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Fluoride-Free Hiyama and Copper- and Amine-Free Sonogashira Coupling in Air in a Mixed Aqueous Medium by a Series of PEPPSI[‡]-Themed Precatalysts

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Keywords: Carbenes / Palladium / Cross-coupling / Hiyama reaction / Sonogashira reaction

A new series of robust, user-friendly, and highly active PEPPSI-themed (pyridine-enhanced precatalyst preparation, stabilization and initiation) (NHC)PdX_2(pyridine)-type (X = Cl, Br) precatalysts of C4–C5 saturated imidazole- (**1**–**4**) and triazole-based (**5** and **6**) N-heterocyclic carbenes for the Hiyama and Sonogashira couplings under amenable conditions are reported. Specifically **1**–**6** efficiently catalyze the fluoride-free Hiyama coupling of aryl halides with $PhSi(OMe)_3$ and CH_2=$CHSi(OMe)_3$ in air in the presence of NaOH as a base in a mixed aqueous medium (dioxane/H_2O, 2:1 v/v). Along the same lines, these **1**–**6** precatalysts also promote the Cu-free and amine-free Sonogashira coupling of aryl bromides and iodides with phenylacetylene in air and in a mixed aqueous medium (DMF/H_2O, 3/1 v/v). The complexes **1**–**6** were synthesized by the direct reaction of the respective imidazolinium and triazolium halide salts with $PdCl_2$ in pyridine in the presence of K_2CO_3 as a base. DFT studies on the catalytically relevant palladium(0) (NHC)Pd(pyridine) precursors **1a**–**6a** reveal significant donation from the N-heterocyclic carbene lone pair onto the unfilled σ^* orbital of the *trans* Pd–pyridine bond. This weakens the Pd-bound "throw-away" pyridine ligand, and its dissociation marks the initiation of the catalytic cycle.

Introduction

Of late, the Hiyama[1] coupling is becoming increasingly popular for the construction of biaryl frameworks along the lines of the highly preferred Suzuki–Miyaura[2] reaction, involving organoboron reagents, and the Migita–Kosugi–Stille[3] reaction, employing organotin reagents, which are routinely used in the synthesis of biaryl targets. The recent success of the Hiyama coupling originates from the new found prospect of organosilicon compounds as organometallic nucleophiles in palladium-mediated cross-coupling reactions.[4] With regard to this it is worth noting that the organosilicon reagents, because of their low cost, easy availability, environmentally benign nature, reagent stability, functional group tolerance, and amenable reaction conditions, have aroused interest in recent times. Furthermore, as the Hiyama coupling significantly eliminates the purification difficulties associated with the use of organoboron reagents in the Suzuki–Miyaura reactions as well as the handling of the toxic byproducts associated with the organotin reagents in the Migita–Kosugi–Stille reactions, the Hiyama coupling thus holds greater promise than these two now-popular coupling reactions.

An important challenge of Hiyama coupling lies in enhancing the nucleophilicity of the organosilicon reagents, which are inherently inert nucleophiles and hence unreactive owing to the small electronegativity difference between Si and C.[4] However, in the presence of an anionic activator like the most commonly used F^- ion or others like, OH^- or OR^- ions, the nucleophilicity of the organosilicon reagent increases as a result of the coordination of the anion to Si thereby making the Si center pentacoordinate and anionic. An important objective therefore lies in developing fluoride-free activation of the organosilicon reagent owing to the environmental issues associated with fluorine. An ingenious method of activation that deserves special mention is that of the "strain release Lewis acidity" encountered in siletane, which provides the first successful alternative to fluorosilanes.[5] With regard to this our aim is in designing highly efficient and robust Pd precatalysts of N-heterocyclic carbenes for the fluoride-free Hiyama couplings under amenable conditions. It is worth noting that although phosphanes have been commonly used as catalysts for the Hiyama coupling,[4] the utility of the N-heterocyclic carbenes in this area remain largely unexplored.

[‡] Pyridine-Enhanced Precatalyst Preparation, Stabilization and Initiation

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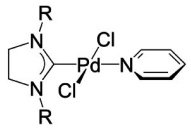
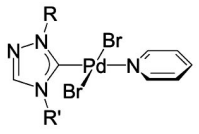
Besides the Hiyama coupling, our other interest is in Sonogashira coupling as it provides a much needed pathway for the construction of the "enyne" framework common in many bioactive molecules[6] as well as in materials related applications.[7] Despite its new-found popularity, the Sonogashira cross-coupling reactions suffer from many limitations like requiring stringent anaerobic conditions and it yields unwanted homocoupled side products alongside the desired cross-coupled products. Thus, a worthwhile objective in this area lies in achieving more amenable conditions for the coupling reaction. A careful scrutiny of the mechanistic pathway of the Sonogashira coupling reveals that the coupling reactions proceed via the formation of a Cu–acetylide species, which is extremely air and moisture sensitive, potentially explosive and yields unwanted homocoupled products in the presence of oxygen or under oxidizing conditions.[7] Hence, it is not surprising that the Cu-free Sonogashira coupling, which holds the possibility of making the reaction more tolerant towards the aerobic conditions, is becoming increasingly popular these days. However, many of the Cu-free Sonogashira couplings involve the use of amines that are not considered environmentally friendly.[7b] Thus, achieving Sonogashira coupling under both the amine-free and Cu-free conditions remains an extremely important objective today. In this context it is worth mentioning that we have recently reported a series of highly active Pd precatalysts supported over *N*/*O*-functionalized N-heterocyclic carbenes for the amine-free Sonogashira couplings of aryl iodides with terminal alkynes in air in a mixed aqueous solvent.[8] We also established that precatalysts with electron-rich metal centers are better for the cross-coupling reaction.

Our research revolves around exploring the utility of *N*/*O*-functionalized N-heterocyclic carbenes[9] in biomedical applications[10] as well as in chemical catalysis,[11] with special emphasis on developing robust, user-friendly, and highly efficient precatalysts for the Pd-mediated C–C cross-coupling reactions[8,12] and hence, here in this contribution, we report on the use of a series of new PEPPSI-themed (NHC)PdX$_2$(pyridine) (X = halide) complexes of the C4–C5 saturated imidazole- (**1**–**4**) and triazole-based (**5** and **6**) N-heterocyclic carbenes for the two highly important but relatively less explored C–C cross-coupling reactions namely the Hiyama and Sonogashira couplings (Figure 1).



R = 2,6-*i*Pr$_2$C$_6$H$_3$ (**1**)
R = 2,6-Et$_2$C$_6$H$_3$ (**2**)
R = 2,4,6-Me$_3$C$_6$H$_2$ (**3**)
R = 2,6-Me$_2$C$_6$H$_3$ (**4**)

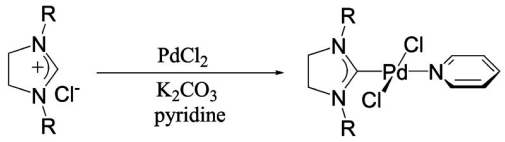


R = *i*Pr, R' = CH$_2$Ph (**5**)
R = CH$_2$CONH*t*Bu, R' = CH$_2$Ph (**6**)

Figure 1. PEPPSI–themed (NHC)PdX2(pyridine) (X = halide) complexes of the C4–C5 saturated imidazole- (**1**–**4**) and triazole-based (**5** and **6**) N-heterocyclic carbenes.

Results and Discussion

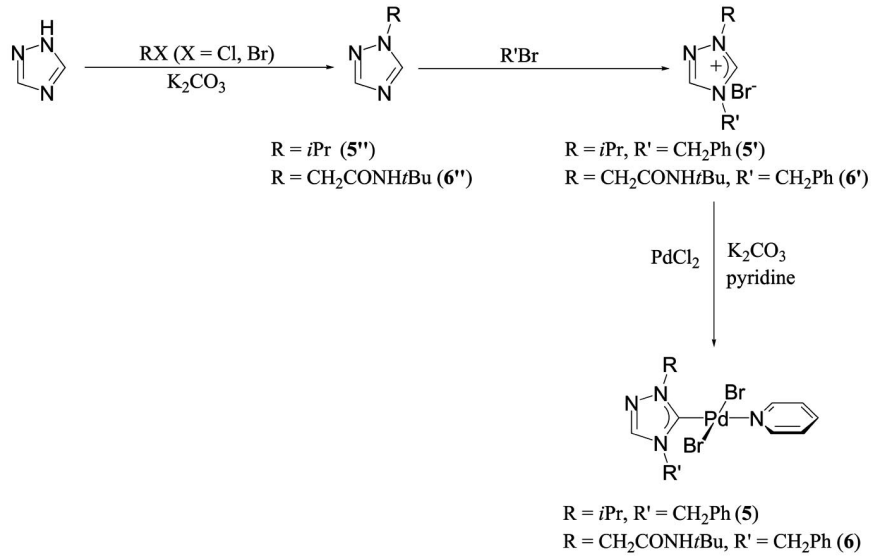
The complexes **1**–**4**, with a C4–C5 saturated imidazole ring (Scheme 1), and the complexes **5** and **6** (Scheme 2), with a triazole ring, were synthesized from the respective imidazolinium chloride and triazolium bromide salts by the reaction with $PdCl_2$ in pyridine in the presence of K_2CO_3 as a base. The formation of the metal complexes were evident from the distinctive metal-bound carbene (Pd–$C_{carbene}$) peak, which appeared at ca. 184.6–186.3 ppm for the C4–C5 saturated imidazole complexes **1**–**4** and at 153.6–159.0 ppm for the triazole complexes **5** and **6** in the ^{13}C NMR spectrum at a significantly downfield shifted resonance relative to that of the imidazolinium (160.0–161.3 ppm)[13–15] and triazolium (143.7–143.8 ppm) N*C*HN peaks of the starting 1igand precursors.



R = 2,6-*i*Pr$_2$C$_6$H$_3$ (**1**)
R = 2,6-Et$_2$C$_6$H$_3$ (**2**)
R = 2,4,6-Me$_3$C$_6$H$_2$ (**3**)
R = 2,6-Me$_2$C$_6$H$_3$ (**4**)

Scheme 1.

Of foremost importance to a PEPPSI-themed precatalyst like **1**–**6** is the loosely bound pyridine moiety that appears at a different region from that of the free pyridine in the ^{1}H NMR spectrum.[16] However, the definitive proof came from the X-ray diffraction study, which confirmed the presence of the metal-bound pyridine moiety in the **1**–**6** complexes (see Figures 2–3 and Figures S1–S4 in the Supporting Information). In particular, the Pd–$N_{pyridine}$ distance in **1** [2.106(6) Å], **2** [2.107(2) Å], **3** [2.0950(16) Å], **4** [2.096(3) Å], **5** [2.092(8) Å], and **6** [2.100(3) Å] was comparable to that of its related unsaturated analogues namely, the non-functionalized aryl-substituted *trans*-[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]PdCl$_2$(3-chloropyridine) [2.137(2) Å],[17b] or with the *N*/*O*-functionalized ones like, the *trans*-[1-benzyl-3-(*tert*-butylaminocarbonylmethyl)imidazol-2-ylidene]PdCl$_2$(pyridine) [2.089(3) Å],[12b] *trans*-[1-(2-hydroxycyclohexyl)-3-benzylimidazol-2-ylidene]PdCl$_2$(pyridine) [2.096(3) Å],[12b] and *trans*-[1-(*o*-methoxybenzyl)-3-(*tert*-butyl)imidazol-2-ylidene]PdBr$_2$(pyridine) [2.100(8) Å].[12b] It is worth noting that owing to the strong *trans* influence of the N-heterocyclic carbene (NHC) ligand, the Pd bound pyridine moiety is expected to be considerably weakly bonded. Hence, quite expectedly, the Pd–$N_{pyridine}$ distance [2.092(8)–2.107(2) Å] in the complexes **1**–**6** was found to be longer than that in the complexes without the NHC ligand e.g. 2.040(3) Å in [2,6-bis(2′-indolyl)pyridine]Pd(pyridine),[18] 2.037(3) Å in [bis(bis(2-pyridylmethyl)amine-*N*,*N*′,*N*′′)]Pd(pyridine)](ClO$_4^-$)$_2$,[19] and 2.038(4) Å in [(2,2′:6′,2′′-terpyridine)Pd(pyridine)](ClO$_4^-$)$_2$.[20] It is noteworthy that a weakly-bound pyridine moiety is a strategic



Scheme 2.

hallmark of a PEPPSI-themed precatalyst. The pyridine moiety is considered to be a "throwaway" ligand as it paves way for the incoming substrate.[17]

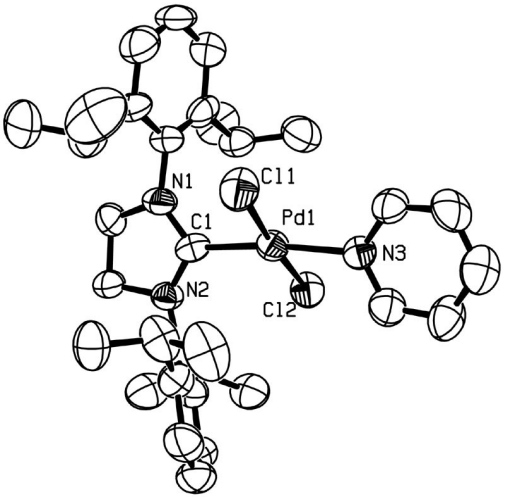


Figure 2. ORTEP drawing of **1** with thermal ellipsoids shown at the 50% probability level. Selected bond lengths [Å] and angles [°]: N(1)–C(1) 1.334(9), N(2)–C(1) 1.317(9), Pd(1)–C(1) 1.993(7), Pd(1)–Cl(1) 2.294(2), Pd(1)–N(3) 2.106(6), C(1)–Pd(1)–N(3) 174.2(3), C(1)–Pd(1)–Cl(1) 93.7(2).

In order to gain insight about the relative electronic influence of the C4–C5 saturated imidazole- and triazole-based N-heterocyclic carbene ligands on the metal center, detailed density functional theory (DFT) studies were carried out on the catalytically relevant palladium(0) (NHC)-Pd(pyridine)-type precursors **1a**–**6a**. Specifically, the geometry optimization followed by single-point calculations were performed on **1a**–**6a** at the B3LYP/SDD, 6-31G(d) level of theory after applying suitable modifications on the structures obtained from X-ray analysis. Further insight into the

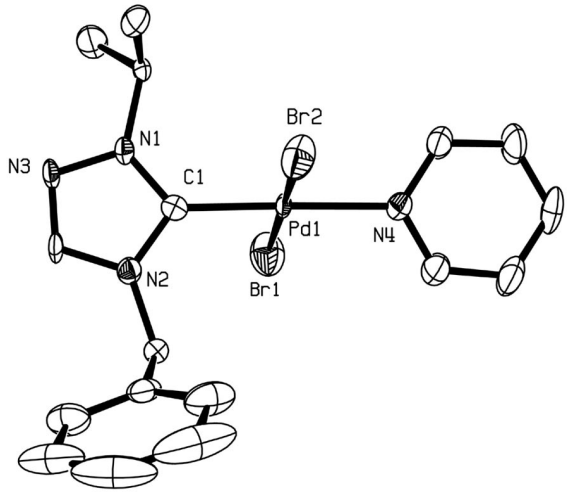


Figure 3. ORTEP drawing of **5** with thermal ellipsoids shown at the 50% probability level. Selected bond lengths [Å] and angles [°]: N(1)–C(1) 1.341(12), N(2)–C(1) 1.375(12), Pd(1)–C(1) 1.950(9), Pd(1)–Br(1) 2.3669(15), Pd(1)–N(4) 2.092(8), C(1)–Pd(1)–N(4) 178.6(3), C(1)–Pd(1)–Br(1) 88.5(3).

nature of the bonding in **1a**–**6a** was obtained from the post-wave function analysis using the natural bond orbital (NBO) method.[21]

It is quite interesting that both the C4–C5-saturated imidazole- and the triazole-based ligands were found to be of comparable electron-donating abilities as was evident from the natural and Mulliken charge analyses, which showed that the metal and carbene centers were of comparable electron densities in **1a**–**6a** (see Tables S8–S13, Supporting Information). In all of the cases, as a result of electron donation from the free NHC ligand fragment onto the metal center in the Pd–pyridine moiety, there was a de-

crease in electron density on the carbene carbon in **1a**–**6a** with respect to that in the free NHC ligand fragment along with a concomitant increase in the electron density on the metal center in **1a**–**6a** with respect to that in the Pd–pyridine fragment (see Tables S8–S13, Supporting Information). Furthermore, a comparison of the electronic configuration of the metal center in **1a**–**6a** relative to that of the Pd–pyridine fragment revealed that the electron donation from the carbene center of the free NHC ligand fragment occurred at the 5s orbital of palladium (see Tables S14–S15, Supporting Information). The natural bond order (NBO) analysis revealed that the NHC–Pd bond is composed of the interaction between a $C_{carbene}$ (sp^2) orbital with an sd hybrid Pd orbital (see Table S16, Supporting Information).

In order to further probe the nature of the Pd–carbene interaction in **1a**–**6a**, particularly with regard to the extent of the $NHC\xrightarrow{\sigma}Pd(NC_5H_5)$ forward donation, designated by *d*, and the $NHC\xleftarrow{\pi}Pd(NC_5H_5)$ backward donation, designated by *b*, occurring in these complexes, charge decomposition analyses[22] were performed. It is worth noting that both the C4–C5 saturated imidazole- (**1**–**4**) and the triazole-based (**5** and **6**) species were found to be predominantly $NHC\xrightarrow{\sigma}Pd(NC_5H_5)$ donating (*d*) with very little $NHC\xleftarrow{\pi}Pd(NC_5H_5)$ backward bonding (*b*) ability as was duly attested by a high *d*/*b* ratio (2.60–2.94) observed in these species (see Table S17, Supporting Information).

The NHC–Pd interaction was further probed by constructing a molecular orbital correlation diagram from the individual fragment molecular orbitals (FMOs) of the free NHC ligand fragment and the Pd–pyridine fragment in **1a**–**6a** using the *AOMix* software[23] (Figures 4–5 and Figures S5–S8, Supporting Information). In all the cases, the NHC–Pd σ-bonding molecular orbitals [**1a** (HOMO-11, HOMO-25), **2a** (HOMO-11, HOMO-21), **3a** (HOMO-11, HOMO-19), **4a** (HOMO-11, HOMO-19), **5a** (HOMO-9, HOMO-17), and **6a** (HOMO-11, HOMO-22)] were found to be deeply seated, thereby, implying the inert nature of the NHC–Pd σ bond. This also explains the fact that it is relatively less vulnerable towards electrophilic or nucleophilic attacks. It is worth noting that contrary to the inert nature of the NHC–Pd bond that arises from the low lying NHC–Pd σ-bonding molecular orbitals in **1a**–**6a**, the other metal–carbene bonds in carbene complexes like the Fischer and Schrock carbene complexes are generally much more reactive and are attacked by electrophiles and nucleophiles.[24]

Of foremost importance is the NHC–Pd σ-bonding molecular orbital [**1a** (HOMO-11), **2a** (HOMO-11), **3a** (HOMO-11), **4a** (HOMO-11), **5a** (HOMO-9), and **6a** (HOMO-11)], which showed an interaction of the carbene lone pair of the free NHC-ligand fragment with the σ*-antibonding orbital of the Pd–pyridine bond indicating a strong *trans* influence of the NHC moiety resulting in the weakening of the Pd–pyridine bond in **1a**–**6a**. A comparison of the extent of interaction between the carbene lone pair with the σ*-antibonding Pd–pyridine orbital in the C4–C5 saturated imidazole- **1a**–**4a** and the triazole-based **5a** and **6a** species, revealed that a slightly higher carbene lone pair donation to the σ*-antibonding Pd–pyridine orbital was observed for the C4–C5-saturated imidazole-based **1a**–**4a** systems (10%) as compared to the triazole-based **5a** and **6a** ones (7–8%), which suggests that the Pd–pyridine moiety is more weakly bound in **1a**–**4a** than in **5a** and **6a** (see Table S18). Indeed, the Pd–pyridine bond dissociation energy D_e (Pd–pyridine) computed at the B3LYP/SDD, 6-31G(d) level of theory

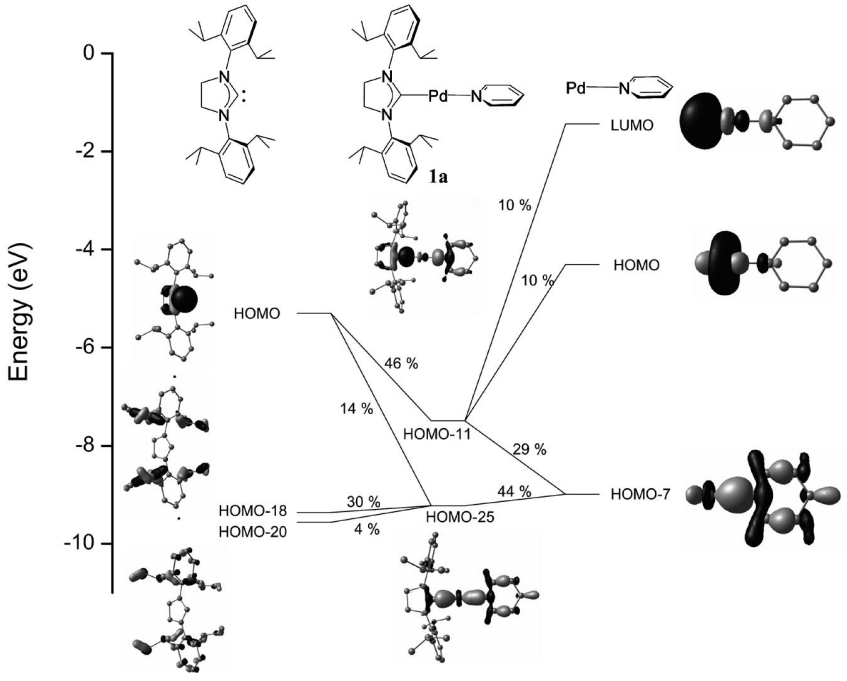


Figure 4. Orbital interaction diagram showing the major contributions of the NHC–palladium bond in **1a**.

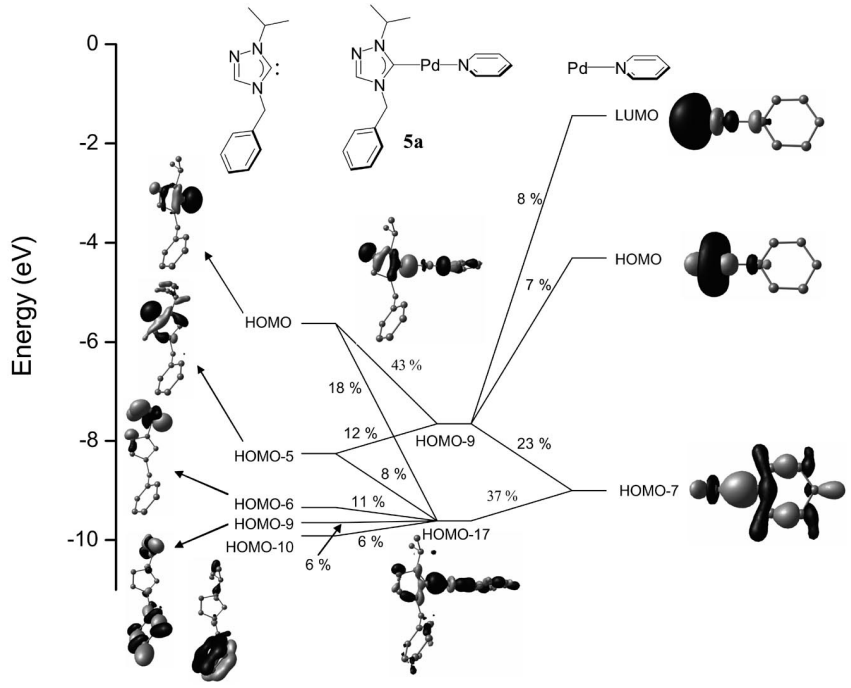
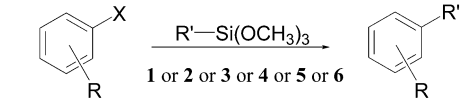


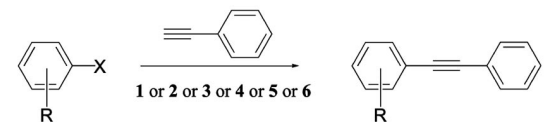
Figure 5. Orbital interaction diagram showing the major contributions of the NHC–palladium bond in **5a**.

showed a marginally weaker Pd–pyridine bond [27.0–27.5 kcal/mol] in **1a**–**4a** than in **5a** and **6a** [28.1–29.4 kcal/mol]. A similar trend was observed for the $C_{carbene}$–Pd bond dissociation energy D_e ($C_{carbene}$–Pd) with a slightly weaker $C_{carbene}$–Pd bond [55.3–56.1 kcal/mol] in **1a**–**4a** than in **5a** and **6a** [56.3–58.1 kcal/mol].

Quite significantly, the **1**–**6** complexes were found to be efficient precatalysts for two important but rather less explored cross-coupling reactions namely, the Hiyama coupling under the highly preferred fluoride-free conditions [Equation (1) and Table 1] and the Sonogashira coupling, also under much desired Cu-free and amine-free conditions [see Equation (2) and Table 2].



R = $COCH_3$, NO_2, OCH_3, CH_3
R' = Ph, vinyl
X = I, Br, Cl (1)



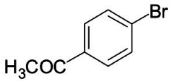
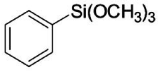
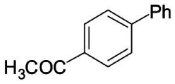
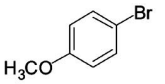
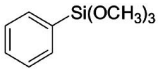
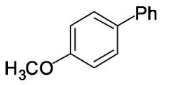
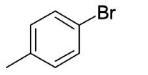
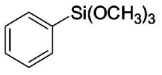
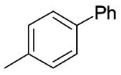
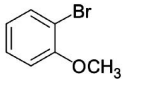
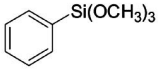
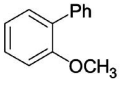
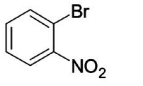
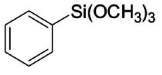
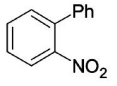
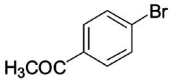
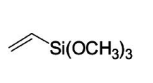
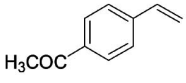
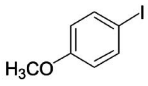
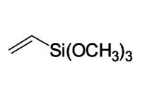
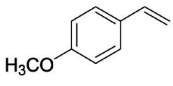
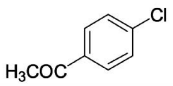
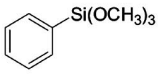
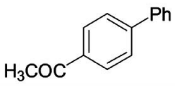
X = Br, I
R = CN, $COCH_3$, CHO, NO_2, H, CH_3, OCH_3 (2)

In particular, the fluoride-free Hiyama couplings of aryl halides with $PhSi(OMe)_3$ and CH_2=$CHSi(OMe)_3$ were carried out at 2 mol-% of the precatalysts **1**–**6** in air in the presence of NaOH as a base in a mixed aqueous medium (dioxane/H_2O, 2:1 v/v) in good to excellent yields at 80 °C (Table 1). A significant enhancement of the product yield of up to 91% for the C4–C5 saturated imidazole complexes **1**–**4** and of up to 84% for the triazole complexes **5** and **6** was observed relative to the control experiment performed with $PdCl_2$ under the same conditions (Table S19, Supporting Information). Thus, high efficiency and robustness form the key attributes of these PEPPSI-themed **1**–**6** precatalysts, performed in air in a mixed aqueous medium under fluoride-free Hiyama conditions.

A comparison of the performances of these **1**–**6** precatalysts with the other reported catalysts is important, particularly the N-heterocyclic-based ones for the Hiyama cross-coupling reactions. The utility of N-heterocyclic carbenes in Hiyama coupling still remains largely unexplored and we are aware of one other isolated report of the use of N-heterocyclic carbene where under "Ligand Assisted Catalysis (LAC)" conditions for Hiyama coupling, promoted by a fluoride coinitiator by Nolan and co-workers,[25] the couplings of aryl bromides and chlorides were attained at 3 mol-% of the precatalyst loading at 80 °C in 1–6 h. It is worth noting that in our case, apart from achieving the fluoride-free conditions, well-characterized precatalysts **1**–**6**, instead of the in situ generated ones under the "Ligand Assisted Catalysis (LAC)" conditions, were employed for Hiyama couplings in air and in a mixed aqueous medium.

There are only a handful of examples[26] of fluoride-free Hiyama couplings in which a OH^- anion was used as the coinitiator instead of a fluoride source, along the lines of the precatalysts **1**–**6**. With regard to this, it is worth noting that because of the small electronegativity difference between Si and C the organosilicon compounds are inherently

Table 1. Selected results of the Hiyama cross-coupling reaction of aryl halides (ArX, X = I, Br, Cl) catalyzed by **1**–**6**.

Entry	Reagent	Reagent	Product	Time (h)	Yield[a]					
					1	**2**	**3**	**4**	**5**	**6**
1[b]				4	>99	>99	>99	>99	>99	96
2[b]				4	>99	>99	>99	>99	>99	>99
3[b]				4	>99	80	>99	>99	>99	>99
4[b]				4	61	72	81	89	86	93
5[b]				16	74	94	>99	>99	62	53
6[c]				16	15	28	41	45	17	22
7[c]				7	41	29	27	22	32	26
8[b]				16	30	7	14	22	31	7

[a] The yields (%) were determined by GC using diethylene glycol dibutyl ether as an internal standard. [b] Reaction conditions: 1.00 mmol of aryl halides, 1.20 mmol of phenyltrimethoxysilane, 3.00 mmol of NaOH, 2 mol-% of catalyst **1**, **2**, **3**, **4**, **5**, or **6** and 6 mL of dioxane/H_2O (2:1), at 80 °C. [c] Reaction conditions: 0.50 mmol of aryl halides, 1.00 mmol of vinyltrimethoxysilane, 2.00 mmol of NaOH, 2 mol-% of catalyst **1**, **2**, **3**, **4**, **5**, or **6** and 6 mL of dioxane/H_2O (2:1), at 80 °C.

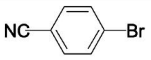
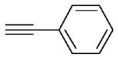
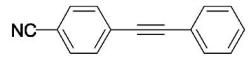
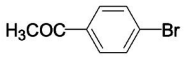
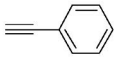
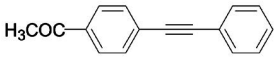
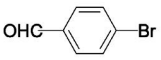
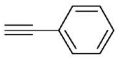
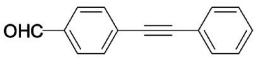
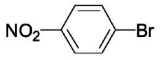
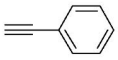
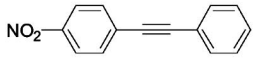
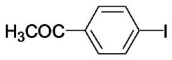
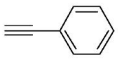
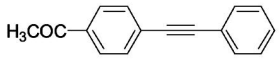
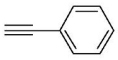
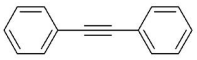
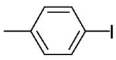
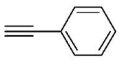
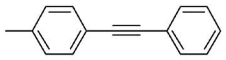
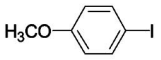
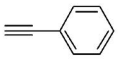
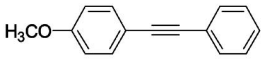
weak nucleophiles, which require activation from a fluoride ion or any other source of anion that significantly enhances the nucleophilicity of the organosilicon compounds by coordination to the Si center thereby making it pentacoordinate and anionic.[4]

Apart from the fluoride-free Hiyama coupling, these **1**–**6** precatalysts were equally efficient in carrying out the Sonogashira coupling under highly desirable Cu-free and amine-free conditions. Specifically, all of the complexes **1**–**6**, at 3 mol-% precatalyst loading, carried out the Cu-free and amine-free Sonogashira coupling of aryl bromides and aryl iodides with phenyl acetylene in the presence of Cs_2CO_3 as a base under amenable conditions in air and in a mixed aqueous medium at 90 °C in good to excellent yields (Table 2). The influence of the NHC ligand in **1**–**6** on catalysis is palpable after having performed a control experiment with $PdCl_2$ and shows up to 77% enhancement of the product yield for the C4–C5 saturated imidazole complexes **1**–**4** and up to 70% for the triazole complexes **5** and **6** (see Table S20, Supporting Information). Apart from the Cu-free and amine-free conditions the other most remarkable aspect of the catalysis is the extremely short reaction time of 1 h in which these cross-couplings occurred.

Being Cu-free the Sonogashira coupling by complexes **1**–**6** tolerates the aerobic environment unlike the much familiar Cu-assisted Sonogashira coupling that is air- and moisture-sensitive and often yields significant amounts of unwanted homocoupled products in the presence of an oxygen or oxidizing environment. Additionally, being amine-free by virtue of using Cs_2CO_3 as a base, the Sonogashira coupling by **1**–**6** is thus environmentally friendly.

Despite the Sonogashira coupling being relatively more explored than the Hiyama coupling, the examples of the utility of N-heterocyclic carbenes in the Sonogashira reaction are still few in number.[27] Though many of the reports are under "Ligand Assisted Catalysis (LAC)" conditions, we are aware of only three examples in which structurally characterized catalyst precursors have been used along the lines of the **1**–**6** precatalysts. For example, *trans*-[(3-pyrrolidinocarbamoyl-1-methylimidazolin-2-ylidene)(1-methylimidazole)]PdI_2[28] was used for aryl bromides and iodide substrates while [1,1′-dimethyl-3,3′-methylene-4-diimidazolin-2,2′-diylidene]PdI_2[29] was used under Cu-free conditions for the aryl bromide substrates. In this regard, we have recently reported highly efficient Pd-based precatalysts namely, *trans*-[1-benzyl-3-(3,3-dimethyl-2-oxobutyl)imidazol-2-ylidene]$_2PdBr_2$[8] and *cis*-[1-benzyl-3-(*tert*-butylaminocarbonylmethyl)imidazol-2-ylidene]$_2PdCl_2$[8] for the Sonogashira coupling under amine-free conditions for aryl iodide substrates. Hence, the complexes **1**–**6** represent the first examples of the use of well-defined N-heterocyclic carbene-based precatalysts for the Sonogashira coupling under both Cu-free and amine-free conditions.

Table 2. Selected results of the Sonogashira cross-coupling reaction of aryl halides (ArX, X = Br, I) catalyzed by **1**–**6**.[a]

Entry	Reagent	Reagent	Product	Yield[b] 1	2	3	4	5	6
1				>99	>99	88	>99	>99	78
2				69	90	96	97	54	63
3				63	>99	78	73	92	51
4				59	58	56	56	51	51
5				>99	>99	>99	>99	93	96
6				89	89	94	86	87	98
7				68	64	91	64	75	81
8				57	53	63	45	55	53

[a] Reaction conditions: 0.49 mmol of aryl halides (ArX, X = Br, I), 0.98 mmol of phenylacetylene, 2 mmol of Cs_2CO_3, 3 mol-% of catalyst **1**, **2**, **3**, **4**, **5**, or **6** and 10 mL of DMF/H_2O (3:1), at 90 °C for 1 h. [b] The yields (%) were determined by GC using diethylene glycol dibutyl ether as an internal standard.

Lastly, it is worth noting that consistent with the weakly bound nature of the pyridine moiety in these PEPPSI-themed **1**–**6** precatalysts as observed in the X-ray crystallographic and DFT studies, the formation of free pyridine was indeed confirmed by GC and GCMS analysis for a representative precatalyst **4** under both the Hiyama and the Sonogashira conditions.

Conclusion

In summary, a series of robust, user-friendly and highly active PEPPSI themed (NHC)PdX_2(pyridine)-type (X = halide) precatalysts of C4–C5 saturated imidazole- (**1**–**4**) and triazole-based (**5** and **6**) N-heterocyclic carbenes are reported for the fluoride-free Hiyama and Cu-free and amine-free Sonogashira couplings. These precatalysts carried out the cross-coupling reactions under amenable conditions in air in a mixed aqueous medium in good to excellent yields. The DFT studies showed that owing to the strong σ donation from the N-heterocyclic carbene ligand to the metal in the **1**–**6** precatalysts, the Pd-bound "throwaway" pyridine ligand is significantly weakened and its dissociation marks the initiation of the catalytic cycle.

Experimental Section

General Procedures: All manipulations were carried out using standard Schlenk techniques. Solvents were purified and degassed by standard procedures. 1,3-Bis(2,6-diisopropylphenyl)imidazolinium chloride,[13] 1,3-bis(2,6-diethylphenyl)imidazolinium chloride,[14] 1,3-bis(2,4,6-trimethylphenyl)imidazolinium chloride,[15] 1,3-bis-(2,6-dimethylphenyl)imidazolinium chloride,[15] and 1-isopropyl-1,2,4-triazole (**5′′**)[30] were synthesized according to literature procedures. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded in $CDCl_3$ with a Varian 400 MHz NMR spectrometer. ^1H NMR peaks are labeled as singlet (s), doublet (d), triplet (t), multiplet (m), and septet (sept). Infrared spectra were recorded with a Perkin–Elmer Spectrum One FT-IR spectrometer. Mass spectrometry measurements were performed with a Micromass Q-Tof spectrometer. GC spectra were obtained on a Schimadzu gas chromatograph GC-15A equipped with a FID. GC–MS spectra were obtained with a Hewlett Packard GCD-1800 A equipped with an EI source. Elemental Analysis was carried out with a Thermo Quest FLASH 1112 SERIES (CHNS) Elemental Analyzer. X-ray diffraction data for compounds **1**–**6** were collected with an Oxford Diffraction Excaliber-S diffractometer and crystal data collection and refinement parameters are summarized in Table S1 (see Supporting Information). The structures were solved by direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 6.10).[31]

CCDC-626236 (for **1**), CCDC-634320 (for **2**), CCDC-634319 (for **3**), CCDC-632564 (for **4**), CCDC-666361 (for **5**), and CCDC-668971 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of *trans*-[1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene]$PdCl_2(NC_5H_5)$ (1): A mixture of 1,3-bis(2,6-diisopropylphenyl)-imidazolinium chloride (0.574 g, 1.34 mmol), $PdCl_2$ (0.238 g,

1.34 mmol), and K_2CO_3 (0.927 g, 6.72 mmol) was heated at 90 °C in pyridine (ca. 4 mL) for 16 h. The solvent was then removed under vacuum, after which the residue was washed with aqueous $CuSO_4$ solution (2.01 g in ca. 30 mL of H_2O) and the organic component was extracted with ethyl acetate (ca. 3 × 10 mL). The organic layer was collected and solvent was removed under vacuum to obtain the product **1** as a yellow solid (0.588 g, 68%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 8.51 (d, $^3J_{HH}$ = 7 Hz, 2 H, *o*-NC_5H_5), 7.52 (t, $^3J_{HH}$ = 7 Hz, 1 H, *p*-NC_5H_5), 7.41 (t, $^3J_{HH}$ = 8 Hz, 2 H, *p*-C_6H_3), 7.30 (d, $^3J_{HH}$ = 8 Hz, 4 H, *m*-C_6H_3), 7.08 (t, $^3J_{HH}$ = 7 Hz, 2 H, *m*-NC_5H_5), 4.06 (s, 4 H, CH_2), 3.59 [sept, $^3J_{HH}$ = 7 Hz, 4 H, $CH(CH_3)_2$], 1.56 [d, $^3J_{HH}$ = 7 Hz, 12 H, $CH(CH_3)_2$], 1.26 [d, $^3J_{HH}$ = 7 Hz, 12 H, $CH(CH_3)_2$] ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): δ = 186.3 (NCN-Pd), 151.4 (*o*-NC_5H_5), 147.7 (*ipso*-C_6H_3), 137.4 (*p*-NC_5H_5), 135.6 (*o*-C_6H_3), 129.5 (*m*-C_6H_3), 124.6 (*p*-C_6H_3), 124.1 (*m*-NC_5H_5), 54.0 (NCH_2CH_2N), 28.9 [$CH(CH_3)_2$], 26.9 [$CH(CH_3)_2$], 24.4 [$CH(CH_3)_2$] ppm. IR data (KBr pellet): $\tilde{\nu}$ = 3173 (m), 2960 (s), 2925 (m), 2866 (m), 1634 (m), 1482 (s), 1451 (s), 1401 (s), 1385 (m), 1362 (w), 1328 (w), 1299 (m), 1273 (s), 1222 (w), 1076 (w), 1054 (w), 802 (m), 757 (m), 698 (m), 636 (w) cm^{-1}. $C_{32}H_{43}Cl_2N_3Pd$ (647.03): calcd. C 59.40, H 6.70, N 6.49; found C 60.05, H 7.25, N 6.19.

Synthesis of *trans*-[1,3-Bis(2,6-diethylphenyl)imidazolin-2-ylidene]-$PdCl_2(NC_5H_5)$ (2): A mixture of 1,3-bis(2,6-diethylphenyl)imidazolinium chloride (0.573 g, 1.54 mmol), $PdCl_2$ (0.272 g, 1.54 mmol), and K_2CO_3 (1.06 g, 7.71 mmol) was heated at 90 °C in pyridine (ca. 7 mL) for 14 hours. The solvent was then removed under vacuum, after which the residue was washed with aqueous $CuSO_4$ solution (2.01 g in ca. 30 mL of H_2O) and the organic component was extracted with ethyl acetate (ca. 3 × 10 mL). The organic layer was collected and solvent was removed under vacuum to obtain the product **2** as a yellow solid (0.509 g, 56%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 8.34 (d, $^3J_{HH}$ = 7 Hz, 2 H, *o*-NC_5H_5), 7.50 (t, $^3J_{HH}$ = 7 Hz, 1 H, *p*-NC_5H_5), 7.40 (t, $^3J_{HH}$ = 7 Hz, 2 H, *p*-C_6H_3), 7.29 (d, $^3J_{HH}$ = 7 Hz, 4 H, *m*-C_6H_3), 7.05 (t, $^3J_{HH}$ = 7 Hz, 2 H, *m*-NC_5H_5), 4.08 (s, 4 H, CH_2), 3.29–3.19 (m, 4 H, CH_2CH_3), 2.87–2.78 (m, 4 H, CH_2CH_3), 1.35 (t, $^3J_{HH}$ = 8 Hz, 12 H, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): δ = 185.4 (NCN-Pd), 151.4 (*o*-NC_5H_5), 143.1 (*ipso*-C_6H_3), 137.5 (*p*-NC_5H_5), 136.4 (*o*-C_6H_3), 129.3 (*m*-C_6H_3), 126.4 (*p*-C_6H_3), 124.1 (*m*-NC_5H_5), 52.4 (NCH_2CH_2N), 24.9 (CH_2CH_3), 15.1 (CH_2CH_3) ppm. IR data (KBr pellet): $\tilde{\nu}$ = 2962 (s), 2923 (s), 2874 (m), 1679 (w), 1490 (s), 1465 (s), 1306 (m), 1278 (s), 1043 (m), 867 (w), 803 (m), 779 (m), 755 (m), 689 (m), 637 (w), 552 (w) cm^{-1}. $C_{28}H_{35}Cl_2N_3Pd$ (590.92): calcd. C 56.91, H 5.97, N 7.11; found C 57.23, H 5.88, N 7.66.

Synthesis of *trans*-[1,3-Bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene]$PdCl_2(NC_5H_5)$ (3): A mixture of 1,3-bis(2,4,6-trimethylphenyl)-imidazolinium chloride (0.331 g, 0.996 mmol), $PdCl_2$ (0.171 g, 0.966 mmol), and K_2CO_3 (0.666 g, 4.83 mmol) was heated at 90 °C in pyridine (ca. 4 mL) for 16 h. The solvent was then removed under vacuum, after which the residue was washed with aqueous $CuSO_4$ solution (2.01 g in ca. 30 mL of H_2O) and the organic component was extracted with ethyl acetate (ca. 3 × 10 mL). The organic layer was collected and solvent was removed under vacuum to obtain the product **3** as a yellow solid (0.294 g, 52%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 8.43 (d, $^3J_{HH}$ = 7 Hz, 2 H, *o*-NC_5H_5), 7.52 (t, $^3J_{HH}$ = 7 Hz, 1 H, *p*-NC_5H_5), 7.08 (t, $^3J_{HH}$ = 7 Hz, 2 H, *m*-NC_5H_5), 7.02 (s, 4 H, *m*-C_6H_2), 4.03 (s, 4 H, CH_2), 2.58 (s, 12 H, *o*-CH_3), 2.33 (s, 6 H, *p*-CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): δ = 184.6 (NCN-Pd), 151.5 (*o*-NC_5H_5), 138.6 (*ipso*-C_6H_3), 137.5 (*p*-NC_5H_5), 137.4 (*o*-C_6H_3), 135.1 (*m*-C_6H_3), 129.7 (*p*-C_6H_3), 124.0 (*m*-NC_5H_5), 51.2 (NCH_2CH_2N), 21.3 (*p*-CH_3), 19.5 (*o*-CH_3) ppm. IR data (KBr pellet): $\tilde{\nu}$ = 2919 (s), 2863 (m), 1675 (m), 1605 (m), 1490 (s), 1450 (s), 1303 (m), 1268 (s), 1073 (m), 1034 (m), 856 (m), 801 (w), 757 (m), 693 (m), 639 (w), 576 (w) cm^{-1}. $C_{26}H_{31}Cl_2N_3Pd$ (562.87): calcd. C 55.48, H 5.55, N 7.47; found C 54.52, H 5.88, N 6.90.

Synthesis of *trans*-[1,3-Bis(2,6-dimethylphenyl)imidazolin-2-ylidene]-$PdCl_2(NC_5H_5)$ (4): A mixture of 1,3-bis(2,6-dimethylphenyl)imidazolinium chloride (0.202 g, 0.644 mmol), $PdCl_2$ (0.114 g, 0.644 mmol), and K_2CO_3 (0.444 g, 3.22 mmol) was heated at 85 °C in pyridine (ca. 4 mL) for 16 hours. The solvent was then removed under vacuum, after which the residue was washed with aqueous $CuSO_4$ solution (2.01 g in ca. 30 mL of H_2O) and the organic component was extracted with ethyl acetate (ca. 3 × 10 mL). The organic layer was collected and solvent was removed under vacuum to obtain the product **4** as a yellow solid (0.234 g, 68%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 8.36 (d, $^3J_{HH}$ = 7 Hz, 2 H, *o*-NC_5H_5), 7.51 (t, $^3J_{HH}$ = 7 Hz, 1 H, *p*-NC_5H_5), 7.27 (t, $^3J_{HH}$ = 7 Hz, 2 H, *p*-C_6H_3), 7.21 (d, $^3J_{HH}$ = 7 Hz, 4 H, *m*-C_6H_3), 7.05 (t, $^3J_{HH}$ = 7 Hz, 2 H, *m*-NC_5H_5), 4.06 (s, 4 H, CH_2), 2.63 (s, 12 H, *o*-CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): δ = 184.7 (NCN-Pd), 151.4 (*o*-NC_5H_5), 137.8 (*ipso*-C_6H_3), 137.6 (*p*-NC_5H_5), 137.5 (*o*-C_6H_3), 129.0 (*m*-C_6H_3), 128.9 (*p*-C_6H_3), 124.1 (*m*-NC_5H_5), 51.1 (NCH_2CH_2N), 19.6 (*o*-CH_3) ppm. IR data (KBr pellet): $\tilde{\nu}$ = 3126 (m), 3017 (w), 2958 (w), 2923 (w), 2854 (w), 1722 (w), 1634 (m), 1605 (m), 1496 (m), 1447 (m), 1400 (s), 1307 (w), 1277 (m), 1257 (w), 1218 (w), 1097 (w), 1072 (w), 1018 (w), 988 (w), 787 (w), 757 (w), 738 (w), 696 (w), 636 (w), 575 (w) cm^{-1}. $C_{24}H_{27}Cl_2N_3Pd$ (534.82): calcd. C 53.90, H 5.09, N 7.86; found C 53.10, H 4.43, N 7.73.

Synthesis of 4-Benzyl-1-isopropyl-1,2,4-triazolium Bromide (5′): A mixture of 1-isopropyl-1,2,4-triazole (3.27 g, 29.5 mmol), and benzyl bromide (5.04 g, 29.5 mmol) was heated at 70 °C for 2 h. The reaction mixture was washed in hot hexane (ca. 2 × 10 mL) and dried under vacuum to obtain the product **5′** as a white solid (5.91 g, 71%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 11.3 [s, 1 H, N-C(5)*H*-N], 8.98 [s, 1 H, N-C(3)*H*-N], 7.69 (d, $^3J_{HH}$ = 7 Hz, 2 H, *o*-C_6H_5), 7.38 (br., 3 H, *m* & *p*-C_6H_5), 5.85 (s, 2 H, CH_2), 4.92 [sept, $^3J_{HH}$ = 7 Hz, 1 H, $CH(CH_3)_2$], 1.62 [d, $^3J_{HH}$ = 7 Hz, 6 H, $CH(CH_3)_2$] ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): δ = 143.8 [N-*C*(5)H-N], 140.9 [N-*C*(3)H-N], 132.4 (*ipso*-C_6H_5), 129.4 (*o*-C_6H_5), 129.3 (*m*-C_6H_5), 129.2 (*p*-C_6H_5), 56.2 (CH_2), 51.3 [$CH(CH_3)_2$], 21.5 [$CH(CH_3)_2$] ppm. IR data (KBr pellet): $\tilde{\nu}$ = 3100 (m), 3036 (s), 2982 (s), 2805 (w), 1811 (w), 1637 (w), 1585 (m), 1515 (m), 1500 (m), 1457 (w), 1445 (m), 1425 (m), 1407 (s), 1390 (s), 1371 (w), 1356 (m), 1313 (w), 1296 (m), 1181 (m), 1154 (s), 1072 (w), 1037 (w), 998 (w), 939 (w), 912 (w), 791 (w), 719 (s), 696 (s), 617 (s), 590 (w), 506 (w), 458 (w) cm^{-1}. HRMS (ES): *m*/*z* = 202.1337 [(NHC) + H]$^+$, calcd. 202.1344.

Synthesis of *trans*-[4-Benzyl-1-isopropyl-1,2,4-triazol-5-ylidene]-$PdBr_2(NC_5H_5)$ (5): A mixture of 4-benzyl-1-isopropyl-1,2,4-triazolium bromide (0.161 g, 0.571 mmol), $PdCl_2$ (0.101 g, 0.571 mmol), and K_2CO_3 (0.393 g, 2.85 mmol) was heated at 90 °C in pyridine (ca. 4 mL) for 14 h. The solvent was then removed under vacuum, after which the residue was washed with aqueous $CuSO_4$ solution (2.01 g in ca. 30 mL of H_2O) and the organic component was extracted with ethyl acetate (ca. 3 × 10 mL). The organic layer was collected and solvent was removed under vacuum to obtain the product **5** as a yellow solid (0.132 g, 48%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 8.96 (d, $^3J_{HH}$ = 7 Hz, 2 H, *o*-NC_5H_5), 7.71 (t, $^3J_{HH}$ = 7 Hz, 1 H, *p*-NC_5H_5), 7.64 [s, 1 H, N-C(3)*H*-N], 7.45 (d, $^3J_{HH}$ = 7 Hz, 2 H, *o*-C_6H_5), 7.35 (m, 3 H, *m*-C_6H_5, *p*-C_6H_5), 7.29 (t, $^3J_{HH}$ = 7 Hz, 2 H, *m*-NC_5H_5), 5.68 [br., 3 H, CH_2, $CH(CH_3)_2$],

1.54 [d, $^3J_{HH}$ = 7 Hz, 6 H, CH(CH_3)$_2$] ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C): δ = 153.6 (N*C*N-Pd), 152.9 (*o*-NC_5H_5), 142.4 [N-*C*(3)H-N], 138.2 (*p*-NC_5H_5), 133.8 (*ipso*-C_6H_5), 129.6 (*o*-C_6H_5), 129.4 (*m*-C_6H_5), 129.3 (*p*-C_6H_5), 124.8 (*m*-NC_5H_5), 55.7 (*C*H$_2$), 53.3 [*C*H(CH$_3$)$_2$], 22.0 [CH(*C*H$_3$)$_2$] ppm. IR data (KBr pellet): $\tilde{\nu}$ = 3136 (w), 2981 (m), 1604 (w), 1540 (m), 1450 (s), 1367 (m), 1254 (m), 1226 (m), 1166 (m), 1050 (m), 860 (m), 803 (m), 758 (m), 718 (s), 692 (s) cm^{-1}. $C_{17}H_{20}Br_2N_4Pd$ (546.60): calcd. C 37.36, H 3.69, N 10.25; found C 37.85, H 3.52, N 10.38.

Synthesis of 1-(*tert*-Butylaminocarbonylmethyl)-1,2,4-triazole (6′′): A mixture of triazole (4.52 g, 65.5 mmol), *N*-*tert*-butyl-2-chloroacetamide (9.82 g, 65.5 mmol), and K_2CO_3 (10.8 g, 78.6 mmol) in CH_3CN (ca. 50 mL) was refluxed for 14 h. The reaction mixture was then filtered and the filtrate was removed under vacuum to obtain a residue, which was dissolved in chloroform (ca. 30 mL) and washed with H_2O (50 mL). The organic layer was collected and dried under vacuum to give the product **6′′** as a brown viscous liquid (5.36 g, 45%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 8.09 [s, 1 H, N-C(5)*H*-N], 7.91 [s, 1 H, N-C(3)*H*-N], 6.21 (br., 1 H, N*H*), 4.66 (s, 2 H, CH_2), 1.26 [s, 9 H, C(CH_3)$_3$] ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C): δ = 164.4 (*C*O), 150.6 [N-*C*(5)H-N], 144.3 [N-*C*(3)H-N], 51.5 (*C*H$_2$), 50.8 [*C*(CH$_3$)$_3$], 27.6 [C(*C*H$_3$)$_3$] ppm. IR data (nujol): $\tilde{\nu}$ = 1679 (s) (ν_{CO}) cm^{-1}. HRMS (ES): *m*/*z* = 183.1245 [M + 1]$^+$, calcd. 183.1246.

Synthesis of 4-Benzyl-1-(*tert*-butylaminocarbonylmethyl)-1,2,4-triazolium Bromide (6′): A mixture of 1-(*tert*-butylaminocarbonylmethyl)-1,2,4-triazole (3.82 g, 21.0 mmol) and benzyl bromide (3.59 g, 21.0 mmol) in CH_2Cl_2 (ca. 10 mL) was refluxed for 6 h, after which a precipitate separated out. The precipitate was washed with hot petroleum ether (ca. 2 × 10 mL) and dried under vacuum to obtain the product **6′** as an off white solid (5.46 g, 74%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 10.6 [s, 1 H, N-C(5)*H*-N], 8.68 [s, 1 H, N-C(3)*H*-N], 7.94 (br., 1 H, N*H*), 7.53 (d, $^3J_{HH}$ = 7 Hz, 2 H, *o*-C_6H_5), 7.45–7.43 (m, 3 H, *m*-C_6H_5, *p*-C_6H_5), 5.67 (s, 2 H, CH_2Ph), 5.48 (s, 2 H, CH_2), 1.37 [s, 9 H, C(CH_3)$_3$] ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C): δ = 162.6 (*C*O), 143.7 [N-*C*(5)H-N], 143.5 [N-*C*(3)H-N], 131.7 (*ipso*-C_6H_5), 130.1 (*o*-C_6H_5), 129.8 (*m*-C_6H_5), 129.5 (*p*-C_6H_5), 55.4 (*C*H$_2$Ph), 52.6 (*C*H$_2$), 52.4 [*C*(CH$_3$)$_3$], 28.8 [C(*C*H$_3$)$_3$] ppm. IR data (KBr pellet): $\tilde{\nu}$ = 1674 (s) (ν_{CO}) cm^{-1}. HRMS (ES): *m*/*z* = 273.1711 [(NHC) + H]$^+$, calcd. 273.1715.

Synthesis of *trans*-4-Benzyl-[1-(*tert*-butylaminocarbonylmethyl)-1,2,4-triazol-5-ylidene]PdBr$_2$(NC$_5$H$_5$) (6): A mixture of 4-benzyl-1-(*tert*-butylaminocarbonylmethyl)-1,2,4-triazolium bromide (0.467 g, 1.32 mmol), $PdCl_2$ (0.234 g, 1.32 mmol), and K_2CO_3 (0.912 g, 6.61 mmol) was heated at 90 °C in pyridine (ca. 4 mL) for 14 h. The solvent was then removed under vacuum, after which the residue was washed with aqueous $CuSO_4$ solution (4.01 g in ca. 30 mL of H_2O) and the organic component was extracted with ethyl acetate (ca. 3 × 10 mL). The organic layer was collected and the solvent removed under vacuum to obtain the product **6** as a yellow solid (0.521 g, 64%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 8.98 (d, $^3J_{HH}$ = 7 Hz, 2 H, *o*-NC_5H_5), 7.82 [m, 2 H, *p*-NC_5H_5 and N-C(3)*H*-N], 7.53 (d, $^3J_{HH}$ = 8 Hz, 2 H, *o*-C_6H_5), 7.47–7.44 (m, 3 H, *m*-C_6H_5, *p*-C_6H_5), 7.39 (t, $^3J_{HH}$ = 7 Hz, 2 H, *m*-NC_5H_5), 6.13 (br., 1 H, N*H*), 5.80 (s, 2 H, CH_2Ph), 5.34 (s, 2 H, CH_2), 1.36 [s, 9 H, C(CH_3)$_3$] ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C): δ = 164.5 (*C*O), 159.0 (N*C*N-Pd), 152.8 (*o*-NC_5H_5), 143.5 [N-*C*(3)H-N], 138.4 (*p*-NC_5H_5), 133.2 (*ipso*-C_6H_5), 129.6 (*o*-C_6H_5), 129.5 (*m*-C_6H_5), 129.4 (*p*-C_6H_5), 124.9 (*m*-NC_5H_5), 57.2 (*C*H$_2$Ph), 53.5 (*C*H$_2$), 52.3 [*C*(CH$_3$)$_3$], 28.7 [C(*C*H$_3$)$_3$] ppm. IR data (KBr pellet): $\tilde{\nu}$ = 1688 (s) (ν_{CO}) cm^{-1}. $C_{20}H_{25}Br_2N_5OPd{\cdot}0.5NC_5H_5$ (657.23): calcd. C 41.12, H 4.22, N 11.72; found C 40.93, H 3.98, N 11.88.

Computational Methods: The density functional theory calculations were performed on the palladium (0) (NHC)Pd(pyridine)-type species, **1a**–**6a**, using the GAUSSIAN 03[32] suite of quantum chemical programs. The Becke three parameter exchange functional in conjunction with the Lee–Yang–Parr correlation functional (B3LYP) has been employed in this study.[33,34] The Stuttgart-Dresden effective core potential (ECP), representing 19 core electrons, along with valence basis sets (SDD) is used for palladium.[35] All other atoms are treated with the 6-31G(d) basis set.[36] All stationary points are characterized as minima by evaluating Hessian indices on the respective potential energy surfaces. Tight SCF convergence (10^{-8} a.u.) was used for all calculations. Natural bond orbital (NBO) analysis was performed using the NBO 3.1 program implemented in the GAUSSIAN 03 package.

Inspection of the metal–ligand donor–acceptor interactions was carried out using the charge decomposition analysis (CDA).[22] CDA is a valuable tool in analyzing the interactions between molecular fragments on a quantitative basis, with an emphasis on the electron donation.[37] The orbital contributions in the geometry optimized palladium(0) (NHC)Pd(pyridine)-type species **1a**–**6a** can be divided into three parts:

(i) σ-donation from the [NHC→Pd(pyridine)] fragment,

(ii) π-back donation from the [NHC←Pd(pyridine)] fragment, and

(iii) repulsive polarization (r).

The CDA calculations were performed using the program *AOMix*,[23] using the B3LYP/SDD, 6-31G(d) wave function. Molecular orbital (MO) compositions and the overlap populations were calculated using the *AOMix* Program. The analysis of the MO compositions in terms of occupied and unoccupied fragment orbitals (OFOs and UFOs, respectively), the construction of orbital interaction diagrams, and the charge decomposition analysis (CDA) was performed using the *AOMix-CDA*.[38]

General Procedure for the Hiyama Coupling Reaction

Coupling with Phenyltrimethoxysilane: In a typical run, performed in air, a 25 mL vial was charged with a mixture of aryl halides, PhSi(OMe)$_3$, NaOH, and diethylene glycol dibutyl ether (internal standard) in a molar ratio of 1:1.2:3:1. Complex **1**, **2**, **3**, **4**, **5**, or **6** (2 mol-%) was then added to the mixture (Table 1). Finally, a mixed solvent (dioxane/H_2O, 2:1 v/v, 6 mL) was added to the reaction mixture and heated at 80 °C for an appropriate period of time, after which it was filtered and the product was analyzed by gas chromatography using diethylene glycol dibutyl ether as an internal standard.

Coupling with Vinyltrimethoxysilane: In a typical run, performed in air, a 25 mL vial was charged with a mixture of aryl halides, CH_2=CHSi(OMe)$_3$, NaOH, and diethylene glycol dibutyl ether (internal standard) in a molar ratio of 1:2:4:1. Complex **1**, **2**, **3**, **4**, **5**, or **6** (2 mol-%) was added to the mixture (Table 1). Finally, a mixed solvent (dioxane/H_2O, 2:1 v/v, 6 mL) was added to the reaction mixture and heated at 80 °C for an appropriate period of time, after which it was filtered and the product was analyzed by gas chromatography using diethylene glycol dibutyl ether as an internal standard.

General Procedure for the Sonogashira Coupling Reaction: In a typical run, performed in air, a 25 mL vial was charged with a mixture of aryl halides, arylalkyne, Cs_2CO_3, and diethylene glycol dibutyl ether (internal standard) in a molar ratio of 1:2:4:1. Complexes **1**, **2**, **3**, **4**, **5**, or **6** (3 mol-%) was added to the mixture (Table 2). Finally, a mixed solvent (DMF/H_2O, 3:1 v/v, 10 mL) was added to the reaction mixture and heated at 90 °C for 1 h, after which it was

filtered and the product was analyzed by gas chromatography using diethylene glycol dibutyl ether as an internal standard.

Pyridine Dissociation under Hiyama Conditions: $PhSi(OMe)_3$ (0.714 g, 3.60 mmol), NaOH (0.361 g, 9.00 mmol), diethylene glycol dibutyl ether (internal standard) (0.015 g, 0.071 mmol), and a representative catalyst, complex **4** (0.037 g, 0.071 mmol) in CH_3CN (6 mL), were placed in a 25 mL vial. The reaction mixture was heated at 70 °C for 4 h, after which it was filtered and the reaction mixture was analyzed by GC and GCMS, which showed the formation of 45% pyridine under the reaction conditions.

Pyridine Dissociation under Sonogashira Conditions: Phenylacetylene (0.300 g, 0.294 mmol), Cs_2CO_3 (1.30 g, 4.00 mmol), diethylene glycol dibutyl ether (internal standard) (0.016 g, 0.073 mmol), and a representative catalyst, complex **4** (0.039 g, 0.073 mmol) in CH_3CN (6 mL), were placed in a 25 mL vial. The reaction mixture was heated at 70 °C for 1 h, after which it was filtered and the reaction mixture was analyzed by GC and GCMS, which showed the formation of 29% pyridine under the reaction conditions.

Supporting Information (see also the footnote on the first page of this article): CIF file giving crystallographic data for **1**–**6**, control experiment tables, X-ray metrical data comparison table, Ortep plots of **2**, **3**, **4**, and **6**, the B3LYP coordinates of the optimized geometries for **1a**–**6a**, NBO tables, CDA table and orbital interaction diagrams of **2a**, **3a**, **4a** and **6a**.

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