solvents. In the ^{1}H-NMR spectra, the chemical shifts in the NH protons also supported the formation of Pd^{II}–nitron complexes. The NH protons were observed at 9.01, 9.05, 9.16, and 8.95 ppm for complexes **6–9**, respectively. In the ^{1}H-NMR spectrum of complexes **8** and **9**, the **8**/**9** balance was observed. The chemical shifts of the $C_{carbene}$ peak of the Pd^{II} complexes (**6–9**) were observed at 154.7, 139.7, 159.2, and 151.6 ppm, respectively. In complex **6**, the Pd^{II} ion was coordinated by two bromine [Pd1–Br1 = 2.4159(17) Å and Pd1–Br2 = 2.4576(16) Å], one nitrogen [Pd1–N1 = 2.095(9) Å] and one carbon [Pd1–C6 = 1.959(10) Å] atoms, thus showing distorted square planar coordination geometry. The molecules of complex **6** were connected by C–H···π and π···π interactions. Atom C10 in the molecule at (x, y, z) acted as a hydrogen-bond donor to the C14–C19 phenyl ring in the molecule at (x + 1, y, z), thereby forming a C(9) chain running parallel to [100] (Fig. 3).

Catalytic studies

Alpha-alkylation of ketones with alcohols

To investigate the potential of the nitron complexes (**1–9**) for α-alkylation reactions, acetophenone (**20a**) and benzyl alcohol (**21a**) were selected as benchmark substrates (Table 1). The reaction was carried out in toluene (1 mL) at 130 °C under an air atmosphere for 2 h in the presence of complexes **1–9** as the catalyst and KOH (0.1 mmol). According to the literature, for this reaction, KOH is one of the best bases and toluene is the best solvent.[18] All the complexes, except **5**, transformed the reaction with 100% yield. The selectivity of the products (ketone : alcohol ratio) of complexes **1–5** was 76 : 24, 72 : 28, 94 : 6, 82 : 18 and 87 : 6%, respectively. The Ir^{III} complexes of nitron (**3** and **4**) exhibited better selectivity than Ru^{II} and Rh^{III} complexes towards the formation of ketone. The effect of different metal catalysts and oxidation states like Ir^{I}/Ir^{III} on the catalytic activity was examined. In this reaction, high valent Ir^{III} complex **3** performed better in the α-alkylation of acetophenone to form 1-phenyl ethanol, while low valent Ir^{I} complex **5** showed lower activity, especially when the Ir^{III} center was stabilized by the strongly chelating 1-Ph substituent

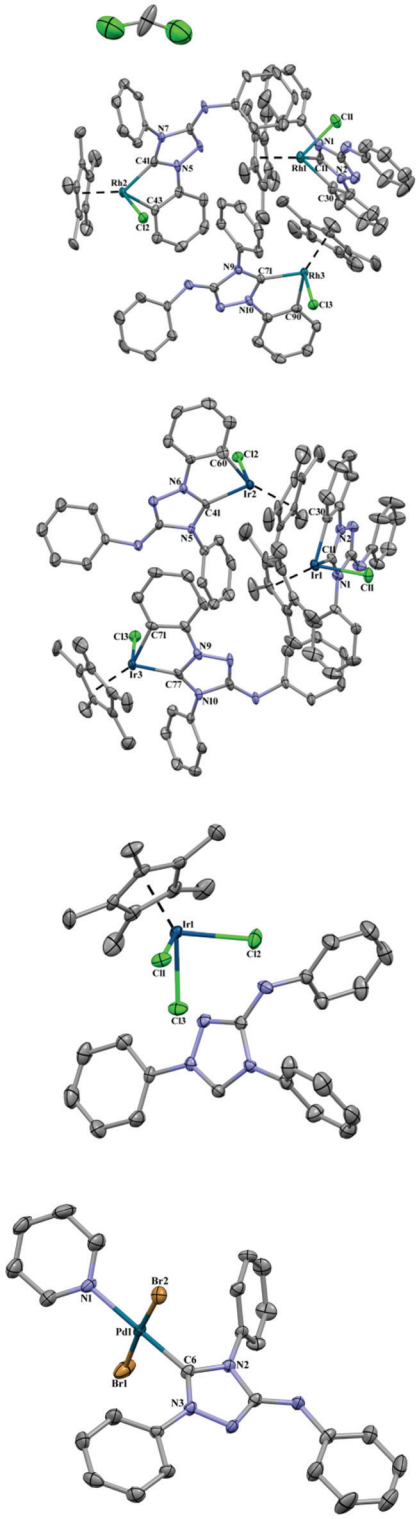
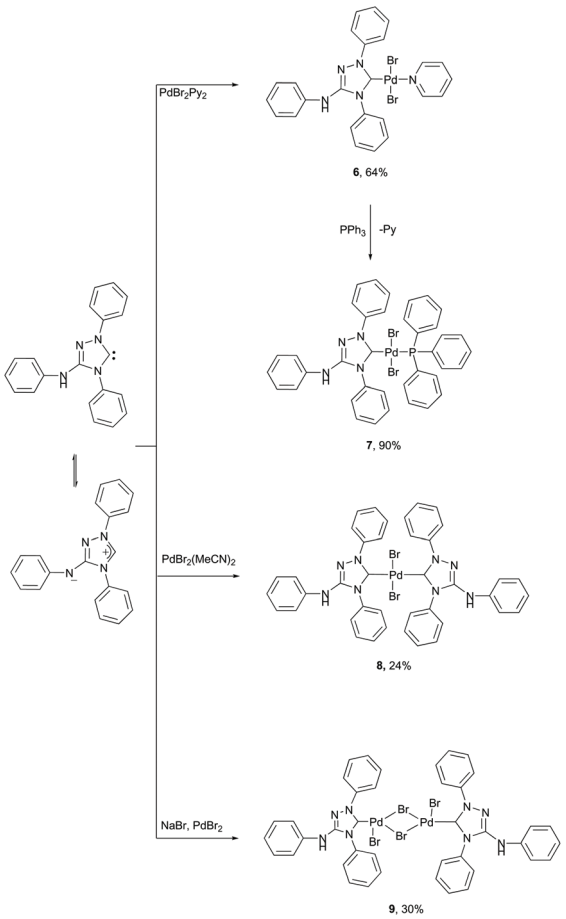
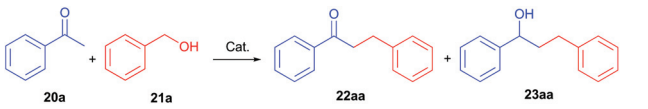


Fig. 3 The molecular structure of complexes **2**, **3**, **4** and **6** (from top to bottom).



Scheme 2 Synthetic pathway for complexes **6–9**.

Table 1 The effects of catalyst, base and temperature on the alkylation of **20a** with **21a**[a]

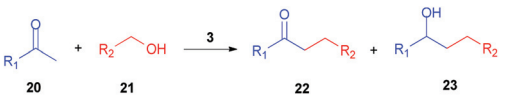


Entry	Cat.	Base	Conversion (%)	Selectivity (%)	
				22aa	**23aa**
1	**1**	KOH	100	76	24
2	**2**	KOH	100	72	28
3	**3**	KOH	100	94	6
4	**4**	KOH	100	82	18
5	**5**	KOH	78	87	6
6	**6**	KOH	100	60	40
7	**7**	KOH	100	46	54
8	**8**	KOH	100	53	47
9	**9**	KOH	100	75	25
10[b]	$[Cp^*IrCl_2]_2$	KOH	90	51	49
11	$[Cp^*IrCl_2]_2$/nitron	KOH	100	53	47
12	**3**	NaOH	100	48	52
13	**3**	KO^{t}Bu	100	81	19
14	**3**	NaO^{t}Bu	67	29	37
15[c]	**3**	KOH	100	88	12
16[d]	**3**	KOH	100	95	5
17[e]	**3**	KOH	85	75	25

[a] Reaction conditions: **20a** (1.00 mmol), **21a** (1.00 mmol), base (0.10 mmol), catalyst (0.10 mol%), toluene (1.00 mL), time (2 h), temperature (130 °C), under air. [b] Cat. (0.05 mol%). [c] T = 120 °C. [d] T = 140 °C. [e] Catalyst (0.01 mol%). Yields were determined using ^{1}H-NMR spectroscopy using diethyleneglycol-di-*n*-butylether as an internal standard.

of nitron. Complex **3** was selected as the main catalyst for further studies although all catalysts (except **5**) completed the reaction with 100% yield, since the ketone product is the desired product in this reaction. In the catalytic reaction with **5**, 1-phenylethanol was observed as a by-product in the solution after 2 hours and the conversion was not completed (Table 1, entry 5). According to the results of the *in situ* study, the selectivity of the α-alkylation of ketone was reduced (Table 1, entry 11). Also, $[Cp^*IrCl_2]_2$ had the same selectivity as the *in situ* study. Inspired by this progress, we also focused on the α-alkylation of acetophenone with benzyl alcohol using Pd^{II}–nitron complexes **6–9** (Table 1, entries 6–9). To the best of our knowledge, the catalytic properties of Pd^{II}–NHC complexes on the alpha-alkylation of ketones with alcohol are yet to be explored although the α-alkylation reaction of ketones with alcohols is also a kind of C–C coupling reaction. Among Pd^{II}–nitron complexes, the highest selectivity to **22aa** was obtained with dimeric Pd^{II}–nitron complex **9**. It was observed that the catalytic selectivity of the palladium complexes increased with the amount of metal. With our preliminary studies, Pd–NHC catalysts can also perform this reaction and we think that it should be evaluated in detail in future studies. Replacing KOH with NaOH or KO^{t}Bu did not improve the selectivity and NaO^{t}Bu could not even complete the conversion (Table 1, entries 12–14). The ideal temperature was set at 130 °C (Table 1, entries 15 and 16). Therefore, the conversion was conducted to explore the effect of base and catalyst towards selective alpha(α)-alkylation production. Finally, reaction parameters were optimized with iridium catalyst (**3**) for 2 hours in 1 mL of toluene at 130 °C. When the catalyst amount was decreased to 0.05 mol%, it was observed that the conversion was not completed (Table 1, entry 17). With the optimal reaction conditions determined, the α-alkylation of benzyl alcohol with different ketone derivatives was investigated, and the results are outlined in Table 2. The reactions of benzyl alcohol with ketone derivatives bearing halogen atoms, namely 4′-chlorine, 2′-chlorine and 4′-bromine produced yields of 82–92% (Table 2, entries 2–4). For the electron-donating substituents, such as methoxy, methyl, and dimethyl, α-alkylated products were obtained with high yields of 98, 95 and 91%, respectively (Table 2, entries 5–7). Higher catalytic yields were achieved using 1-(naphthalene-2-yl)ethanone and 1-tetralone, resulting in products 1-(naphthalen-2-yl)-3-phenylpropan-1-one (95%) and 2-benzyl-3,4-dihydronaphthalen-1(2*H*)-one (96%), respectively (Table 2, entries 8 and 9). The α-alkylation of acetophenone with alcohol derivatives was also investigated to further explore the scope of the reaction (Table 2). Transformation of acetophenone with various primary alco-

Table 2 Scope of α-alkylation ketones of alcohols[a]



20 21 22 23

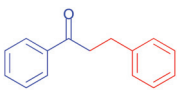
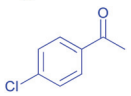
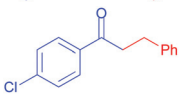
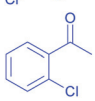
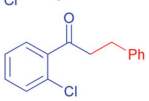
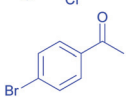
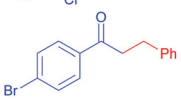
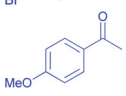
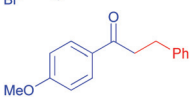
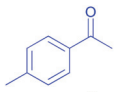
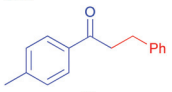
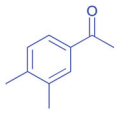
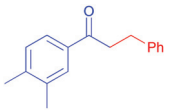
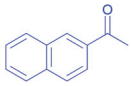
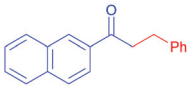
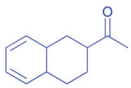
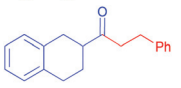
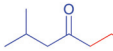
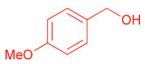
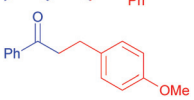
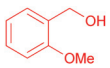
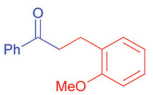
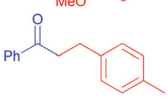
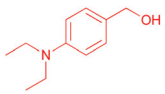
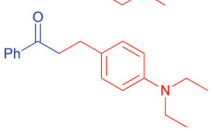
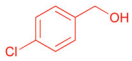
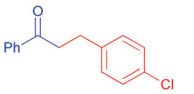
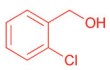
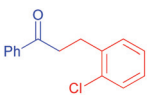
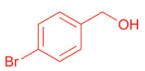
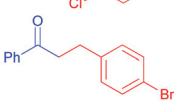
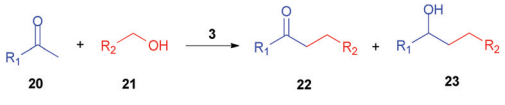
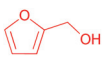
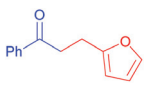
Entry	Ketone (**20**) or Alcohol	Product (**22**)	Yield **22** : **23**%
1			92 : 8 (90 : 10)[b]
2			90 : 10 (87 : 13)[b]
3			92 : 8
4			82 : 18 (81 : 19)[b]
5			98 : 2 (98 : 2)[b]
6			95 : 5 (91 : 9)[b]
7			91 : 9
8			95 : 5 (87 : 13)[b]
9			96 : 4
10			79 : 21
11			97 : 3 (97 : 3)[b]
12			92 : 8
13			88 : 12 (85 : 15)[b]
14			89 : 11
15			91 : 9 (88 : 12)[b]
16			93 : 7
17			84 : 16 (82 : 18)[b]

Table 2 *(Contd.)*



20 21 22 23

Entry	Ketone (**20**) or Alcohol	Product (**22**)	Yield **22** : **23**%
18			86 : 14
19			78 : 22 (72 : 28)[b]
20			64 : 36

[a] Reaction conditions: ketone (**20**) (1.00 mmol), alcohol (**21**) (1.00 mmol), KOH (0.10 mmol), **3** (0.10 mol%), toluene (1.00 mL), time (2 h), temperature (130 °C), under air, analysed by NMR. [b] Isolated yields. Benzyl alcohol was used as alcohol in the entries 1–10. Acetophenone was used as ketone in the entries 11–20.

hols, including electron-donating, electron-withdrawing, heteroaromatic, and aliphatic alcohols, produced yields ranging from 64 to 97% (Table 2, entries 11–20). We also reported isolated product yields for a select few examples (Table 2). α-Alkylated products and their derivatives have biological uses in pharmacology and medicine, such as Phloretin.[26] Under similar reaction conditions, we achieved a TOF value of 230 h^{-1} with [chloro(*N*-phenyl-*N*-octylethylenediamine)(η^6-*p*-cymene)ruthenium(II)] hexaflorophophate.[15h] The Ir^{III} complex (**3**) in our study reached a TOF value of 470 h^{-1}. Chen and co-workers prepared bidentate Ru^{II} complexes with a pyridonate fragment and reported a TOF value reaching 3680 h^{-1} in the α-alkylation of ketones with alcohols using KO^{t}Bu as a base.[15c] The results due obtained from this study are considered to be promising for the easy synthesis of the catalyst and the commercial availability of the NHC ligand at a low cost. The α-alkylation of **20a** with **21a** was monitored by NMR spectroscopy in d_8-toluene to gain further insight into the reaction mechanism. Products and Ir–H formation were observed as soon as the reaction started. The Ir–H species persisted throughout the reaction. A hydride peak appeared in the hydridic region of the ^{1}H-NMR spectrum (δ = −17.4 ppm) with the formation of 1,3-diphenylpropan-1-one and 1,3-diphenylpropan-1-ol, which suggested that the catalytically active species were related to Ir–H formation (Fig. 4). The peaks of the substrates (**20a** and **21a**) disappeared in the ^{1}H-NMR spectrum within 15 minutes after the reaction began. For a practical availability, gram-scale reaction was carried out using acetophenone with benzyl alcohol, and the ketone 1,3-diphenylpropan-1-one was obtained in an 89% product yield (Scheme 3).

We monitored the time profile of the α-alkylation of ketone reaction with ^{1}H-NMR spectroscopy (Fig. 5). According to the observations, the conversion of substrates to **22aa** and **23aa** completed within 15 min. The possible mechanism of the α-alkylation of ketones with primary alcohols is given in Scheme 4. The mechanism began with the dehydrogenation of

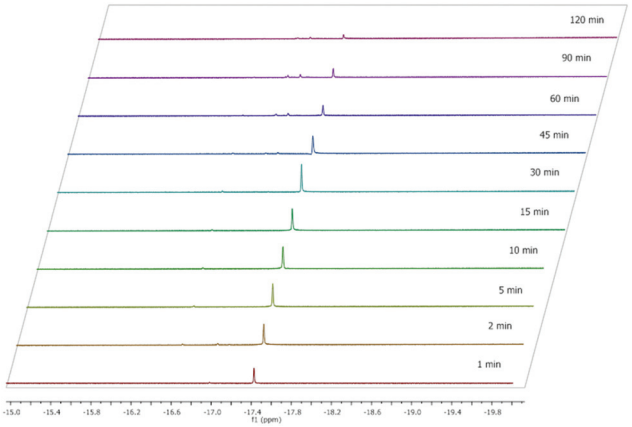
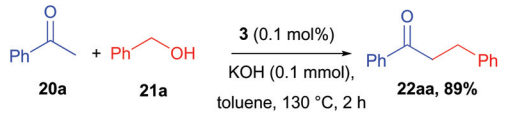


Fig. 4 ^{1}H-NMR monitoring of the hydride signal of Ir-hydride (located at –17.40 ppm and zoomed in): **20a** (1.0 mmol), **21a** (1.0 mmol), KOH (0.1 mmol), cat. **3** (5 mmol %), toluene-d_8 (1 ml), temperature (130 °C).



Scheme 3 Gram-scale synthesis of **22aa**.[a] [a]Reaction conditions: **20a** (1.0 g, 8.33 mmol), **21a** (0.9 g, 8.33 mmol), **3** (0.1 mol%), KOH (5.6 mg, 0.10 mmol), toluene (10.0 mL), 130 °C, under an air atmosphere. Isolated yield.

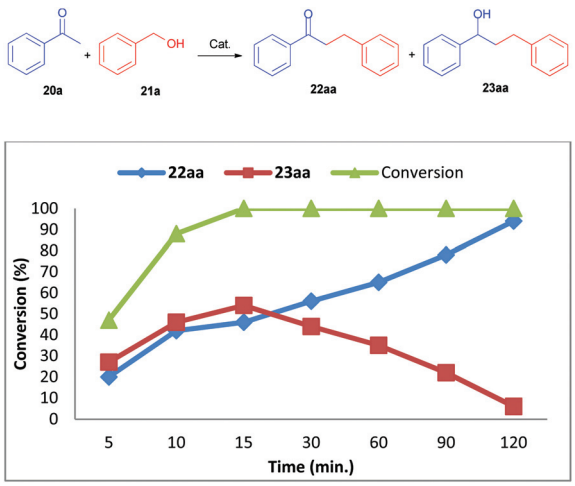
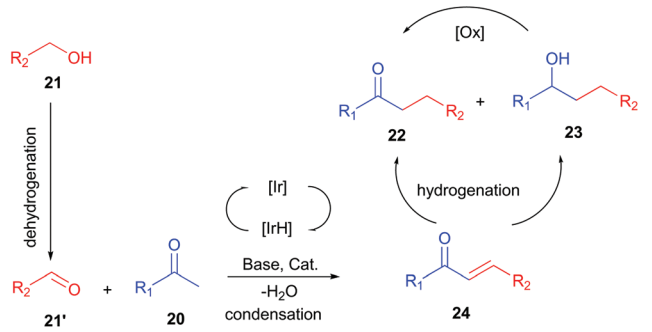


Fig. 5 Time profile of the α-alkylation of acetophenone (**20a**) and benzyl alcohol (**21a**). Reaction conditions: **20a** (1.00 mmol), **21a** (1.00 mmol), KOH (0.10 mmol), **3** (0.10 mol%), toluene (1.00 mL), time (2 h), temperature (130 °C), under air. Conversions and ratios were determined by ^{1}H NMR analyses.

the primary alcohol (**21**) to the carbonyl compound (**21′**) with the aid of catalyst **3**. During aldehyde (**21′**) formation, the system releases hydrogen and this hydrogen may help to form iridium hydride. The two carbonyl compounds (**20** and **21′**) produced α, β-unsaturated ketone (**24**) in the presence of a base. The α, β-unsaturated ketone (**24**) intermediate was reduced with iridium hydride, which resulted in ketone (**22**) and alcohol (**23**) products. Finally, the oxidation of alcohol (**23**) increased the ketone product (**22**) over time. The most important points of this mechanism are that the hydrogen released by dehydrogenation of the alcohol is borrowed by the catalyst for the formation of iridium hydride and this hydrogen is further used in the reduction of enone.[16d] If benzaldehyde is used directly instead of alcohol in the first step, the cross-aldol condensation reaction occurs.[19]

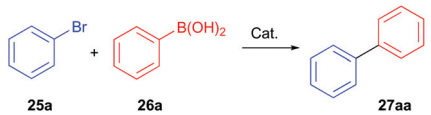


Scheme 4 Plausible reaction mechanism for α-alkylation of ketones with primary alcohols.

Suzuki–Miyaura cross-coupling reactions

In the last decade, palladium-catalyzed Suzuki–Miyaura reactions have become the most popular cross-coupling method in classical chemical synthesis.[14] In the current study, catalytic reactions were carried out in H_2O/2-propanol (1.5 : 0.5 mL) at room temperature under an air atmosphere in the presence of a catalyst and KOH (0.5 mmol). To compare the effect of the catalytic activity of Pd^{II}–nitron complexes **6–9**, the reaction of bromobenzene with phenylboronic acid was selected as a reference reaction. The progress of the reaction was monitored by gas chromatography. The catalytic yields of complexes **6–9** were 88, 74, 82, and 76%, respectively (Table 3). The catalytic activity of complex **6** was 88%, which was relatively higher compared to complexes **7**, **8**, and **9** (Table 3, entries 1–4). The ligands on the metal atom had a substantial effect on the catalytic activity. The solvent system was a mixture of H_2O/2-propanol (1.5/0.5 mL), which was more effective than H_2O and 2-propanol (Table 3, entries 5 and 6). H_2O helps to activate phenylboronic acid, while 2-propanol enhances the activity of aryl halides. In this study, decreasing the ratios of catalyst loading from 0.1% to 0.025% resulted in 1,1′-biphenyl with 78% yield (Table 3, entry 9). Besides, only 18% yield was obtained using [$PdBr_2Py_2$], which indicated the importance of the nitron ligand for the catalytic reaction (Table 3, entry 10). A control experiment was applied without any precatalyst, and no product formation was detected (Table 3, entry 11). Different bases, such as NaOH, $NaHCO_3$, Cs_2CO_3, K_2CO_3, and KO^{t}Bu, which are soluble in water, were also scanned (Table 3, entries 12–16). KOH and KO^{t}Bu were identified as the ideal bases for this reaction with 88 and 87% yields, respectively (Table 3,

Table 3 The effects of solvent, base and catalysts on the Suzuki–Miyaura reaction of **24a** with **25a**[a]



25a **26a** **27aa**

Entry	Complex	Cat. (mol%)	Solvent	Base	Yield (%)
1	**6**	0.1	H_2O/2-propanol	KOH	88
2	7	0.1	H_2O/2-propanol	KOH	74
3	**8**	0.1	H_2O/2-propanol	KOH	82
4	**9**	0.05	H_2O/2-propanol	KOH	76
5	**6**	0.1	2-Propanol	KOH	65
6	**6**	0.1	H_2O	KOH	73
7	**6**	0.075	H_2O/2-propanol	KOH	81
8	**6**	0.050	H_2O/2-propanol	KOH	80
9	**6**	0.025	H_2O/2-propanol	KOH	78
10	$PdBr_2Py_2$	0.1	H_2O/2-propanol	KOH	18
11	**6**	—	H_2O/2-propanol	KOH	—
12	**6**	0.1	H_2O/2-propanol	NaOH	76
13	**6**	0.1	H_2O/2-propanol	$NaHCO_3$	41
14	**6**	0.1	H_2O/2-propanol	Cs_2CO_3	62
15	**6**	0.1	H_2O/2-propanol	K_2CO_3	65
16	**6**	0.1	H_2O/2-propanol	KO^{t}Bu	87
17[b]	**6**	2nd recycle	H_2O/2-propanol	KOH	72
18[b]	**6**	3rd recycle	H_2O/2-propanol	KOH	68
19[b]	**6**	4th recycle	H_2O/2-propanol	KOH	67
20[b]	**6**	5th recycle	H_2O/2-propanol	KOH	52

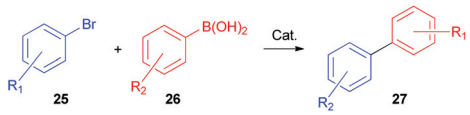
[a] Reaction conditions: 4-bromobenzene (1.0 mmol), phenylboronic acid (1.0 mmol), base (0.5 mmol), 0.5 mL 2-propanol + 1.5 mL H_2O or solvent (2.0 mL), RT, 0.5 h, under air. Yields were determined by gas chromatography. [b] Reuse experiments.

entries 1 and 16). The possibility of reusing catalysts **6** for the Suzuki–Miyaura coupling reaction was examined. After each reaction, the reaction mixture was filtered, and the black solid residue was used for the next reaction. The yields for the second, third, fourth, and fifth cycles were 72, 68, 67, and 52%, respectively. The results showed that the catalyst was still active at the end of the fifth cycle (Table 3, entries 17–20).

The electron-donating properties of N-heterocyclic carbenes change with the effect of heteroatoms on the ring, especially at the backbone of the structure.[20] The literature similarly contains reports on these types of Pd-(1,2,4-triazol-5-ylidine) complexes.[21] Chernyshev *et al.* synthesized alkyl- and benzyl-substituted Pd^{II}-(1,2,4-triazol-5-ylidine) complexes and observed that these complexes could be used as efficient catalysts for the Suzuki–Miyaura reaction.[22] Padelkova *et al.* also investigated the effects of 1,2,4-triazol-5-ylidine substituents on the catalytic activity.[24]

Under the optimized conditions, we extended the reaction scope using different aryl bromides and arylboronic acid derivatives (Table 4). Firstly, phenylboronic acids containing electron-donating groups at the *para* position, namely OCH_3 and CH_3 were tested, and good yields were obtained with 4-methoxy-1,1′-biphenyl and 4-methyl-1,1′-biphenyl (Table 4, entries 2 and 3). Phenylboronic acids containing electron-withdrawing groups such as F, Cl, and CHO produced 4-fluoro-1,1′-biphenyl, 4-chloro-1,1′-biphenyl, and [1,1′-biphenyl]-4-carbal-

Table 4 Suzuki–Miyaura coupling reactions of aryl bromides and phenylboronic acids under the optimized conditions[a]



25 **26** **27**

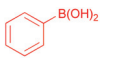
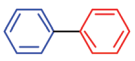
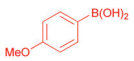
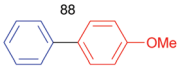
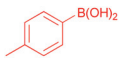
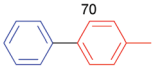
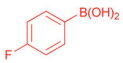
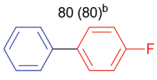
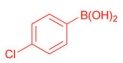
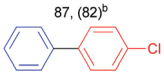
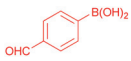
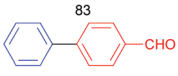
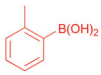
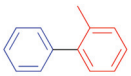
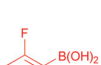
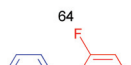
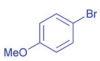
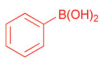
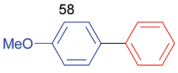
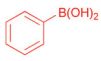
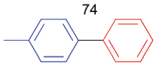
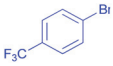
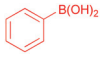
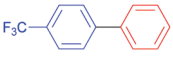
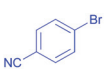
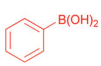
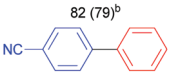
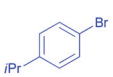
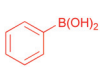
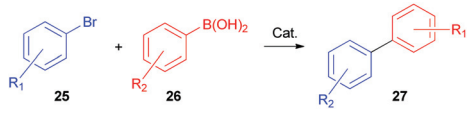
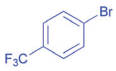
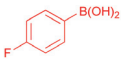
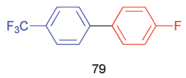
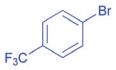
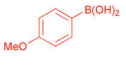
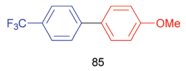
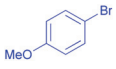
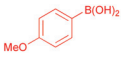
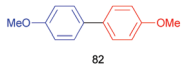
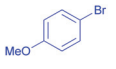
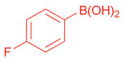
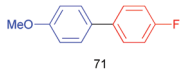
Entry	Aryl bromide (**25**)	Arylboronic acid (**26**)	Product, yield (27%)
1			
2			88 
3			70 
4			80 (80)[b] 
5			87, (82)[b] 
6			83 
7			68 
8			64 
9			58 
10			74 
11			84 
12			82 (79)[b] 
13			71 (69)[b]
14			78
15			54
16			48 34

Table 4 *(Contd.)*



Entry	Aryl bromide (**25**)	Arylboronic acid (**26**)	Product, yield (27%)
17			 79
18			 85
19			 82
20			 71

[a] Reaction conditions: aryl bromide (1.0 mmol), arylboronic acid (1.0 mmol), KOH (0.5 mmol), 6 (0.1 mol%), 0.5 mL 2-propanol + 1.5 mL H_2O, RT, 30 min, under air. [b] Isolated yield. Yields were determined by gas chromatography.

dehyde with excellent yields of 87%, 83%, and 68%, respectively (Table 4, entries 4–6). When the F and CH_3 groups at the *para* position of phenylboronic acids were displaced by the *ortho* position, the catalytic activity was reduced to 64% for 2-methyl-1,1′-biphenyl and 58% for 2-fluoro-1,1′-biphenyl (Table 4, entries 7 and 8). Furthermore, different aryl bromides were also examined (Table 4, entries 9–17). Aryl bromides consisting of electron-donating substituents, OCH_3, CH_3, and $C(CH_3)_3$, gave the corresponding products 4-methoxy-1,1′-biphenyl, 4-methyl-1,1′-biphenyl and 4-isopropyl-1,1′-biphenyl with good yields of 74, 84 and 78%, respectively (Table 4, entries 9,10 and 13). Aryl bromides containing electron-withdrawing groups, namely CF_3 and CN also resulted in good yields (82% and 71%) in coupling reactions with the products of 4-(trifluoromethyl)-1,1′-biphenyl and [1,1′-biphenyl]-4-carbonitrile (Table 4, entries 11 and 12). However, when sterically hindered aryl bromides were used, the product yields were decreased. Fluorinated aromatic compounds were used in medically active compounds to inhibit the oxidation of the aromatic ring and increase lipophilicity, which inhibits drug delivery.[23] The reaction of 4-bromobenzotrifluoride with 4-flouro-phenylboronic acid and 4-methoxyphenylboronic acid produced 79% and 85% yields for the coupling products. Our results demonstrated that the Pd^{II} complexes containing nitron can be used in Suzuki–Miyaura cross-coupling reactions.

Liu *et al.* proposed two possible reaction pathways involving a $Pd^{0/II/0}$ and a $Pd^{II/IV/II}$ catalytic cycle for the Suzuki–Miyaura coupling reactions.[25] We performed DFT calculations to investigate which of these mechanisms were preferred by our complexes during the Suzuki–Miyaura coupling reaction (Fig. 6). To determine which pathway the Suzuki–Miyaura Coupling

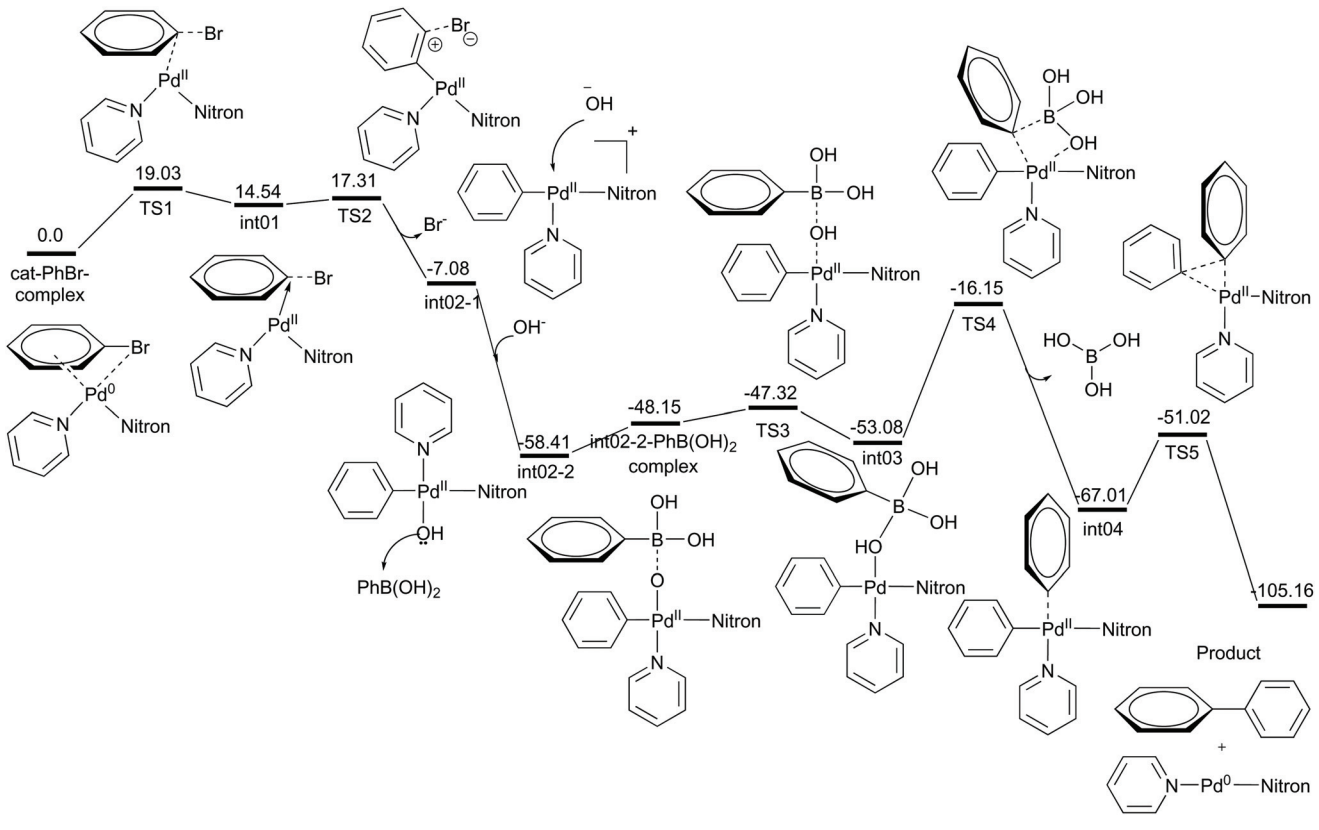
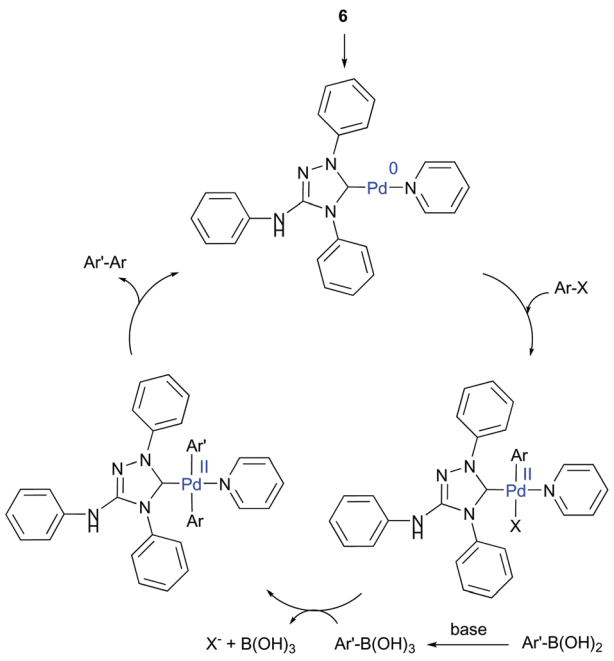


Fig. 6 The $Pd^{0/II/0}$ pathway and its free energy profile calculated with the DFT-B3LYP method in water. Energies are given in kcal mol^{-1}.

reaction would prefer, both reaction pathways were computationally investigated using the DFT-B3LYP method. The $Pd^{0/II/0}$ pathway was calculated with the DFT-B3LYP method (Fig. 6). Unfortunately, we were unable to locate any transition state structure for the oxidation step of the other pathway $Pd^{II/IV/II}$. Our scan jobs indicate that the approach of PhBr to the Pd^{II} center continuously increases the electronic energy instead of passing from a maximum. This may infer the PhBr ligand not having enough power to oxidize Pd^{II} to Pd^{IV}. On the other hand, we were able to determine the whole $Pd^{0/II/0}$ pathway with the DFT-B3LYP hydride functional in water. In the early stage of the mechanism, a stable PhBr-catalyst complex forms and the activation barrier of the first step were determined relative to this complex. Then, the Pd^0 catalyst concertedly breaks the C–Br bond of PhBr and Pd^0 oxidize to Pd^{II} with an activation free energy of 19 kcal mol^{-1}. In the next step, bromide anion leaves the complex with very low activation energy letting the formation of an int02-1 cation which barrierlessly forms an int02-2 intermediate complex. The addition of the $PhB(OH)_2$ reagent initiates the transmetallation step. After the formation of int02-2 and $PhB(OH)_2$ complex, it readily converts into int03 complex. Then, the phenyl group attached to the boron atom in int03 attacks to Pd^{II} center. Since this Ph migration needs rather high energy, and this step (transmetallation) becomes the rate-determining step with an activation free energy of ~37 kcal mol^{-1}. In the last step, the reduction of the Pd^{II} complex, reproduction of the Pd^0 catalyst, and the formation of a diaryl product occur simultaneously with moderate activation energy (16 kcal mol^{-1}). Also, the possible mechanism of the Suzuki–Miyaura C–C coupling reactions is summarized (Scheme 5).



Scheme 5 Proposed mechanisms of Suzuki–Miyaura coupling reactions.

Conclusions

In conclusion, a series of Ru^{II}, Rh^{III}, $Ir^{I,III}$ and Pd^{II} complexes bearing the mesoionic NHC ligand were successfully synthesized and fully characterized. The X-ray diffraction spectra of complexes **1**, **2**, **3**, **5**, and **6** were obtained by the diffusion of diethyl ether into the concentrated solutions of the complexes in dichloromethane. Complexes **1–9** exhibited high catalytic activities for the α-alkylation of ketones with alcohols with a low catalyst loading (0.1 mol%) and base amount (10 mol%) under the air atmosphere. The Ir-hydride species were detected by ^{1}H-NMR spectroscopy at −17.40 ppm. The palladium complexes **6–9** were tested as active precatalysts for the Suzuki–Miyaura cross-coupling reaction. The PEPPSI-type complex **6** catalyzed this reaction in a short time at room temperature. The DFT calculations indicated that the $Pd^{0/II/0}$ pathway is more favorable than the other pathway which requires further oxidation of Pd^{II} to Pd^{IV}.

Experimental

All experimental applications of organometallic compounds were carried out under an inert atmosphere using standard Schlenk line techniques. All complexes were synthesized in dry acetonitrile. Analytical grade acetonitrile (Merck) was dried over phosphorus(v) oxide and stored over molecular sieves. $[RuCl_2(p\text{-cymene})]_2$ was prepared according to the method reported by Bennett and Smith through the reaction of ruthenium(III) chloride with α-terpinene.[27] $[IrCl_2Cp^*]_2$ was synthesized according to the published procedures by a reaction of iridium(II) chloride and pentamethylcyclopentadiene.[28] All catalytic reactions were carried out under the inert atmosphere on the Carousel 12 Plus Reaction Station system. ^{1}H- and ^{13}C-NMR spectra were recorded using Varian 400 MHz spectrometers and chemical shifts are recorded in ppm. *J* values were given in Hz. NMR chemical shifts were referenced to the solvent signal in $CDCl_3$ and DMSO-d_6. Reagents were purchased from Aldrich or Merck and were used as received. Infrared spectra were recorded on a PerkinElmer Spectrum 100 IR spectrometer using the KBr pellet technique between 4000 and 400 cm^{-1} in the solid state. Other reagents were commercially available and used without further purification.

Synthesis of complex 1

$[Ru(p\text{-cymene})Cl_2]_2$ (980 mg, 1.6 mmol) and nitron (1000 mg, 3.2 mmol) were dissolved in 30 ml of DCM. The mixture was stirred overnight at room temperature, and then DCM was evaporated *in vacuo*. The complex was purified by column chromatography (DCM). The precipitate was recrystallized in DCM/Et_2O. Yield: 447 mg (24%), orange solid. M. p. 242–244 °C. Anal. calcd for $C_{30}H_{29}ClN_4Ru$ (582.10): C, 61.90; H, 5.02; N, 9.62. Found: C, 61.79; H, 5.01; N, 9.59. FT-IR ν_{max}/cm^{-1} in KBr: 3255, 3047 (NH); 2955, 745 (C–H); 1579 (C═N). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.11 (m, 1H, Ph–H), 7.74 (t, J = 4.0 Hz, 4H, Ph–H), 7.50 (m, 3H, Ph–H), 7.35 (m, 2H, Ph–H),

7.04 (m, 4H, Ph–H), 6.14 (s, 1H, N–H), 5.42 (d, J = 6.0 Hz, 1H, *p*-cymene-CH), 5.20 (d, J = 6.0 Hz, 1H, *p*-cymene-CH), 4.67 (d, J = 6.0 Hz, 1H, *p*-cymene-CH), 4.58 (d, J = 6.0 Hz, 1H, *p*-cymene-CH), 2.14 (m, 1H, *p*-cymene-CH(CH_3)$_2$), 1.92 (s, 3H, *p*-cymene-CH_3), 0.84 (d, J = 6.8 Hz, 3H, *p*-cymene-CH(CH_3)$_2$), 0.69 (d, J = 6.8 Hz, 3H, *p*-cymene-CH(CH_3)$_2$). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 188.3, 160.4, 148.9, 145.3, 140.7, 138.1, 134.9, 130.4, 129.3, 124.6, 122.8, 122.5, 117.6, 112.7, 104.9, 99.7, 92.8, 90.2, 89.6, 82.6, 30.9, 23.3, 18.9.

Synthesis of complex 2

The complex **2** was prepared in the same manner as complex **1** using $[Rh(Cp^*)Cl_2]_2$ (150 mg, 0.24 mmol) and nitron (152 mg, 0.48 mmol). The complex was purified by column chromatography (DCM). The precipitate was recrystallized in DCM/Et_2O. Yield: 131.9 mg, (47%), orange solid, m.p. 225–227 °C. Anal. calcd for $C_{30}H_{30}ClN_4Rh$ (584.94): C, 61.60; H, 5.17; N, 9.58. Found: C, 61.37; H, 5.18; N, 9.56. FT-IR ν_{max}/cm^{-1} in KBr: 3414, 3053 (NH); 2913, 749 (C–H); 1579 (C═N). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.97 (br, 2H, Ph–H), 7.77 (t, J = 4.0 Hz, 1H, Ph–H), 7.58 (m, 6H, Ph–H), 7.33 (t, J = 7.6 Hz, 2H, Ph–H), 7.07 (m, 3H, Ph–H), 6.41 (s, 1H, N–H), 1.41 (s, 15H, $C_5(CH_3)_5$). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 182.0 (d, J = 58 Hz, C–Rh), 156.3, 156.0, 149.3, 145.3, 138.1, 136.9, 134.3, 130.4, 130.0, 129.2, 125.7, 122.8, 117.7, 112.4, 98.0, 97.9, 9.3.

Synthesis of complex 3

Complex **3** was prepared in the same manner as complex **1** using $[Ir(Cp^*)Cl_2]_2$ (150 mg, 0.19 mmol) and nitron (119 mg, 0.38 mmol). The complex was purified by column chromatography (DCM). The precipitate was recrystallized in DCM/Et_2O. Yield: 189.6 mg (74%), yellow solid, m.p: 232–234 °C. Anal. calcd for $C_{30}H_{31}ClN_4Ir$ (674.26): C, 53.44; H, 4.48; N, 8.31. Found: C, 53.32; H, 4.46; N, 8.29. FT-IR ν_{max}/cm^{-1} in KBr: 3414, 3062 (NH); 2965, 748 (C–H); 1579 (C═N). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.89 (br, 2H, Ph–H), 7.75 (m, 1H, Ph–H), 7.67 (t, J = 7.6 Hz, 2H, Ph–H), 7.59 (m, 2H, Ph–H), 7.49 (m, 2H, Ph–H), 7.34 (m, 2H, Ph–H), 7.06 (m, 3H, Ph–H) 6.20 (s, 1H, N–H), 1.48 (s, 15H, $C_5(CH_3)_5$). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.1, 156.4, 149.3, 146.4, 138.1, 136.9, 134.0, 130.5, 130.0, 129.2, 125.8, 117.8, 112.5, 98.0, 9.39.

Synthesis of complex 4

Complex **4** was observed as a by-product of the synthesis of complex **3**. Complex **4** was also obtained as the second product from the same column with complex **3**. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 11.85 (s, 1H, N–H), 8.28 (d, J = 8.4 Hz, 2H, Ph–H), 8.01 (d, J = 8.4 Hz, 2H, Ph–H), 7.68 (s, 1H, Ph–H), 7.57 (m, 6H, Ph–H), 7.46 (m, 2H, Ph–H), 7.35 (t, J = 7.6 Hz, 2H, Ph–H), 7.12 (t, J = 7.2 Hz, 1H, Ph–H), 1.56 (s, 15H, $C_5(CH_3)_5$). Yield: 8.5 mg (3%), yellow solid. Anal. calcd for $C_{30}H_{32}Cl_3IrN_4$ (747.18): C, 48.22; H, 4.32; N, 7.50. Found: C, 48.09; H, 4.29; N, 7.51. ^{13}C-NMR (100 MHz, $CDCl_3$): δ 163.7, 149.6, 149.1, 145.3, 135.7, 130.6, 130.1, 129.9, 129.8, 129.2, 129.0, 126.0, 122.7, 122.3, 120.6, 119.2, 117.6, 111.9, 91.6, 9.13.

Synthesis of complex 5

$[Ir(COD)Cl_2]_2$ (150 mg, 0.22 mmol) and nitron (139 mg, 0.44 mmol) were dissolved in 10 ml of toluene. The mixture was stirred overnight at room temperature, and then toluene was evaporated *in vacuo*. The product was purified by column chromatography (DCM). The precipitate was recrystallized in chloroform/pentane. Yield: 196.8 mg (69%), yellow solid, m.p: 213–215 °C. Anal. calcd for $C_{28}H_{28}ClN_4Ir$ (648.22): C, 51.80; H, 4.35; N, 8.64. Found: C, 51.62; H, 4.35; N, 8.61. FT-IR ν_{max}/cm^{-1} in KBr: 3259, 3072 (NH); 2920, 751 (C–H); 1585 (C═N). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.64 (m, 2H, Ph–H), 7.91 (br, 2H, Ph–H), 7.64 (m, 3H, Ph–H), 7.50 (t, J = 7.2 Hz, 3H, Ph–H), 7.43 (m, 2H, Ph–H), 7.34 (m, 2H, Ph–H), 7.06 (t, J = 7.2 Hz, 1H, Ph–H), 6.04 (s, 1H, N–H), 4.57 (m, 2H, COD–H), 2.64 (m, 1H, COD–H), 2.46 (m, 1H, COD–H), 2.01 (m, 1H, COD–H), 1.79 (m, 1H, COD–H), 1.60 (m, 2H, COD–H), 1.40 (m, 2H, COD–H), 1.27 (m, 2H, COD–H). ^{13}C-NMR (100 MHz, DMSO-d_6): δ 181.3, 149.4, 139.6, 137.9, 134.2, 130.2, 129.8, 128.7, 127.5, 123.0, 122.9, 117.6, 86.2, 84.1, 53.1, 52.4, 34.1, 33.7, 32.0, 29.9, 28.5, 22.3, 14.1.

Synthesis of complex 6

Complex **6** was prepared in the same manner as complex **1** using $Pd(Py)_2Br_2$ (473 mg, 1.10 mmol) and nitron (350 mg, 1.10 mmol). The product was purified by column chromatography (DCM). The precipitate was recrystallized in DCM/Et_2O. Yield: 463.0 mg (64%), yellow solid. M.p.: 236–238 °C. Anal. calcd for $C_{25}H_{21}Br_2N_5Pd$ (657.70): C, 45.65; H, 3.22; N, 10.65. Found: C, 45.48; H, 3.21; N, 10.60. FT-IR ν_{max}/cm^{-1} in KBr: 3413, 3054 (NH); 2918, 753 (C–H); 1579 (C═N). ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.01 (s, 1H, N–H), 8.62 (d, J = 7.6 Hz, 2H, Py–H) 8.54 (m, 2H, Py–H), 7.91 (m, 3H, Ph–H), 7.72 (m, 6H, Ph–H), 7.53 (m, 2H, Ph–H), 7.45 (t, J = 6.4 Hz, 2H, Ph–H), 7.31 (t, J = 7.6 Hz, 2H, Ph–H), 7.01 (t, J = 7.2 Hz, 1H, Ph–H). ^{13}C-NMR (100 MHz, DMSO-d_6): δ 154.7, 152.3, 151.6, 139.6, 139.4, 139.3, 134.5, 130.7, 130.0, 129.6, 129.3, 129.1, 125.6, 123.7, 123.0, 119.1.

Synthesis of complex 7

[(Nitron)Pd(Py)Br_2] (150 mg, 0.23 mmol) was dissolved in 15 mL DCM and then PPh_3 (60 mg, 0.23 mmol) was added. The mixture was stirred at room temperature for 15 min. DCM was evaporated *in vacuo*. The product was purified by column chromatography (DCM). Yield: 174 mg (90%), yellow solid, m.p.: 227–229 °C. Anal. calcd for $C_{38}H_{31}Br_2N_4PPd$ (840.88): C, 54.28; H, 3.72; N, 6.66. Found: C, 54.13; H, 3.69; N, 6.67. FT-IR ν_{max}/cm^{-1} in KBr: 3410, 3052 (NH); 2923, 747 (C–H); 1584 (C═N). ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.05 (s, 1H, N–H), 8.54 (t, J = 8.4 Hz, 2H, Ph–H), 7.87 (t, J = 4.0 Hz, 2H, Ph–H), 7.76 (m, 3H, Ph–H), 7.60 (m, 6H, Ph–H), 7.38 (m, 15H, PPh_3–PhH), 7.00 (t, J = 7.2 Hz, 1H, Ph–H). ^{13}C-NMR (100 MHz, DMSO-d_6): δ 139.7 (d, J = 24 Hz, C–Pd), 134.9, 134.8, 130.9, 130.8, 130.3, 129.9, 129.5, 129.4, 129.3, 128.5, 128.4, 123.2, 119.0.

Synthesis of complex 8

$PdBr_2(MeCN)_2$ (250 mg, 0.96 mmol) and nitron (300 mg, 0.96 mmol) were dissolved in 30 mL of DCM. The mixture was stirred overnight at room temperature and then DCM was evaporated *in vacuo*. The product was purified by column chromatography (DCM : MeOH = 99 : 1). Yield: 205.2 mg (24%), yellow solid, m.p.: 212–214 °C. FT-IR ν_{max}/cm^{-1} in KBr: 3415, 3051 (NH); 2921, 755 (C–H); 1588 (C═N). ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.16 (s, 2H, N–H), 8.25 (d, J = 8.0 Hz, 4H, Ph–H), 7.77 (m, 12H, Ph–H), 7.65 (m, 4H, Ph–H), 7.52 (d, J = 8.4 Hz, 4H, Ph–H), 7.31 (t, J = 7.6 Hz, 4H, Ph–H), 7.01 (t, J = 6.8 Hz, 2H, Ph–H). ^{13}C-NMR (100 MHz, DMSO-d_6): δ 159.2, 151.8, 139.3, 138.7, 133.8, 131.2, 130.6, 130.1, 130.1, 129.6, 129.3, 129.2, 128.8, 124.3, 123.8, 123.0, 119.0.

Synthesis of complex 9

$PdCl_2$ (400 mg, 2.25 mmol), nitron (705 mg, 2.25 mmol) and NaBr (696 mg, 6.76 mmol) were dissolved in 10 mL of dry DMSO. The reaction mixture was stirred overnight at 90 °C under argon atmosphere. Then, DMSO was vacuumed. The residue was dissolved in DCM. The resulting salts were filtered. The product was purified by column chromatography (DCM : MeOH = 99 : 1). Yield: 781.1 mg (30%), orange solid, decomposition: 197–199 °C. FT-IR ν_{max}/cm^{-1} in KBr: 3413, 3059 (NH); 2924, 753 (C–H); 1586 (C═N). ^{1}H-NMR (400 MHz, DMSO-d_6): δ 8.95 (s, 2H, N–H), 8.49 (d, J = 8.0 Hz, 4H, Ph–H), 7.72 (m, 14H, Ph–H), 7.50 (d, J = 8.4 Hz, 4H, Ph–H), 7.29 (t, J = 7.6 Hz, 4H, Ph–H) 6.99 (t, J = 6.8 Hz, 2H, Ph–H). ^{13}C-NMR (100 MHz, DMSO-d_6): δ 151.6, 139.5, 139.4, 139.2, 138.8, 130.1, 130.0, 129.6, 129.5, 129.3, 129.2, 129.0, 124.4, 124.0, 123.1, 123.0, 119.1.

General procedure for the alpha-alkylation of ketones with alcohols

KOH (0.1 mmol, 5.6 mg) and toluene (1.0 mL) were added to a Radley's tube under air. Catalyst (0.1 mol%), ketones (1.0 mmol) and alcohols (1.0 mmol) were added in that order and stirred at 130 °C for 2 h. The reaction mixture was cooled to room temperature and filtered. The conversion and selectivity were analyzed by ^{1}H-NMR spectroscopy.

General procedure for the Suzuki–Miyaura C–C coupling reaction

A Radley's tube was charged with aryl halide (1.0 mmol), phenylboronic acid (1.0 mmol), KOH (0.5 mmol) and catalyst (0.1 mol%) in a 2-propanol–H_2O mixture (2 mL, 0.5 : 1.5). The mixture was stirred at room temperature for 30 min under an air atmosphere. Ethyl acetate was added to the mixture and the organic phase was monitored by gas chromatography.

Theoretical calculations

All of the DFT calculations were performed with the Gaussian 09 package.[29] Geometry optimizations were carried out using the B3LYP functional with the LANL2DZ basis set[30] (effective core potentials (ECP) of the LANL2DZ basis set were employed for Pd and Br atoms).[31] Vibrational frequencies were computed analytically at the same level of theory to confirm whether the structures are minima (no imaginary frequencies) or transition states (only one imaginary frequency). All transition state structures were confirmed to connect the corresponding reactants and products by intrinsic reaction coordinate (IRC) calculations.[32] Solvation effects were taken into account by the PCM model.[33]

X-ray crystallography

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 1883006 for **1**, 1883005 for **2**, 1883008 for **3**, 1883007 for **4** and 1841200 for **6**.†

Conflicts of interest

There are no conflicts to declare.

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