Palladium(II) and Gold(I) Complexes of a New O-Functionalized N-Heterocyclic Carbene Ligand: Synthesis, Structures, and Catalytic Application

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Synthetic and structural studies of Pd(II) and Au(I) complexes of a new O-functionalized N-heterocyclic carbene ligand, namely, 1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene, are reported. Specifically, the N-heterocyclic carbene precursor 1-(*o*-methoxybenzyl)-3-*tert*-butylimidazolium bromide (**1a**) was synthesized by the reaction of 2-methoxybenzyl bromide and *tert*-butylimidazole in 44% yield. The Au(I) and Pd(II) complexes [1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene]AuCl (**1c**) and [1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene]$_2$PdCl$_2$ (**1d**) were prepared in 77% and 89% yields, respectively, by the commonly used silver carbene transfer route from the silver complex {[1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene]$_2$Ag}$^+$Br$^-$ (**1b**). The silver complex **1b** was in turn synthesized from the reaction of **1a** with Ag_2O. The molecular structures of the complexes **1c** and **1d** have been determined by X-ray diffraction studies, which revealed that the gold complex **1c** possessed a linear geometry while the palladium complex **1d** had a trans-square-planar geometry at their respective metal centers. The Pd(II) complex **1d** was found to be an efficient catalyst for Suzuki−Miyaura type cross-coupling reactions of phenylboronic acid and aryl halides (ArX, X = Br, I) in high yields and turnover numbers (up to 109 600).

Introduction

Being central to many important cross-coupling reactions such as Hiyama,[1] Kumada,[2] Negishi,[3,4] Suzuki,[5] and Stille[6−8] reactions, Pd has revolutionalized transition-metal-mediated C−C bond forming reactions in a big way over the last three decades and is now duly recognized for its catalytic utility in synthetic organic chemistry. Its versatility, ease of use, and efficiency are key factors that have brought such unprecedented success in metal-mediated cross-coupling reactions.[9] Though the frequently used Pd precatalysts are still the phosphine-based ones such as [Pd(PPh$_3$)$_4$],[10] a growing number of reports of N-heterocyclic carbene based analogues have been emerging lately.[11−14] Despite significant advancements reported for phosphine-based systems,[15,16] there remains a need for more user-friendly precatalysts, as the phosphine-based species are expensive, sensitive to air, and difficult to handle and thus are of limited availability.[9] N-heterocyclic carbenes (NHCs) provide a viable alternative, as they are better σ-donors and yield precatalysts that are more stable to air, moisture, and heat and are more tolerant toward oxidizing conditions than their

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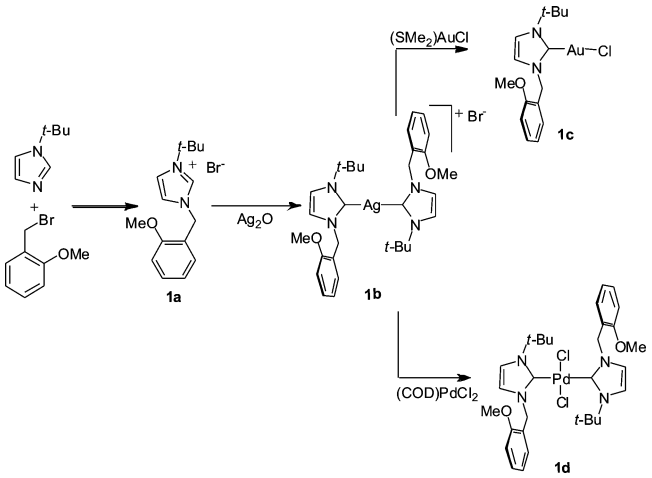
Scheme 1



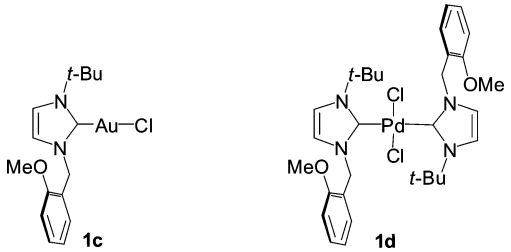


Figure 1.

phosphine counterparts. More importantly, the phosphines, apart from being expensive, are also required in excess quantities, as they often exhibit leaching of bare metals from the soluble precatalysts and also show considerable P−C bond cleavage at elevated temperatures.[14a,17] The N-heterocyclic carbenes, however, do not suffer from such shortcomings and thus are not needed in excess during catalysis. Significant improvements have been reported on the ancillary ligand design front, both for the in situ generation of catalysts[17,18] as well as for the well-defined catalysts.[12−14] As the ligand-assisted catalysis (LAC) involving in situ generation of catalysts suffers from many limitations such as uncertainty in stoichiometry and composition of the active species, difficulty in controlling the catalysis rate and catalyst efficiency, and unnecessary waste of precious Pd and NHC precursors and poses difficulties in the mechanistic understanding of the results, we became interested in designing well-defined precatalysts for our study. Furthermore, well-defined catalysts display shorter reaction times[19] and also reduce unwanted side reactions.[14a]

The Suzuki−Miyaura reaction offers a powerful and general methodology for the construction of C−C bonds and is perhaps the most widely used transition-metal-mediated cross-coupling reaction today.[20] The popularity of the Suzuki−Miyaura reaction is due to the ready availability of reactants that are nontoxic and air- and water-stable, its simplicity of use, ease of waste disposal, and, more importantly, its extreme versatility and high regio- and stereoselectivity.[21] It is worth noting that recently several highly active Pd precatalysts supported over N-heterocylic carbenes have been reported by Herrmann[13] and Organ.[19]

The central theme of one of our core program revolves around designing N-heterocylic carbene based complexes of late transition metals for their utility in chemical catalysis. In this regard, we have recently reported several Ag−NHC compounds[22] and the first example of a Au−NHC-based initiator[23] for the bulk ring-opening polymerization of L-lactide. Our motivation in this program is derived from the exceptional success exhibited by N-heterocyclic carbenes in the realm of chemical catalysis, as they have found applications in a wide gamut of important transformations such as olefin metathesis,[24] hydrogenation,[25] hydroformylation,[26] hydrosilylation,[27] hydroboration,[28] carbene-transfer reactions,[29] etc. in addition to the C−C bond forming reactions[12−14] discussed earlier. As the role played by N-heterocyclic carbenes has thus far been very promising in the development of Pd-based precatalysts for cross-coupling reactions,[9] we set out to explore the utility of other new Pd−NHC complexes in the coupling reactions. Specifically, we decided to synthesize Pd complexes supported over new functionalized N-heterocyclic carbenes in order to study their catalytic potential in C−C bond forming reactions.

In this contribution, we report the Pd−NHC complex [1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene]$_2$PdCl$_2$ (**1d**), which displays high activity toward Suzuki−Miyaura type cross-coupling reactions of phenylboronic acid and aryl halides (ArX,

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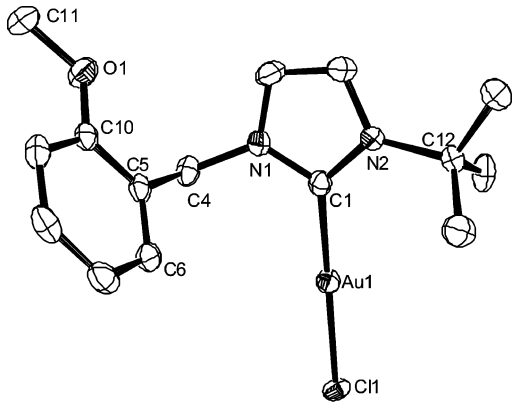


Figure 2. ORTEP drawing of **1c** with thermal ellipsoids shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): N(1)−C(1) = 1.347(5), N(2)−C(1) = 1.347(5), Au(1)−C(1) = 1.979(4), Au(1)−Cl(1) = 2.2872(10); C(1)−Au(1)−Cl(1) = 179.74(11).

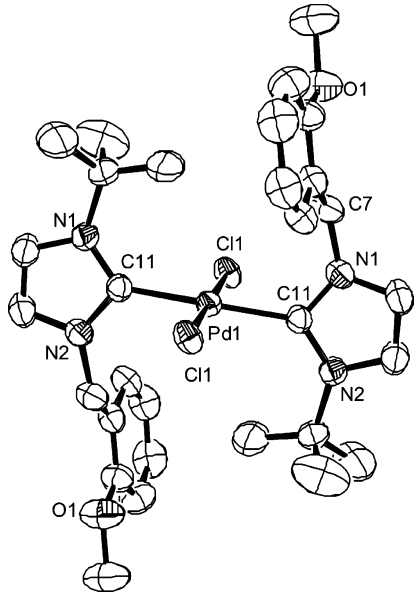


Figure 3. ORTEP drawing of **1d** with thermal ellipsoids shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): N(1)−C(11) = 1.356(7), N(2)−C(11) = 1.364(7), Pd(1)−C(11) = 2.036(5), Pd(1)−Cl(1) = 2.3531(12); Cl(1)−Pd(1)−C(11) = 91.61(15), C(11)−Pd(1)−C(11) = 180.0(4).

X = Br, I). We also report the syntheses and structural characterizations of the Au−NHC complex [1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene]AuCl (**1c**) and the Pd−NHC complex **1d**, supported over a new O-functionalized N-heterocyclic carbene ligand: namely, 1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene.

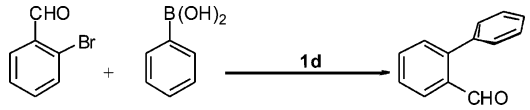
Results and Discussion

A new neutral O-functionalized N-heterocyclic carbene ligand, namely, 1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene, having a methoxy-functionalized sidearm, was designed with the intent of stabilizing metal complexes with enhanced catalytic attributes. In this regard it is noteworthy that a similar anionic aryloxy O-functionalized N-heterocyclic carbene analogue, 1-(3,5-di-*tert*-butyl-2-hydroxybenzyl)-3-R-imidazol-2-ylidene (R = *i*-Pr, benzyl),[30] has been recently reported, and its Fe complex[31] showed activity toward the ring-opening polymerization of ϵ-caprolactone. Also worth mentioning is that another class of analogous anionic aryloxy O-functionalized N-heterocyclic carbene ligands, namely, 1-(3-(adamantan-1-yl)-2-hydroxy-5-methylphenyl)-3-(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene and its variants, has been reported by Grubbs[32] and these displayed a novel type of ring-opening reaction of N-heterocyclic carbenes.[33] Specifically, the new O-functionalized imidazolium bromide salt 1-(*o*-methoxybenzyl)-3-*tert*-butylimidazolium bromide (**1a**) was prepared by the direct alkylation of *tert*-butylimidazole with 2-methoxybenzyl

Table 1. X-ray Crystallographic Data for 1c and 1d

	1c	**1d**
lattice	monoclinic	monoclinic
formula	$C_{15}H_{20}AuClN_2O$	$C_{15}H_{20}ClN_2OPd_{0.50}$
formula wt	476.75	332.98
space group	*I*2/*a*	$P2_1/c$
a (Å)	16.5313(19)	8.740
b (Å)	11.2567(18)	12.687
c (Å)	17.275(7)	14.204
α (deg)	90.00	90.00
β (deg)	99.65(2)	104.17
γ (deg)	90.00	90.00
V (Å^3)	3169.1(15)	1527.1
Z	8	4
temp (K)	150(2)	293(2)
radiation (λ, Å)	0.710 73	0.709 30
ρ(calcd) (g cm^{-3})	1.998	1.448
μ(Mo Kα) (mm^{-1})	9.450	0.816
θ_{max} (deg)	24.99	11.4200−13.5600
no. of data	2804	2694
no. of params	185	178
R1	0.0199	0.0492
wR2	0.0429	0.1337
GOF	1.084	1.066

Table 2. Selected Results of Suzuki Coupling of *o*-Bromobenzaldehyde with Phenylboronic Acid Catalyzed by 1d[a]



entry	amt of **1d** (mmol)	amt of **1d** (mol %)	time (h)	tield[b] (%)	TON
1	7.5×10^{-3}	3.5×10^{-1}	12	>99	288
2	1.9×10^{-3}	8.6×10^{-2}	12	>99	1110
3	7.5×10^{-4}	3.5×10^{-2}	12	>99	2880
4	3.7×10^{-4}	1.7×10^{-2}	12	>99	6000
5	1.8×10^{-4}	8.6×10^{-3}	12	>99	11700
6	4.3×10^{-5}	2.0×10^{-3}	12	>99	50600
7	2.0×10^{-5}	9.2×10^{-4}	12	45	49700
8	2.0×10^{-5}	9.2×10^{-4}	24	>99	109600

[a] Reaction conditions: 2.16 mmol of aryl halide, 2.64 mmol of phenylboronic acid, 3.24 mmol of K_2CO_3, complex **1d**, 30 mL of CH_3CN, 85 °C. [b] Determined by GC using diethylene glycol di-*n*-butyl ether as an internal standard.

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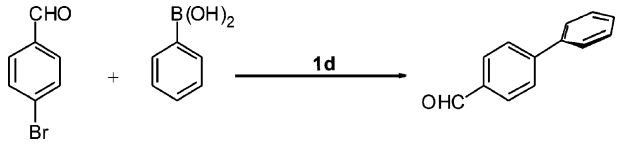
bromide in 44% yield (Scheme 1). The ^{1}H NMR spectrum of **1a** showed the diagnostic, highly downfield shifted imidazolium (NC*H*N) resonance at 10.6 ppm. The bridging methylene (CH_2) moiety appeared as a singlet at 5.64 ppm in the ^{1}H NMR spectrum and at 58.4 ppm in the ^{13}C NMR spectrum. In the electrospray mass spectrum the 1-(*o*-methoxybenzyl)-3-*tert*-butylimidazolium cation appeared as a *m*/*z* 245 peak in 100% abundance.

The treatment of the imidazoilum bromide salt **1a** with Ag_2O yielded the silver complex **1b** by the procedure reported by Lin.[34] Consistent with the formation of **1b**, the ^{1}H NMR spectrum showed the absence of an imidazolium (NC*H*N) resonance at 10.6 ppm owing to the loss of the acidic imidazolium proton of **1a** as result of the reaction with Ag_2O along with the appearance of a diagnostic silver-bound carbene (NC*N*−Ag) peak at 178.3 ppm in the ^{13}C NMR spectrum of **1b**. The HRMS data of **1b** gave a peak at *m*/*z* 595.2177 corresponding to the cationic fragment {[1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene]$_2$Ag}$^+$ (calculated *m*/*z* 595.2202).

The treatment of the silver complex **1b** with (SMe_2)AuCl yielded the gold complex [1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene]AuCl (**1c**; Figure 1) in 77% yield along with the formation of AgBr precipitate. In this context it is worth mentioning that though several methods have been reported for synthesizing Au−NHC complexes, namely, (i) cleavage of electron-rich olefins,[35] (ii) carbene transfer from group 6 carbonyl complexes,[36] (iii) reactions of azolium salts or free NHCs with Au(I) precursors,[37] (iv) protonation or alkylation of gold azolyl complexes,[38] and (v) transmetalation via the reaction of Ag(I)−NHC complexes with Au(I) precursors,[34] the milder conditions of the transmetalation pathway make it an attractive choice. The ^{1}H NMR spectrum of **1c** showed the bridging methylene (CH_2) and the methoxy (OCH_3) resonances appearing as singlets at 5.47 and 3.88 ppm, respectively. The diagnostic gold-bound carbene (N*C*N−Au) peak appeared at 169.2 ppm in the ^{13}C NMR spectrum.

The molecular structure of the gold complex **1c** has been determined by X-ray diffraction studies (Figure 2). The X-ray structure of **1c** revealed the formation of a neutral monomeric (NHC)AuCl type complex in which the metal center was bound to a N-heterocyclic carbene ligand on the one side and to a chloride on the other. The geometry around the metal center is linear (∠C(1)−Au(1)−C1(1) = 179.74(11)°) and is consistent with the d^{10} configuration of Au(I) in **1c**.[39] The structure of **1c** is analogous to those of other reported neutral monomeric (NHC)AuCl type complexes such as [1-(2-hydroxycyclohexyl)-3-(*N*-*tert*-butylacetamido)imidazol-2-ylidene]AuCl, recently reported by us,[23] and [1,3-R$_2$-imidazol-2-ylidene]AuCl complexes (R = mesityl, 2,6-diisopropylphenyl, cyclohexyl, adamentyl), reported by Nolan and co-workers.[40] The bond distances Au−C_{carb} (1.979(4) Å) and Au−Cl (2.2872(10) Å) are consistent with single-bond character, as they are marginally shorter than the sum of the individual covalent radii (d_{Au-C} = 2.108 Å; d_{Au-Cl} = 2.326 Å).[41,42] Another notable feature of the **1c** structure is that the methoxy O of the functionalized 1-N substitutent (*o*-methoxybenzyl) was oriented away from the metal center, with the O1···Au1 distance being 6.041 Å.

Table 3. Selected Results of Suzuki Coupling of *p*-Bromobenzaldehyde with Phenylboronic Acid Catalyzed by 1d[a]



entry	amt of **1d** (mmol)	amt of **1d** (mol %)	time (h)	yield[b] (%)	TON
1	7.5×10^{-3}	3.5×10^{-1}	12	>99	288
2	2.8×10^{-4}	1.3×10^{-2}	12	>99	7580
3	2.8×10^{-5}	1.3×10^{-3}	12	51	39200

[a] Reaction conditions: 2.16 mmol of aryl halide, 2.64 mmol of phenylboronic acid, 3.24 mmol of K_2CO_3, complex **1d**, 30 mL of CH_3CN, 85 °C. [b] Determined by GC using diethylene glycol di-*n*-butyl ether as an internal standard.

The palladium complex [1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene]$_2$PdCl$_2$ (**1d**) was also synthesized via the transmetalation route by the reaction of the silver complex **1b** with (COD)PdCl$_2$ in 89% yield, following the procedure reported by Tilset and co-workers.[43,44] In this context it is worth mentioning that several other methods have been reported for synthesizing Pd−NHC complexes. For example, a frequently used pathway involves reaction of imidazolium halide salts with Pd(OAc)$_2$.[45,46] Along the same lines, Organ and co-workers[19] reported a convenient preparation of highly active Pd−NHC precatalysts by the reaction of imidazolium halide salts with PdCl$_2$ in air. Another ingenious one-pot synthesis of chiral Pd−NHC complexes by the activation of the C−S bond of methyl levamisolium has been recently reported by Cabeza and co-workers.[47] The complex **1d** is sufficiently air-stable and could be purified by column chromatography. In this regard it is worth mentioning that several air-stable Pd[46,48,49] and Ir[50] complexes of N-heterocyclic carbene ligands have been reported that were purified using column chromatography. In the ^{1}H NMR

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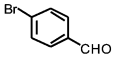
Table 4. Selected Results of Suzuki−Miyaura Cross-coupling Reaction of Aryl Halides (ArX, X = Br, I) Catalyzed by 1d

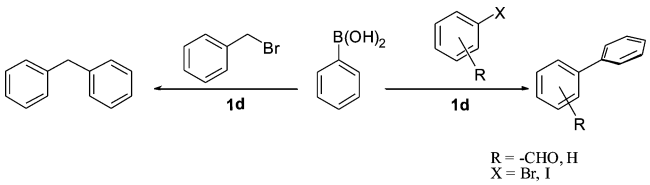
Entry	Reagent[a]	Reagent[a]	**1d**[a] (mol %)	Temp (°C)	Time (hour)	Yield[b] (%)	TON
1			3.5×10^{-1}	85	12	>99	288
2			3.5×10^{-1}	85	12	>99	288
3			3.5×10^{-1}	85	12	41	119
4			3.5×10^{-1}	85	12	42	121

[a] Reaction conditions: 2.16 mmol of aryl halides (ArX, X = Br, I), 2.64 mmol of phenylboronic acid, 3.24 mmol of K_2CO_3, 7.5×10^{-3} mmol of catalyst **1d**, and 30 mL of CH_3CN were taken for each run. [b] Determined by by GC using diethylene glycol di-*n*-butyl ether as an internal standard.

spectrum of **1d**, the bridging methylene (CH_2) and the methoxy (OCH_3) moieties appeared at 6.18 and 3.87 ppm, respectively. The characteristic palladium-bound carbene (N*C*N−Pd) peak appeared at 157.2 ppm in the ^{13}C NMR and falls well within the range, ca. 175−145 ppm, observed for other reported Pd−NHC complexes.[46,49,51]

The definitive proof for the **1d** structure came from X-ray diffraction studies, which showed the formation of a square-planar $(NHC)_2PdCl_2$ type complex having the two N-heterocyclic carbene ligands and two chloride ligands disposed trans to each other (Figure 3). As observed in the case of the **1c** structure, the **1d** structure also showed that the methoxy O of the functionalized sidearm (*o*-methoxybenzyl) did not chelate to the palladium center and was found to be disposed away from the metal center (O1···Pd1 = 5.360 Å). The two equivalent Pd−Cl bond distances (2.3531(12) Å) in **1d** are slightly larger than the sum of the individual covalent radii (d_{Pd-Cl} = 2.273 Å)[41] but compare well with the range observed for other related Pd complexes such as in *trans*-{3-[2-((2,6-diisopropylphenyl)-imino)propyl]-1-methylimidazol-2-ylidene}$PdCl_2$[43] (2.3070(3) Å) and *trans*-{3-[2-(benzylideneamino)cyclohexyl]-4-phenyl-1-propylimidazol-2-ylidene}$PdCl_2$[52] (2.359(2) Å). Interestingly enough, the two equivalent Pd−C_{carb} bond distances (2.036(5) Å) in **1d** are slightly smaller than the sum of the individual covalent radii (d_{Pd-C} = 2.055 Å).[41] In this regard it is worth mentioning that a theoretical study by Cundari[53] and co-workers revealed that up to 4% shortening of a metal−carbene bond can be ascribed to the change in hybridization state of the carbene carbon as a consequence of enhanced s character of the in-plane carbene lone pair σ-bonded to metal in the metal−NHC complexes. Consistent with an almost perfect square-planar geometry in **1d**, the ∠Cl1−Pd1−C11 angle is 91.61(15)° and the ∠C11−Pd1−C11 angle is 180.0(4)°.

The palladium complex **1d** was found to be an efficient catalyst for Suzuki−Miyaura type cross-coupling reactions. Specifically, the coupling of phenylboronic acid and *o*-bromobenzaldehyde to yield biphenyl-2-carbaldehyde was achieved in high yield and turnover numbers at 85 °C after 12 h of reaction time (eq 1 and Table 2). A study of the variation of



(1)

catalyst loading was carried out in order to gauge the upper limit of the catalyst efficiency (Table 2), and in fact, a maximum turnover number of ca. 49 700 and 45% conversion (Table 2, entry 7) were observed by gas chromatography at 9.2×10^{-4} mol % of catalyst loading after 12 h at 85 °C. Further increase in the yield (>99%) and turnover number (to ca. 109 600) were achieved by extending the reaction time to 24 h under the same conditions (Table 2, entry 8). Similar results were obtained for the cross-coupling of phenylboronic acid with *p*-bromobenzaldehyde, which produced biphenyl-4-carbaldehyde (Table 3). High turnover numbers up to ca. 39 200 were observed at 51% conversion by ^1H NMR at 1.3×10^{-3} mol % of catalyst loading after 12 h at 85 °C (Table 3, entry 3). Quite significantly, for the coupling of aryl bromides with phenylboronic acid, the high turnover numbers exhibited by **1d** not only are substantially greater than those reported for the palladium bis-chelating N-heterocyclic carbene complex [methylenebis(*N*-methylimidazol-2-ylidene)]PdI_2 (TON up to 100)[12b] but also are comparable to those reported for a well-known phosphapalladacyclic precatalyst, namely, *trans*-bis(μ-acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II) (TON up to 74 000).[54] It is noteworthy that phosphapalladacyclic complexes are renowned for their proficiencies in cross-coupling reactions, including Suzuki−Miyaura type reactions.[14f,55,56] In this context it is worth mentioning that two highly active Pd−NHC−phosphine cata-

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lysts, namely, *trans*-{[1,3-diisopropyl-1,4,5,6-tetrahydropyrimidine]Pd(PPh_3)$_2$Cl}$^+$Cl$^-$ (TON up to 800 000) and *cis*-[1,3-diisopropyl-1,4,5,6-tetrahydropyrimidine]Pd(PPh_3)Cl_2 (TON up to 1 000 000), exhibiting ultrahigh turnover numbers, have been recently reported by Herrmann and co-workers.[57] Notably, significant emphasis has been placed in recent years on designing cross-coupling catalysts of low catalyst loadings[58] in order to minimize the cost related to the usage of Pd and the ligand (particularly the phosphines), both considered expensive, alongside achieving large-scale synthesis requiring minimum effort in removal of Pd from the final product.[16a]

The palladium precatalyst **1d** successfully carried out Suzuki−Miyaura cross-coupling of a variety of aryl halides (ArX, X = Br, I) substrates (Table 4). Furthermore, the cross-coupling of an aryl iodide, namely, iodobenzene, with phenylboronic acid to give biphenyl was also achieved under analogous conditions. Quite interestingly, the C−C coupling can be extended from the C_{sp^2} carbon center, e.g., in *o*-bromobenzaldehyde, to the C_{sp^3} center in benzyl bromide (Table 4). However, much lower yield (42%) and turnover numbers (121) were observed for benzyl bromide compared to those for *o*-bromobenzaldehyde (yield >99%; TON = 288) obtained under the same reaction conditions.

Conclusion

In summary, two new gold and palladium complexes, namely, [1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene]AuCl (**1c**) and [1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene]$_2$PdCl$_2$ (**1d**), supported over a new O-functionalized N-heterocyclic carbene ligand, have been synthesized. Complexes **1c** and **1d** have been structurally characterized by X-ray diffraction studies, which revealed the formation of a neutral monomeric (NHC)-AuCl type complex in **1c** and a trans-square-planar (NHC)$_2$PdCl$_2$ type complex in **1d**, in accordance with the preferred geometries of the respective metal ions. Notably, in the structures of **1c** and **1d**, chelation of the O-functionalized sidearm to the metal was not observed. The palladium complex **1d** effectively catalyzed Suzuki−Miyaura type cross-coupling of phenylboronic acid and aryl halides (ArX, X = Br, I) in high yield and high turnover numbers.

Experimental Section

General Procedures. All manipulations were carried out using a combination of a glovebox and standard Schlenk techniques. Solvents were purified and degassed by standard procedures. Ag_2O was purchased from SD-Fine Chemicals (India) and used without any further purification. (COD)PdCl_2[59] and (SMe_2)AuCl[60] were prepared according to the reported literature procedures, while 2-methoxybenzyl bromide[61] was prepared by a procedure modified from that reported in the literature. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded in $CDCl_3$ on a Varian 400 MHz NMR spectrometer. ^{1}H NMR peaks are labeled as singlet (s), doublet (d), and multiplet (m). Infrared spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer. Mass spectrometric measurements were done on a Micromass Q-Tof spectrometer. GC spectra were measured on a Shimadzu GC-15A gas chromatograph equipped with an FID detector. X-ray diffraction data for **1c** and **1d** were collected on a NONIUS-MACH3 diffractometer. The crystal data and data collection and refinement parameters are summarized in Table 1. The structures were solved using direct methods and standard difference map techniques and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (version 6.10).

Synthesis of 1-(*o*-Methoxybenzyl)-3-*tert*-butylimidazolium Bromide (1a). A mixture of 2-methoxybenzyl bromide (3.00 g, 14.9 mmol) and *tert*-butylimidazole (1.84 g, 14.9 mmol) was dissolved in toluene (ca. 50 mL), and the reaction mixture was refluxed at 110 °C for 12 h, at which point a sticky solid separated out. The solid was isolated by decanting off the solvent and washed with hot hexane (3 × ca. 10 mL) to obtain the product **1a** as a brown solid (2.16 g, 6.65 mmol; 44% with respect to 2-methoxybenzyl bromide). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 10.6 (s, 1H, NC*H*N), 7.79 (d, 1H, $^3J_{HH}$ = 8 Hz, *m*-C_6H_4), 7.47 (br, 1H, NC*H*CHN), 7.37 (br, 1H, NCHC*H*N), 7.25 (t, 1H, $^3J_{HH}$ = 8 Hz, *p*-C_6H_4), 6.98 (t, 1H, $^3J_{HH}$ = 8 Hz, *m*-C_6H_4), 6.92 (d, 1H, $^3J_{HH}$ = 8 Hz, *o*-C_6H_4), 5.65 (s, 2H, CH_2), 3.90 (s, 3H, OCH_3), 1.72 (s, 9H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C): δ 155.7 (OC_6H_4), 133.0 (N*C*N), 129.8 (*o*-C_6H_4), 129.4 (*m*-C_6H_4), 120.9 (*ipso*-C_6H_4), 120.2 (*p*-C_6H_4), 119.2 (NCH*C*HN), 118.7 (N*C*HCHN), 109.2 (*m*-C_6H_4), 58.4 (*C*H$_2$), 54.0 (O*C*H$_3$), 46.5 (*C*(CH$_3$)$_3$), 28.3 (C(*C*H$_3$)$_3$). IR (KBr pellet): 3012 (m), 2955 (m), 1431 (s), 1417 (s), 1331 (s), 1253 (s), 1236 (s), 1215 (s), 1190 (s), 1161 (m), 1144 (m), 955 (m), 868 (s), 849 (m), 760 (s), 670 (s), 623 (s), 564 cm^{-1} (s). LRMS (ES): *m*/*z* 245 [(NHC)]$^+$. HRMS (ES): *m*/*z* 245.1662 (NHC-ligand)$^+$, calcd 245.1654.

Synthesis of {[1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene]$_2$Ag}$^+$Br$^-$ (1b). A mixture of 1-(*o*-methoxybenzyl)-3-*tert*-butylimidazolium bromide (**1a**; 1.45 g, 4.47 mmol) and Ag_2O (0.519 g, 2.24 mmol) in dichloromethane (ca. 60 mL) was stirred at room temperature for 6 h. The reaction mixture was filtered, and the solvent was removed under vacuum to give the product **1b** as a brown solid (0.876 g, 1.30 mmol; 58% with respect to Ag_2O). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 7.33 (t, 1H, $^3J_{HH}$ = 8 Hz, *p*-C_6H_4), 7.24 (d, 1H, $^3J_{HH}$ = 8 Hz, *m*-C_6H_4), 7.12 (br, 1H, NC*H*CHN), 7.02 (br, 1H, NCHC*H*N), 6.95 (t, 1H, $^3J_{HH}$ = 8 Hz, *m*-C_6H_4), 6.91 (d, 1H, $^3J_{HH}$ = 8 Hz, *o*-C_6H_4), 5.33 (s, 2H, CH_2), 3.88 (s, 3H, OCH_3), 1.72 (s, 9H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C): δ 178.3 (N*C*N−Ag), 156.9 (OC_6H_4), 130.0 (*o*-C_6H_4), 129.7 (*m*-C_6H_4), 123.8 (*ipso*-C_6H_4), 120.7 (*p*-C_6H_4), 119.8 (NCH*C*HN), 118.6 (N*C*HCHN), 110.6 (*m*-C_6H_4), 57.5 (*C*H$_2$), 55.2 (O*C*H$_3$), 51.7 (*C*(CH$_3$)$_3$), 31.6 (C(*C*H$_3$)$_3$). IR (KBr pellet): 3089 (w), 2971 (s), 2929 (m), 2339 (s), 1658 (w), 1558 (m), 1456 (m), 1370 (s), 1262 (w), 1229 (m), 1149 (w), 1108 (w), 1025 (w), 796 (w), 737 (s), 573 cm^{-1} (w). HRMS (ES): *m*/*z* 595.2177 [(NHC)$_2$Ag]$^+$, calcd 595.2202. Anal. Calcd for $C_{30}H_{40}AgBrN_4O_2$·CH_2Cl_2: C, 48.90; H, 5.56; N, 7.36. Found: C, 48.07; H, 4.81; N, 8.43.

Synthesis of [1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene]AuCl (1c). A mixture of {[1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene]$_2$Ag}$^+$Br$^-$ (**1b**; 0.825 g, 1.22 mmol) and (SMe_2)AuCl (0.720 g, 2.44 mmol) in dichloromethane (ca. 40 mL) was stirred at room temperature for 6 h, at which point the formation of an off-white AgBr precipitate was observed. The reaction mixture was filtered, and the solvent was removed under vacuum to obtain the product **1c** as a brown solid (0.446 g, 0.938 mmol; 77% with respect to **1b**). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 7.41 (d, 1H, $^3J_{HH}$ = 8 Hz, *m*-C_6H_4), 7.33 (t, 1H, $^3J_{HH}$ = 8 Hz, *p*-C_6H_4), 7.03 (br, 1H, NC*H*CHN), 6.97 (br, 2H, NC*H*CHN and *o*-C_6H_4), 6.92 (t,

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1H, $^3J_{HH}$ = 8 Hz, *m*-C_6H_4), 5.47 (s, 2H, CH_2), 3.88 (s, 3H, OCH_3), 1.84 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): δ 169.2 (N*C*N−Au), 157.0 (OC_6H_4), 130.4 (*o*-C_6H_4), 130.1 (*m*-C_6H_4), 123.6 (*ipso*-C_6H_4), 120.9 (NCH*C*HN), 119.1 (*p*-C_6H_4), 118.2 (N*C*HCHN), 110.5 (*m*-C_6H_4), 58.7 (CH_2), 55.3 (OCH_3), 51.2 ($C(CH_3)_3$), 31.6 ($C(CH_3)_3$). IR (KBr pellet): 3174 (w), 3145 (w), 3065 (w), 3004 (w), 2971 (m), 2837 (w), 2713 (w), 1601 (m), 1563 (w), 1496 (s), 1464 (s), 1445 (s), 1406 (s), 1367 (m), 1343 (w), 1291 (m), 1253 (s), 1219 (s), 1193 (m), 1162 (w), 1109 (m), 1052 (m), 1024 (s), 936 (w), 868 (w), 834 (w), 765 (s), 750 (s), 728 (m), 703 (w), 687 (m), 643 (w), 595 (w), 556 (w), 538 cm^{-1} (w). HRMS (ES): *m*/*z* 441.1232 $[(NHC)Au]^+$, calcd 441.1241. Anal. Calcd for $C_{15}H_{20}AuClN_2O$: C, 37.79; H, 4.23; N, 5.88. Found: C, 38.36; H, 4.51; N, 6.61.

Synthesis of [1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene]$_2$PdCl$_2$ (1d). A mixture of {[1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene]$_2$Ag}$^+$Br$^-$ (**1b**; 1.00 g, 2.32 mmol) and (COD)$PdCl_2$ (0.331 g, 1.16 mmol) was refluxed in acetonitrile (ca. 30 mL) at 85 °C for 6 h, at which point the formation of an off-white AgBr precipitate was observed. The reaction mixture was filtered, and the solvent was removed under vacuum to obtain a yellow solid, which was purified using column chromatography by eluting it with a mixed solvent (10% MeOH in $CHCl_3$) to obtain the pure product **1d** as a brown solid (0.857 g, 1.29 mmol; 89% with respect to **1b**). ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 7.61 (d, 1H, $^3J_{HH}$ = 8 Hz, *o*-C_6H_4), 7.31 (t, 1H, $^3J_{HH}$ = 8 Hz, *p*-C_6H_4), 7.01 (d, 1H, $^3J_{HH}$ = 3 Hz, NC*H*CHN), 6.96 (t, 1H, $^3J_{HH}$ = 8 Hz, *m*-C_6H_4), 6.91 (d, 1H, $^3J_{HH}$ = 8 Hz, *m*-C_6H_4), 6.79 (d, 1H, $^3J_{HH}$ = 3 Hz, NCHC*H*N), 6.18 (s, 2H, CH_2), 3.87 (s, 3H, OCH_3), 2.09 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): δ 157.2 (N*C*N−Pd), 135.9 (OC_6H_4), 131.9 (*ipso*-C_6H_4), 131.0 (*o*-C_6H_4), 122.1 (*p*-C_6H_4), 121.8 (NCH*C*HN), 121.2 (N*C*HCHN), 119.0 (*m*-C_6H_4), 110.6 (*m*-C_6H_4), 60.0 (CH_2), 55.4 (OCH_3), 48.3 ($C(CH_3)_3$), 29.9 ($C(CH_3)_3$). IR (KBr pellet): 3138 (w), 2971 (m), 2936 (m), 2837 (w), 1603 (m), 1463 (m), 1440 (m), 1415 (m), 1372 (m), 1290 (w), 1246 (s), 1110 (m), 1049 (w), 1025 (m), 949 (w), 862 (w), 820 (w), 803 (w), 758 (s), 701 (m), 657 (w), 638 (w), 558 cm^{-1} (w). Anal. Calcd for $C_{30}H_{40}Cl_2N_4O_2Pd{\cdot}CHCl_3$: C, 47.41; H, 5.26; N, 7.13. Found: C, 47.51; H, 5.07; N, 7.60.

General Procedure for the Suzuki Coupling Reaction. In a typical run, a round-bottom flask was charged with a mixture of aryl halides (ArX, X = Br, I), phenylboronic acid, K_2CO_3, and diethylene glycol di-*n*-butyl ether (internal standard) in a molar ratio of 1:1.2:1.5:1 and to this mixture was added [1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene]$_2$$PdCl_2$ (**1d**) at varying mole percent amounts (Tables 2 and 3). Acetonitrile (30 mL) was added to the reaction mixture, and this mixture was refluxed for an appropriate period of time, after which it was filtered and the product was analyzed by gas chromatography using diethylene glycol di-*n*-butyl ether as an internal standard.

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Supporting Information Available: CIF files giving crystallographic data for [1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene]AuCl (**1c**) and [1-(*o*-methoxybenzyl)-3-*tert*-butylimidazol-2-ylidene]$_2$$PdCl_2$ (**1d**). This material is available free of charge via the Internet at http://pubs.acs.org.

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