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Synthesis and Structure of Palladium 1,2,3-Triazol-5-ylidene Mesoionic Carbene PEPPSI Complexes and Their Catalytic Applications in the Mizoroki–Heck Reaction

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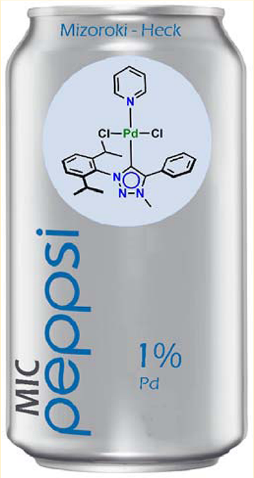
Supporting Information

ABSTRACT: New mono- and bimetallic 1,2,3-triazol-5-ylidene mesoionic carbene (MIC) complexes of Pd have been synthesized, isolated, and characterized. We have described the synthesis of a bis(MIC) complex via transmetalation from a Ag-MIC complex and two PEPPSI-type complexes which are directly available from their respective triazolium salts by treatment with $PdCl_2$ in pyridine. The X-ray structures are reported for all complexes described herein. Interestingly, each complex described exhibits various secondary noncovalent interactions in the solid state of the general type C–H···Cl, which appear to be important for the stabilization of the solid-state structure of the complexes. We further demonstrated the utility of the new PEPPSI complexes in the Mizoroki–Heck reaction. In the case of aryl iodides and electron-deficient bromides, high conversion is observed with methyl acrylate. Hg poisoning tests suggest that, even with an easily dissociated ligand, the reaction likely proceeds via Pd nanoparticles.



INTRODUCTION

The development of N-heterocyclic carbenes (NHCs) for use in organic synthesis has witnessed impressive growth in recent years.[1−7] The high steric bulk and strongly σ-donating properties of these ligands have made them particularly well suited for use in cross-coupling reactions.[8−11] In many cases, the Pd-NHC complex is formed *in situ*, which can result in difficulties with reproducibility and controlling the nature of the Pd complex formed. As a result, many researchers have instead moved toward well-defined preformed Pd^{II} NHC complexes, which are often air and moisture stable and can be used without rigorous anaerobic conditions.[12−15] The reduction of these complexes can then be performed *in situ* to generate the active Pd^0 species, although there can also be difficulties with this process.[16]

Heterocyclic carbenes that are only stabilized by one heteroatom have also attracted significant interest, as they generally act as stronger donors than the more common NHCs.[17−20] These are often termed abnormal carbenes or mesoionic carbenes (MICs), and ligands of this type have been utilized as catalysts in organic synthesis.[21−26] An important development in the chemistry of MICs was reported by Albrecht and co-workers, who demonstrated the feasibility of employing alkylated 1,2,3-triazolium salts as MIC precursors.[27] The facile synthesis of these species, via copper-catalyzed "click reactions",[28] has resulted in the rapid development of these ligands,[29−33] which are effective for a variety of catalytic transformations.[34−41] In particular, Pd-MIC complexes have received significant interest; however, the diversity of the complexes reported (Figure 1) is significantly less than that for analogous NHC complexes.[42−48]

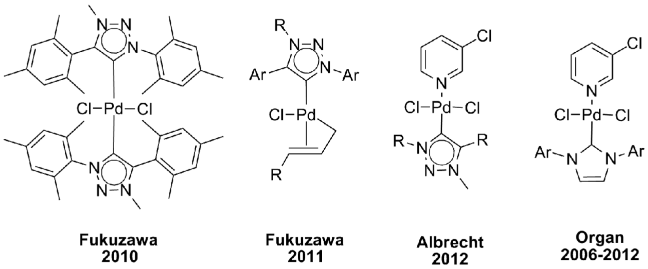


Figure 1. Selected Pd-MIC and Pd-NHC complexes relevant to this study.[13,42,44,49]

During the preparation of this paper, Albrecht and Trzeciak reported the synthesis of a series of triazole MIC-derived PEPPSI[13] (pyridine enhanced precatalyst preparation stabilization and initiation) complexes and investigated their use in the Suzuki–Miyaura reaction.[49] Interestingly, these complexes appear to be less effective than the analogous NHC derivatives

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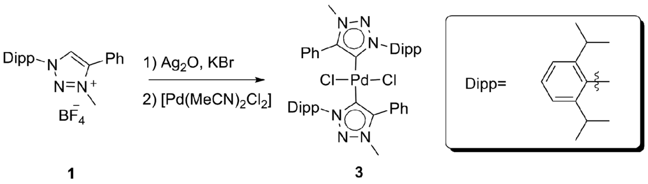
reported by Organ.[50,51] Most importantly, through a detailed analysis, it was shown that these complexes readily decomposed to Pd nanoparticles at elevated temperatures, suggesting significant differences in Pd binding between NHCs and MICs.

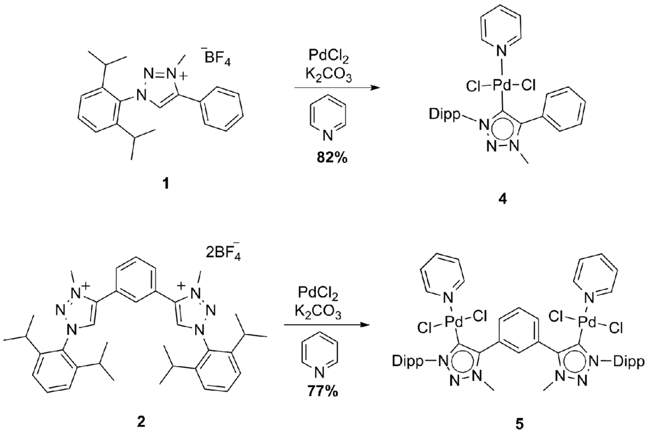
We have also been interested in developing triazole MIC PEPPSI-type complexes for C−C bond forming reactions, in the hopes that the increased electron donor capabilities of these ligands could lead to increased reactivity versus the standard NHCs. Herein we report the synthesis and characterization of mono- and bimetallic PEPPSI-type complexes bearing triazole MIC ligands and an investigation of their catalytic activity in the Mizoroki−Heck reaction of methyl acrylate with aryl iodides and bromides. Similarly to previous reports, mercury poisoning tests suggest that these complexes may readily form Pd nanoparticles at only moderately elevated temperatures.[49] The PEPPSI complexes described herein are conveniently synthesized by a one-step route directly from $PdCl_2$ in the presence of a weak base in good yield, without requiring preactivation with Ag_2O. All palladium complexes have been characterized by X-ray crystallography, as well as ^1H and $^{13}C\{^1H\}$ NMR.

RESULTS/DISCUSSION

Scheme 1. Synthesis of Bis(MIC) Complex 3



Scheme 2. Synthesis of Complexes 4 and 5



Synthesis of Complexes. We recently reported the synthesis of mono- and bimetallic rhodium complexes coordinated to triazole ligands derived from MIC precursors **1** and **2** (**1**, MIC_1; **2**, MIC_2, Schemes 1 and 2).[52] The synthesis of these complexes required transmetalation from Ag-MIC complexes. In order to first investigate their coordination chemistry with Pd, ligand MIC_1 was treated with Ag_2O and KBr in MeCN and then transmetalated to $[Pd(MeCN)_2Cl_2]$ by a procedure similar to the one we reported previously, resulting in the bis(MIC) complex **3** in overall 75% yield (Scheme 1).[52] Formation of the desired complex was confirmed by ^1H NMR, which was characterized by the disappearance of the triazole C−*H* peak. In addition, only one resonance at 3.98 ppm was observed for the triazole methyl group (*trz*-CH_3), indicating the presence of only one MIC-derived Pd complex. The $^{13}C\{^1H\}$ NMR spectrum of **3** displayed the Pd−carbene resonance at 162.9 ppm, which is consistent with bis(MIC) complexes described in the literature.[42,43,47] X-ray-quality crystals were grown via a slow diffusion of hexanes into a concentrated solution of CH_2Cl_2. The crystal structure of complex **3** is displayed in Figure 2, and selected geometrical parameters are reported in Table S1 (Supporting Information).

Fukuzawa and co-workers demonstrated that similar bis(MIC) complexes required very high temperatures (150 °C) to efficiently catalyze the Mizoroki−Heck reaction.[43] Computational analysis by Rösch and co-workers had previously demonstrated the likely benefits of a catalyst which consists of *only one* NHC ligand, as well as a second labile ligand to help stabilize the complex but provides open coordination sites for catalysis to occur.[53] This concept was exploited by Herrmann in his synthesis of heteroleptic NHC phosphine catalysts.[54−56] These results inspired us to investigate the reactivity of PEPPSI-type catalysts[13] derived from triazole MIC ligands in the Mizoroki−Heck reaction. Surprisingly, although there have been several reports of PEPPSI-type catalysts utilized in a variety of C−C and C−N bond forming reactions,[14,50,57] examples of these complexes in the Mizoroki−Heck reaction are rare.[58,59]

Related triazole MIC PEPPSI complexes described by Albrecht and Trzeciak were synthesized by activation first onto Ag_2O, followed by transmetalation to $PdCl_2$ conducted in 3-chloropyridine as the solvent at 100 °C.[49] In our case, we were able to synthesize complexes **4** and **5** bearing Dipp substituents by the reaction of a slight excess of triazolium salts MIC_1 and MIC_2 directly with $PdCl_2$ in pyridine in the presence of K_2CO_3. This resulted in the isolation of the desired compounds in 82% and 77% yields, respectively, after purification by column chromatography (Scheme 2). Although Organ has demonstrated the benefits of 3-chloropyridine as the throwaway ligand,[60] the syntheses of these complexes proved to be problematic, due to significant insolubility of the product. In contrast, both complexes **4** and **5** are soluble in many organic solvents and are air and moisture stable.

The formation of complex **4** was evident by the loss of the singlet resonance at 8.98 ppm corresponding to the C−*H* triazole peak in the ^1H NMR spectrum, as well as the presence of new aromatic peaks corresponding to the coordinated pyridine. Only one *trz*-CH_3 peak was present at 4.14 ppm, indicating the presence of only one MIC-derived complex. The formation of complex **5** was also characterized by the loss of the singlet resonance corresponding to the C−*H* triazole peaks of the triazolium salt in its ^1H NMR spectrum at 8.84 ppm. The highly symmetrical nature of the ^1H NMR spectrum was retained, indicating the likely formation of a bimetallic complex. Similar to our previous results,[52] the formation of syn and anti diastereomers did not seem to be an issue.[61] No cyclometalation was observed, since a broad resonance corresponding to the *o*-C−H of the central benzene was still observed at 8.52 ppm. Interestingly, the $^{13}C\{^1H\}$ NMR spectra of complexes **4** and **5** display C_{MIC}−Pd resonances that are dramatically more upfield than that of complex **3** by 16.1 and 20.8 ppm, respectively. This was also observed for the related PEPPSI MIC complexes previously reported,[49] which may indicate relatively weak Pd−MIC bonds, which in turn may have important ramifications for catalysis (*vide infra*).

X-ray-quality single crystals of **4** were grown by a slow diffusion of hexanes into a concentrated CH_2Cl_2−THF solution

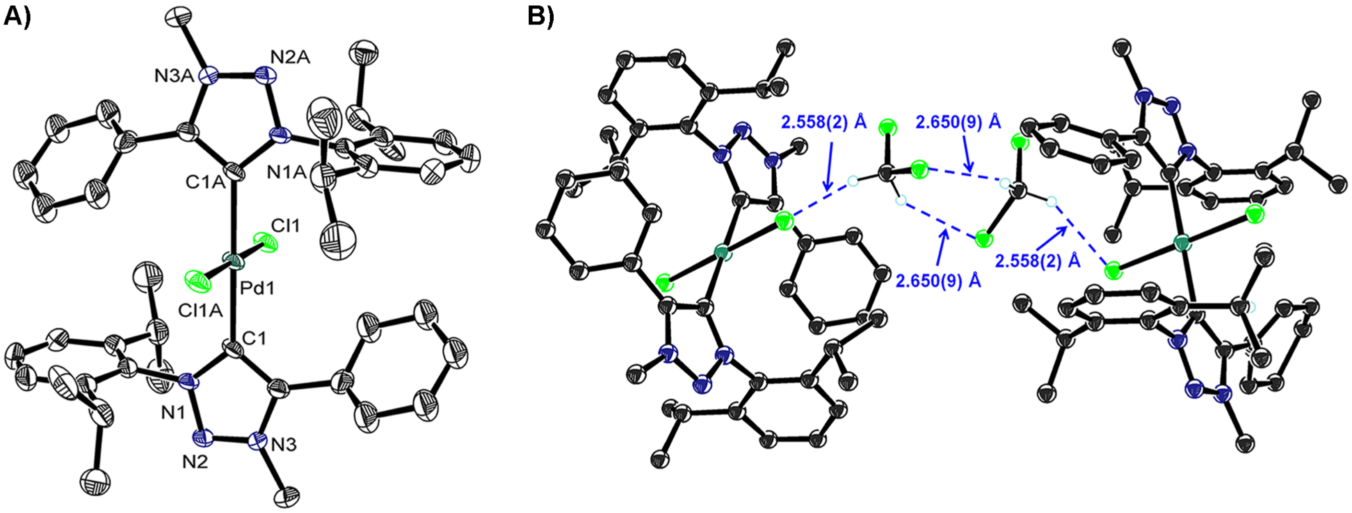


Figure 2. (A) Crystallographically determined structure of $[Pd(MIC_1)_2(Cl)_2]$ (**3**) displaying thermal ellipsoids drawn at the 50% confidence level. Hydrogen atoms and solvent molecules (CH_2Cl_2) are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Pd(1)−C(1), 2.022(6); Pd(1)−Cl(1), 2.3512(15); N(1)−C(1), 1.382(7); N(2)−N(1), 1.344(7); N(2)−N(3), 1.306(7); C(1)−Pd−C(1A), 180.000(1); C(1)−Pd(1)−Cl(1), 90.35(17); Cl(1)−Pd(1)−Cl(2), 180.0. (B) 2D structure of $[Pd(MIC_1)_2(Cl)_2]\cdot 2CH_2Cl_2$ showing the hydrogen C−H···Cl bonds. Hydrogen atoms and solvent molecules are omitted for clarity, with the exception of those involved in hydrogen bonding.

of **4**. The X-ray crystal structure of complex **4** is displayed in Figure 3a, and selected geometrical parameters are reported in Table S1. X-ray-quality single crystals of **5** were grown by a slow diffusion of hexanes into a concentrated CH_2Cl_2 solution of **5**. The X-ray crystal structure of **5** is displayed in Figure 3b, and selected geometrical parameters are reported in Table S1. Upon detailed inspection of the X-ray structures of complexes **3-5**, it appears that all complexes are characterized by multiple weak noncovalent interactions that influence the crystal organization *(vide infra)*. Complexes **4** and **5** were additionally characterized by high resolution mass spectrometry and elemental analysis.

Crystallography. Complex **3** exhibits a square-planar geometry around the palladium metal center with the two MIC ligands oriented trans to one another (Figure 2). The Pd center is lying on a crystallographic inversion center. The triazole rings of the carbene ligands are planar with negligible deviation from planarity, which is represented by the torsion angle (C2N3N2N1) = 1.15°. In addition, the triazole rings of the carbenes are coplanar. The two palladium−MIC bonds are 2.022(6) Å, which is consistent with structurally related Pd bis(NHC) complexes.[22,62] The triazole rings of the MICs are tilted with respect to their corresponding Dipp wingtip groups with a dihedral angle of 46.16°.

Since complex **3** was crystallized from a CH_2Cl_2/THF mixture, we observed CH_2Cl_2 incorporated into the crystal lattice. Interestingly, multiple weak noncovalent interactions were observed between the CH_2Cl_2 molecules and Pd complex **3**, likely playing an important role in crystal packing (see Figure 2B). These contacts may reasonably be considered to be C−H···Cl hydrogen bonds, since they are less than the sum of the van der Waals radii (2.95 Å) and are charge assisted by the opposite charges of anion and cation.[63−67] Strong interactions exist between the terminal chlorine atoms of complex **3** and the hydrogen atoms from a CH_2Cl_2 solvent molecule with H···Cl bond lengths of 2.558(2) and 2.650(9) Å (see Table S2 in the Supporting Information for details). Complex **4** crystallized with two crystallographically independent molecules per asymmetric unit. Complex **4** displays a distorted-square-planar geometry about the Pd atom with the pyridine bound trans to the MIC ligand. The angles between the carbene carbons and nitrogens of the pyridines are of 172.02 and 177.11°. The triazole rings of the carbene ligands in complex **4** are planar, with negligible deviations from planarity represented by the torsion angles (C2N3N2N1) of 0.41° and (C28N8N7N6) of 0.62°. The Pd−C_{MIC} bond lengths of 1.977(5) and 1.973(5) Å are slightly shorter than in complexes **3** and **5**. The plane of the heterocyclic ring of the carbene ligand is tilted with respect to the phenyl group with a dihedral angle of 46.37° and is almost perpendicular to the corresponding Dipp wingtip group with a dihedral angle of 78.07°, probably due to the steric constraints of the isopropyl groups.

Although complex **4** was crystallized from a CH_2Cl_2/THF/hexanes mixture, CH_2Cl_2 was not observed within the crystal structure; however, several weak noncovalent C−H···Cl interactions were observed. These interactions occur between one of the Pd-bound chlorine atoms and the meta hydrogen of the pyridine of a neighboring molecule (H···Cl bond length 2.744(1), 2.879(1), and 2.86(4) Å, Figure 3B). A second interaction is also observed, as the other Pd-bound chlorine atom is interacting with a hydrogen atom of the methyl group of the triazole MIC ring of a neighboring molecule (H···Cl bond length 2.84(3) Å (see Table S3 in the Supporting Information for details).

The X-ray structure of complex **5** clearly displays the bimetallic nature of the complex. The two palladium centers have nearly identical environments, with each of the MICs oriented trans to a pyridine. The heterocyclic rings of the carbene ligand are planar with negligible deviation from planarity, represented by the torsion angles (C23N3N2N1) of 1.37° and (C13N4N5N6) of 0.67°. The Pd−C_{MIC} bond lengths for Pd1 and Pd2 are 2.000(13) and 2.004(13) Å, respectively, which are quite similar to those of structurally related complexes.[49,60] The triazole rings of the carbene ligand are almost perpendicular to their corresponding Dipp wingtip groups, with dihedral angles of 78.62 and 80.75° for Pd1 and Pd2, respectively. The triazole rings are tilted with respect to the central phenyl ring with the angles of 50.22 and 50.34°.

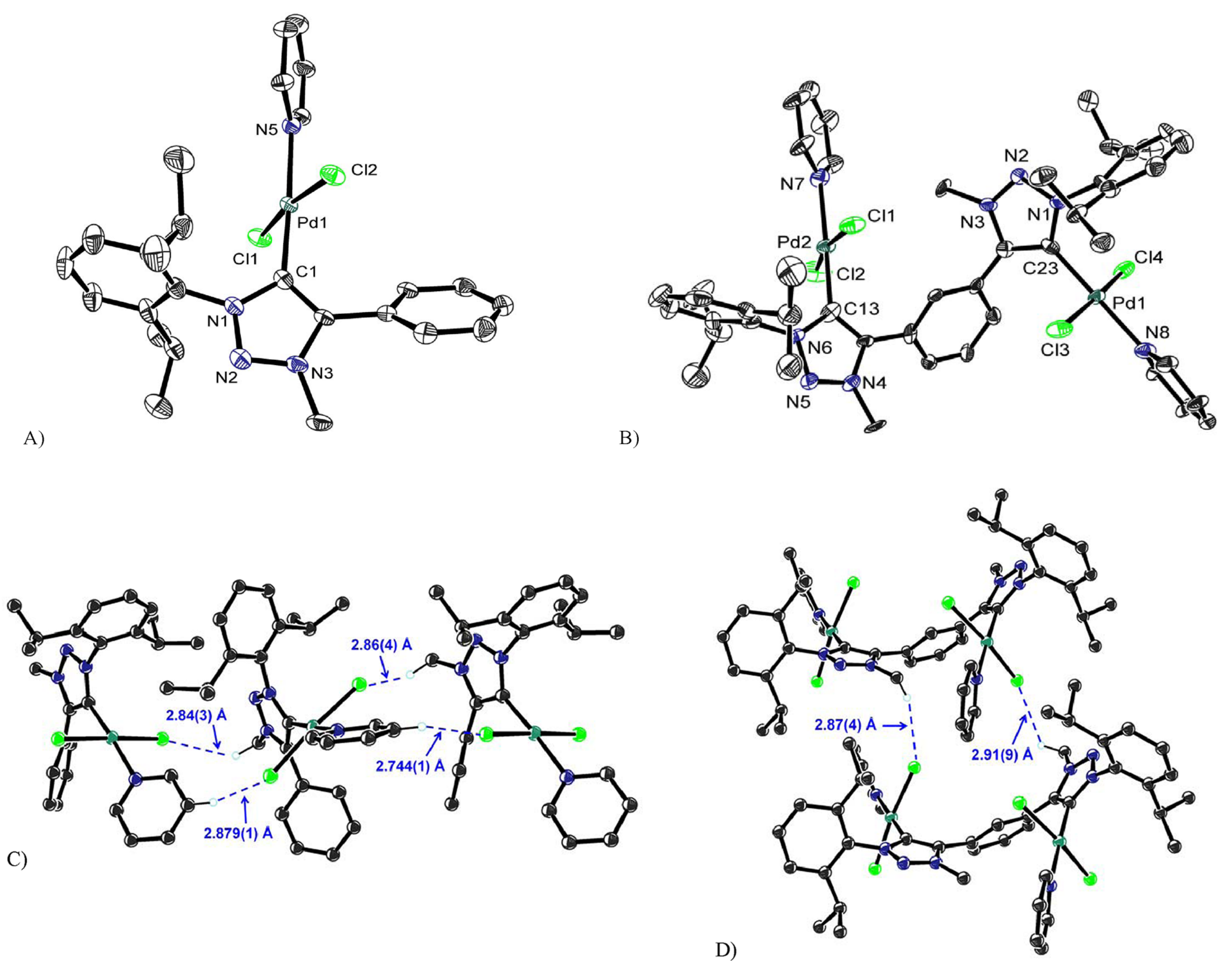


Figure 3. Crystallographically determined structures of (A) $[Pd(MIC_1)(Pyr)(Cl)_2]$ (**4**) and (B) $[(Pd)_2(MIC_2)(Pyr)_2(Cl)_4]$ (**5**), displaying thermal ellipsoids drawn at the 50% confidence level. There are two independent molecules of **4** per asymmetric unit. The second crystallographically independent molecule of **4** has a very similar geometry and was omitted for clarity. (C) 2D structure of $[Pd(MIC_1)(Pyr)(Cl)_2]$, (**4**) showing the hydrogen C−H···Cl bonds. Non-hydrogen-bonding H atoms are omitted for clarity. (D) 2D structure of $[(Pd)_2(MIC_2)(Pyr)_2(Cl)_4]$ (**5**) showing weak C−H···Cl interactions. Hydrogen atoms and solvent molecules are omitted for clarity, with the exception of those involved in hydrogen bonding. Selected interatomic distances (Å) and angles (deg) are as follows. For **4**: Pd(1)−C(1), 1.977(5); Pd(1)−Cl(1), 2.3066(13); Pd(1)−Cl(2), 2.3003(13); N(1)−C(1), 1.367(6); N(2)−N(1), 1.316(6); N(2)−N(3), 1.306(7); Pd(1)−N(5), 2.116(4); C(1)−Pd−N(5), 176.70(17); C(1)−Pd(1)−Cl(1), 89.15(15); C(1)−Pd(1)−Cl(2), 87.84(15); Cl(1)−Pd(1)−Cl(2), 172.02(5). For **5**: Pd(1)−C(23), 2.004(13), Pd(2)−C(13), 2.000(13); Pd(2)−Cl(1), 2.322(4); Pd(2)−Cl(2), 2.324(4); Pd(1)−Cl(3), 2.299(4); Pd(1)−Cl(4), 2.297(4); N(6)−C(13), 1.358(15); N(1)−C(23), 1.349(14); N(2)−N(1), 1.349(13); N(6)−N(5), 1.350(13); N(2)−N(3), 1.300(12); N(4)−N(5), 1.304(12); Pd(2)−N(7), 2.145(11); Pd(1)−N(8), 2.103(11); C(13)−Pd(2)−N(7), 178.8(5); C(23)−Pd(1)−N(8), 178.5(5); C(13)−Pd(2)−Cl(1), 88.3(3); C(13)−Pd(2)−Cl(2), 87.5(3); C(23)−Pd(1)−Cl(4), 89.7(4); C(23)−Pd(1)−Cl(3), 88.5(4); Cl(3)−Pd(1)−Cl(4), 173.34(15); Cl(1)−Pd(2)−Cl(2), 168.63(16).

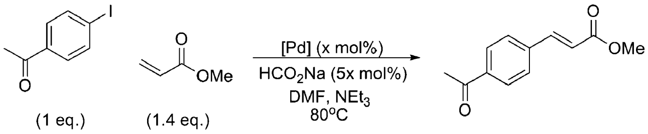
Complex **5** exhibits a distorted-square-planar geometry around the metal centers with visible distortions from planarity with the corresponding angles Cl(1)−Pd(2)−Cl(2) = 168.63(16)° and Cl(3)−Pd(1)−Cl(4) =173.34(15)°. This is likely due to the multiple weak intermolecular noncovalent C−H···Cl interactions (*vide infra*) that appear to have a significant effect on the solid-state structure of complex **5**.

Similarly to complex **4**, weak intermolecular noncovalent interactions in complex **5** exist between the chlorine atoms and one of the pyridine hydrogens (H···Cl bond length 2.87(4) Å), Figure 3D) and a second type of interaction is also observed between one of the Pd-bound chlorine atoms and one of the hydrogen atoms of the methyl group of the triazole carbene in a neighboring molecule (H···Cl bond length 2.91(9) Å) (see Table S4 in the Supporting Information for details).

Catalysis. The Mizoroki−Heck reaction[68] has been extensively studied with a wide variety of Pd-NHC complexes.[22,69−71] Although this reaction is commonly performed with phosphine-ligated catalysts,[72] Pd-NHC complexes benefit from increased thermal stability, which make them ideally suited for the often harsh conditions required in this reaction.[69,73] Some of the most common precatalysts investigated are Pd^{II} bis(NHC) complexes,[43] which are reduced *in situ* to the catalytically active Pd^0 complexes. Several groups, however, have demonstrated the beneficial effect of Pd-NHC complexes sporting hemilabile ligands,[53,56,70,74,75] whose role would be to open up coordinate sites on the Pd center and facilitate binding of the substrate. This prompted us to study the catalytic activity of complexes **4** and **5**. It was our hope that the increased donating capabilities of the ligands **4** and **5** would make them effective catalysts for this reaction under relatively mild conditions.[76]

We began by examining the coupling of *p*-iodoacetophenone and methyl acrylate utilizing complexes **4** and **5** as catalysts (Table 1). Both complexes proved to be competent catalysts for the coupling of aryl iodides using sodium formate as the reducing agent.[77,78] Complete conversion was obtained in 2 h at 80 °C using 1 mol % of complex **5** (2 mol % Pd). In the absence of sodium formate, minimal conversion (<5%) was observed in the same time period, as determined by GC analysis. Decreasing the catalyst loading slowed down the reaction, but good conversion could still be obtained at increased reaction times (entries 2−5). Encouragingly, no Pd black was observed at this temperature, in contrast to the performance of related catalysts in the Suzuki−Miyaura reaction at the same temperature.[49] However, once the catalyst loading was decreased to 0.25 mol %, decomposition become evident, as complete conversion could not be observed even at extended times (entries 3−5). In all cases, the *E* isomer was the only product observed.

Table 1. Optimization Results in the Mizoroki−Heck Reaction



entry	cat.	cat. loading (mol %)[c]	time (h)	yield (%)[d]	TON
1[a]	5	1	2	96	48
2[a]	5	0.5	3	97	97
3[a]	5	0.25	6	40	80
4[b]	5	0.25	24	81	162
5[b]	5	0.125	48	61	244
6[a]	4	2	2	96	48
7[a]	3	2	2	99	49

[a] Conditions: *p*-iodoacetophenone (0.20 mmol), methyl acrylate (0.28 mmol), NEt$_3$ (0.5 mL), DMF (2.5 mL). [b] Conditions: *p*-iodoacetophenone (0.40 mmol), methyl acrylate (0.56 mmol), NEt$_3$ (1.0 mL), DMF (5.0 mL). [c] HCO$_2$Na (5 equiv/[Pd]) as reducing agent. [d] Isolated yields.

Catalyst **4** also proved to be competent in this transformation (entry 6), giving yields comparable to those for catalyst **5**. A direct comparison between complexes **4** and **5** was performed by GC analysis, which revealed nearly identical catalytic behavior for the two complexes (Figure 4). A short induction period was present for **5** relative to **4**, which may be related to the *in situ* reduction to the active Pd^0 species. TOF values at 50% conversion were calculated as 50 and 37 h^{-1} for complexes **4** and **5**, respectively.

Since Trzeciak and Albrecht clearly demonstrated that the Pd-MIC catalysts used in their detailed study of the Suzuki−Miyaura reaction decomposed to Pd nanoparticles,[49] we also examined our catalyst system for the presence of heterogeneous Pd. Thus, we performed a mercury poisoning test by exposing the reaction solution to a large excess of elemental mercury after the reaction had reached 12% conversion as determined by GC analysis. Under these conditions, subsequent conversion to product was inhibited, suggesting that heterogeneous Pd nanoparticles are the active catalyst, despite the fact that Pd black was not visually detected when the reaction was run at 80 °C;[49] however, to definitively show that heterogeneous Pd is the sole active species, significantly more studies would be required.[79−81]

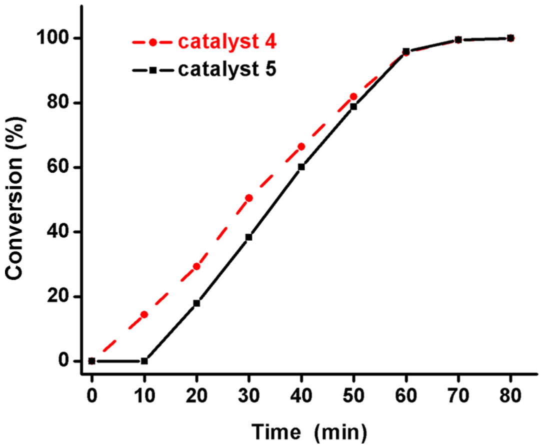
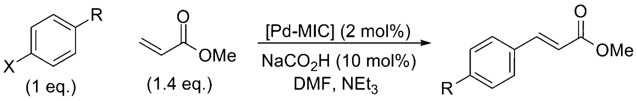


Figure 4. Comparison of catalytic activity for catalysts **4** and **5** in the Mizoroki−Heck reaction at 2% catalyst loading.

Higher temperatures (125 °C instead of 80 °C) and longer reaction times were required in order for electron-deficient aryl bromides to react (Table 2). In all of the experiments performed at 125 °C, Pd black was observed within minutes of the reaction. Regardless, at 125 °C, full conversion of electron-deficient aryl bromides was observed in 5 h. Electron-rich aryl bromides failed to react under these conditions (entry 5), and even after higher temperatures and extended reaction times (150 °C, 24 h), only minimal conversion (<5%) was observed. These results likely indicate significant thermal instabilities of the catalysts, which limits the applicability of the catalyst to less reactive substrates. The precise mode of deactivation of the Pd catalyst is not apparent at this time, but this result is consistent with previous reports highlighting the differences in metal bonding with triazole MIC and NHC complexes and the resulting instability of these species under catalytic conditions.[49]

Table 2. Mizoroki−Heck Reaction of Aryl Iodides and Bromides[a]



entry	substrate	temperature (°C)	time (h)	catalyst	yield (%)
1	X = I, R = CH$_3$	80	2	4	90[b]
				5	93[b]
2	X = I, R = OCH$_3$	80	2	4	95[b]
				5	98[b]
3	X = I, R = C(O)CH$_3$	125	5	4	98[b]
				5	95[b]
4	X = Br, R = NO$_2$	125	5	4	92[b]
				5	97[b]
5	X = Br, R = CH$_3$	125	16	4	trace[c]
				5	5[c]
				3	trace[c]

[a] General conditions: aryl halide (0.20 mmol), methyl acrylate (0.28 mmol), HCO$_2$Na (0.02 mmol), catalyst (0.004 mmol Pd), NEt$_3$ (0.5 mL), DMF (2.5 mL). [b] Isolated yields. [c] Determined by GC.

■ CONCLUSIONS

In conclusion, we have described the synthesis and characterization of several Pd 1,2,3-triazol-5-ylidene MIC complexes. All complexes were characterized by X-ray crystallography and displayed multiple weak noncovalent interactions within the solid structure. We further illustrated the use of complexes **4** and **5** as catalysts in the Mizoroki–Heck reaction. Complexes **4** and **5** behave essentially identically and successfully couple aryl iodides with methyl acrylate in 2 h at 80 °C using 2 mol % Pd. Mercury poisoning tests were performed which suggest the formation of Pd nanoparticles as the active catalyst. Higher temperatures resulted in the decomposition of the catalysts and the obvious formation of Pd black, which limits the utility of these complexes for this transformation. Current work in our laboratory is dedicated to increasing the catalytic activity and thermal stability of these complexes, in order to successfully couple more difficult substrates such as aryl chlorides.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text giving experimental procedures for the synthesis of the Pd-MIC complexes and their use in catalysis tables and CIF files giving crystal data for the complexes described herein. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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