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Dinuclear Triazole-Derived Janus-Type N-Heterocyclic Carbene Complexes of Palladium: Syntheses, Isomerizations, and Catalytic Studies toward Direct C5-Arylation of Imidazoles

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Supporting Information

ABSTRACT: The dipalladium triazolidine-diylidene complex *all-trans*-[$PdBr_2(CH_3CN)]_2$(μ-ditz) (**1**) (ditz = 1,2,4-trimethyltriazolidine-3,5-diylidene) was synthesized via *in situ* deprotonation of the precursor salt with a basic metal precursor. Ligand replacements of *all-trans*-**1** with monodentate or chelating phosphines afforded the dicarbene-bridged complexes *all-cis*-[$PdBr_2(PPh_3)]_2$(μ-ditz) (**2**) and [$PdBr(DPPP)]_2$(μ-ditz)Br_2 (**3**), respectively. Bromido substitution of *all-cis*-**2** gave tetra-acetato complex *all-cis*-[$Pd(CH_3COO)_2(PPh_3)]_2$(μ-ditz) (**4**) with retention of the configuration as the predominant product. In addition, monopalladium triazolin-5-ylidene complexes *trans*-[$PdBr_2(CH_3CN)$(tazy)] (**6**, tazy =1,4-dimethyltriazolin-5-ylidene), *cis*-[$PdBr_2(PPh_3)$(tazy)] (**7**), [PdBr(DPPP)(tazy)]Br (**8**), and *cis*-[$Pd(CH_3COO)_2(PPh_3)$(tazy)] (**9**) were also synthesized as the respective mononuclear equivalents for comparison. A comparative catalytic study revealed the general superiority of dinuclear complexes **1**−**4** over their respective mononuclear counterparts **6**−**9** in the direct C5-arylation reaction of 1-methylimidazoles. Overall, mixed dicarbene/diphosphine complex **3** showed the best catalytic performance.

INTRODUCTION

N-Heterocyclic carbenes (NHCs) have evolved to become universal ligands in organometallic chemistry.[1] Various monodentate NHCs and diNHCs incorporating two mutually linked carbene donors have been extensively investigated. The latter have been exploited as bridging or chelating ligands in their transition metal complexes.[2] In addition, the application of homo- and heterobimetallic diNHC complexes in cooperative catalysis has also received increasing interest.[3]

Recently, we[4] also became interested in the Janus-type diNHC ligand[5] 1,2,4-trimethyltriazolidine-3,5-diylidene (ditz, Figure 1), which was introduced by the group of Bertrand[6] and employed by Peris and co-workers in catalysis.[3] The ditz ligand features two $C_{carbene}$ donors within a single five-membered triazole ring. This unique structural feature renders the two bound metal centers spatially proximate with a fixed distance of only ca. 6 Å,[3a−j] which cannot be achieved by any other diNHC ligand known so far.

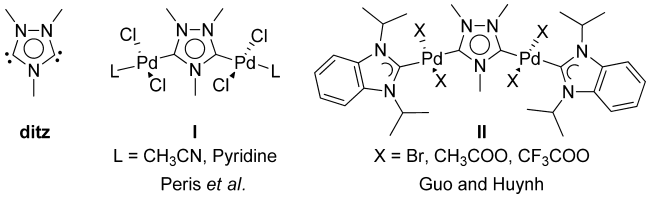

Figure 1. 1,2,4-Trimethyltriazolidine-3,5-diylidene (ditz) and its reported dipalladium complexes of the general formula [$PdX_2L]_2$(μ-ditz).

Although, triazolidine-diylidene ligands have been applied as a bridging ligands in a couple of transition metal complexes, very few dipalladium ditz complexes have been disclosed[3e−g,4a] (**I**/**II**, Figure 1), including the heterotetra(carbene) complexes [$PdX_2(^iPr_2$-bimy)]$_2$(μ-ditz) (**II**, X = Br, CH_3COO, CF_3COO, $^iPr_2$-bimy = 1,3-diisopropylbenzimidazolin-2-ylidene) previously reported by us.[4a]

Theoretically, four isomers are possible for complexes of the general formula [$PdX_2L]_2$(μ-ditz). These include *all-trans*, *cis*−*trans*, *all-cis*−*syn*, and *all-cis*−*anti* configurations, respectively (Chart 1). However, the known dipalladium triazolidine-diylidene complexes (*vide supra*) are dominantly *all-trans*-configured, with both of the Pd(II) centers surrounded by *trans*-oriented ancillary ligands.

An earlier study has revealed that *trans*-oriented Pd(II) mixed carbene/phosphine complexes of the general formula *trans*-[PdX_2(NHC)(PR_3)] (X = halido ligand) slowly isomerize to the electronically preferred *cis* form due to the "transphobia effect".[7] Furthermore, *cis*-configured NHC complexes have also been reported to undergo faster catalyst initiation than their direct *trans* isomers.[8] Thus, with the objective to broaden the structural diversity of dipalladium triazolidine-diylidene complexes, particularly to gain access to *all-cis*-oriented isomers, mono- and diphosphines were employed as supporting ligands in this work. The catalytic behavior of the complexes toward

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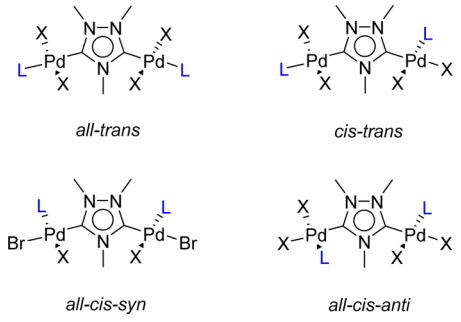
Chart 1. Possible Isomers of $[PdX_2L]_2(\mu$-ditz$)$ Complexes

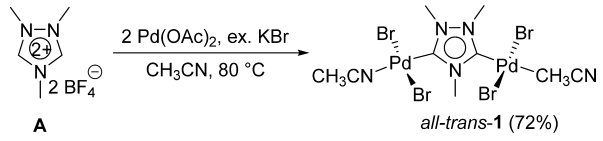


direct C5-arylation of 1-methylimidazoles was also examined. Lastly, to provide insights on potential catalytic cooperativity effects of the two diNHC-bridged Pd(II) centers, we also report the synthesis and a comparative catalytic study of monopalladium triazolin-5-ylidene complexes as mononuclear equivalents.

RESULTS AND DISCUSSION

Although, the dipalladium ditz complex *all-trans*-$[PdCl_2(CH_3CN)]_2(\mu$-ditz$)$ of type **I** (Figure 1) has been reported,[3e] its potential use for further ligand substitution reactions remains unexplored, although the labile acetonitrile ligands in complexes of this type are predestined to undergo displacement. Thus, as a good starting point for us, the analogous *all-trans*-$[PdBr_2(CH_3CN)]_2(\mu$-ditz$)$ complex was synthesized. To be consistent with our previous study and for the purpose of comparison,[4a,7b,c] bromido coligands were chosen. The palladation reaction of dicationic salt ditz$\cdot(H^+BF_4^-)_2$ (**A**),[4a,9] two equivalents of $Pd(OAc)_2$, and excess KBr in CH_3CN, following the reported procedure for the chlorido analogue *all-trans*-$[PdCl_2(CH_3CN)]_2(\mu$-ditz$)$,[3e] afforded *all-trans*-$[PdBr_2(CH_3CN)_2]_2(\mu$-ditz$)$ (**1**) in a decent yield of 72% (Scheme 1).

Scheme 1. Synthesis of Dipalladium Acetonitrile Complex *all-trans*-1



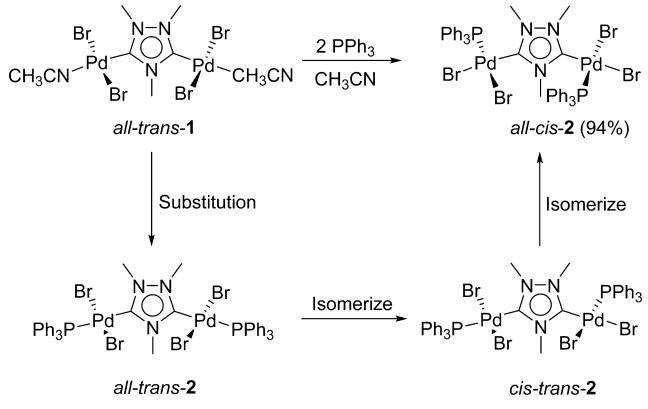
In the ^{1}H NMR spectrum of *all-trans*-**1**, the absence of the downfield resonance characteristic for NCHN protons provided the first evidence of the successful metalation. The three *N*-methyl groups of the triazolidine-diylidene ligand give two singlets with very close chemical shifts at 4.31 and 4.25 ppm with an intensity ratio of 1:2, suggesting a 2-fold symmetry of *all-trans*-**1** in solution.

The formation of *all-trans*-**1** was further corroborated by its ^{13}C NMR spectrum, which displays the carbene signal at 160.6 ppm, falling in the range typically observed for Pd(II) acetonitrile complexes.[3e,7c] In addition, a dominant peak at m/z 749 was observed in the ESI-MS spectrum of *all-trans*-**1**, arising from the $[M + Na]^+$ cationic species.

Complex *all-trans*-**1** is readily soluble in CH_3CN, less soluble in chlorinated solvents, and insoluble in nonpolar solvents such as diethyl ether and *n*-hexane. This compound is fairly air-stable, and no decomposition to palladium black was observed in CH_3CN upon standing for a couple of days. Several attempts to obtain single crystals of good quality for X-ray diffraction study were to no avail. However, the analogous tetrachlorido complex **A** (*vide supra*) was reported to adopt an *all-trans*-configuration.

Complex *all-trans*-**1** can serve as a precursor for further ligand replacement reactions and was treated with two equivalents of PPh_3 in CH_3CN with the aim to access the mixed dicarbene/phosphine complex $[PdBr_2(PPh_3)]_2(\mu$-ditz$)$ (**2**, Scheme 2). It is known that mixed NHC/phosphine

Scheme 2. Synthesis and Isomerization Process of di-Pd(II) ditz/PPh_3 Complex 2



complexes of the type *trans*-$[PdX_2(NHC)(PR_3)]$ (X = halido ligand) slowly convert to the preferred *cis*-configured isomer (*vide supra*).[7] Such isomerization processes have not been studied for dipalladium complexes yet. To provide insight into the potential isomerization process in the case of the more complicated dipalladium mixed dicarbene/bis(phosphine) complex **2** described herein, a NMR tube reaction in CD_3CN was carried out. The interconversion of isomers can be monitored by ^{1}H NMR spectroscopy as depicted in Figure 2.

The ^{1}H NMR signals for the *N*-CH_3 groups of the triazolidine-diylidene ligand are good indicators for the isomerization process. Facile ligand substitution is accomplished quickly in only 5 min, and two new sets of resonance, assigned to *all-trans*-**2** and *cis-trans*-**2**, respectively, emerged (Figure 2).

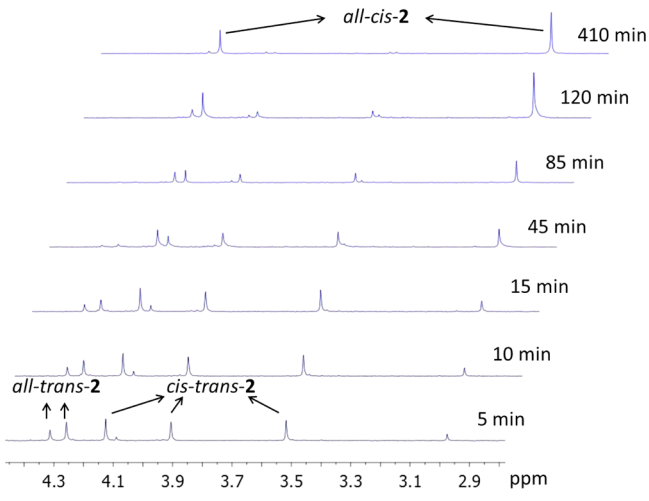


Figure 2. Time-dependent ^{1}H NMR spectra showing the isomerization process of di-Pd(II) mixed ditz/PPh_3 complex **2** in CD_3CN.

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The former gives two singlets with an intensity ratio of 1:2, in line with a 2-fold symmetry of this isomer. As expected, such symmetry is absent in the latter mixed *cis*−*trans* form, which is corroborated by three singlets with an integration ratio of 1:1:1. Notably, the isomer *all-trans*-**2** was almost fully consumed in only 45 min, suggesting that this isomer is thermodynamically unfavorable. This is due to the transphobia effect, which is expressed here as the difficulty to place two strong phosphine donors *trans* to the dicarbene in the *all-trans*-**2** isomer. In contrast, the *cis-trans*-**2** form is slightly more preferred, and the corresponding signals almost disappeared after only ca. 7 h. Finally, signals due to *all-cis*-**2** become dominant, indicating it as the most thermodynamically stable species. It should be noted that this isomerization process can be accelerated at elevated temperature. Heating the reaction mixture in CH_3CN at 80 °C for only ca. 2 h leads to a complete conversion to the *all-cis* isomer.

Complex *all-cis*-**2** was isolated as yellow solid, which is readily soluble in polar solvents such as DMSO, CH_3CN, and CH_2Cl_2, but less soluble in $CHCl_3$ and insoluble in nonpolar solvents, such as diethyl ether and *n*-hexane. In the ^{1}H NMR spectrum of *all-cis*-**2**, the *N*-methyl groups of triazolidine-diylidene ligand give two singlets at 4.08 and 2.96 ppm, which are upfield shifted in comparison to those in *all-trans*-**1**. This is probably due to the shielding effect of the phenyl rings of the *cis*-standing PPh_3 ligands. Only one singlet at 28.0 ppm is observed in the ^{31}P NMR spectrum, supporting the existence of a single isomer. The formation of *all-cis*-**2** was also verified by its ^{13}C NMR spectrum, which displays the carbene signal at 176.7 ppm. A base peak at *m*/*z* 1120 is found in the positive mode ESI-MS spectrum of *all-cis*-**2**, arising from the cationic species $[M - Br + CH_3OH]^+$.

The identity of *all-cis*-**2** was also confirmed by X-ray diffraction analysis on the single crystals obtained by slow evaporation of a concentrated CH_2Cl_2/*n*-hexane solution. The molecular structure is depicted in Figure 3, and selected crystallographic data are listed in Table SI-1 (see Supporting Information).

The dinuclear complex contains two essentially square planar palladium centers, each of which is coordinated by one PPh_3 ligand and two bromido ligands in a *cis*-fashion and linked by a triazolidine-diylidene bridge. The two sterically demanding PPh_3 ligands adopt an *anti*-configuration with respect to the diNHC plane to avoid intramolecular repulsion. The five-membered dicarbene ring is oriented almost perpendicularly to the $PdCPBr_2$ coordination planes with an average dihedral angle of ∼77°. The Pd−$C_{carbene}$(ditz) bond lengths of 1.968(5) and 1.976(5) Å in *all-cis*-**2** are found to be markedly shorter compared to those (cf. 2.026(7), 2.034(7) Å) in the previously reported hetero(tetra)carbene counterpart *all-trans*-[$PdBr_2$-(^{i}Pr$_2$-bimy)]$_2$(μ-ditz) of type **II** (Figure 1).[4a] This observation is attributed to the stronger *trans*-influence exerted by the ^{i}Pr$_2$-bimy carbene ligand in the latter. Owing to the same reason, the interpalladium distance of 5.969 Å in *all-cis*-**2** is also pronouncedly shorter than that in *all-trans*-[$PdBr_2$(^{i}Pr$_2$-bimy)]$_2$(μ-ditz).[4a] To the best of our knowledge, complex *all-cis*-**2** is the first dipalladium triazolidine-diylidene complex adopting an *all-cis*-configuration.

To further explore the structural diversity of ditz-bridged dipalladium complexes, the reactivity of *all-trans*-**1** toward diphosphine ligands was examined. Hence, the precursor complex *all-trans*-**1** was treated with two equivalents of the DPPP ligand (DPPP = 1,3-bis(diphenylphosphino)propane), affording the desired bis(diphosphine) complex [PdBr(DPPP)]$_2$(μ-ditz)Br_2

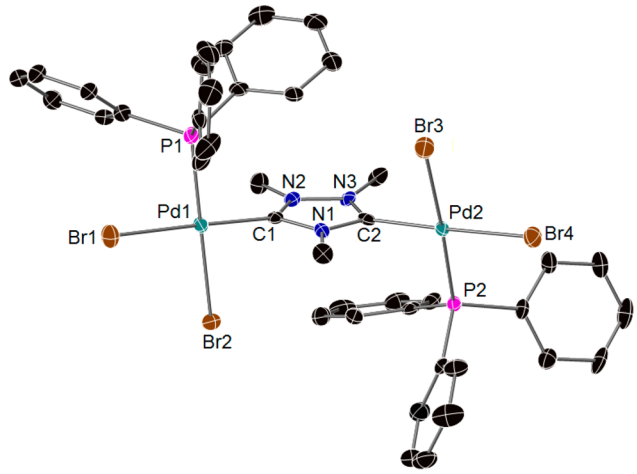
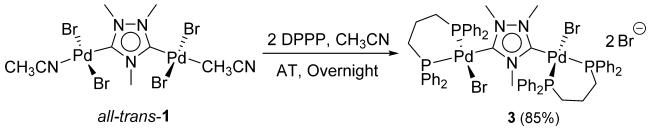


Figure 3. Molecular structure of *all-cis*-**2** showing 50% probability ellipsoids. Hydrogen atoms, solvent molecules, and disordered atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Pd1−C1 1.968(5), Pd1−P1 2.2663(15), Pd1−Br1 2.4496(7), Pd1−Br2 2.4701(7), Pd2−C2 1.976(5), Pd2−P2 2.2693(14), Pd2−Br4 2.4568(7), Pd2−Br3 2.4598(7); C1−Pd1−P1 94.07(15), C1−Pd1−Br1 176.10(15), P1−Pd1−Br1 86.72(4), C1−Pd1−Br2 85.08(14), P1−Pd1−Br2 178.19(5), Br1−Pd1−Br2 94.24(2), C2−Pd2−P2 92.58(15), C2−Pd2−Br4 174.09(15), P2−Pd2−Br4 92.27(4), C2−Pd2−Br3 84.60(14), P2−Pd2−Br3 177.09(4), Br4−Pd2−Br3 90.50(2).

Scheme 3. Synthesis of Dipalladium(II) Mixed Dicarbene/Diphosphine Complex 3



(**3**) as an off-white solid in a high yield of 85% (Scheme 3). Attempts to synthesize analogous bis(DPPF) complex (DPPF = 1,1′-bis(diphenylphosphino)ferrocene) gave multiple inseparable products.

Complex **3** is readily soluble in polar solvents such as DMSO and DMF and less soluble in CH_2Cl_2. In the ^{31}P NMR spectrum of **3** recorded in d_6-DMSO, two sharp doublets at 9.68 and −1.85 ppm with a coupling constant of ^2J(P−P) = 35 Hz are found. These resonances are in good agreement with the data found for other palladium(II)-DPPP complexes.[10] The ^{1}H NMR spectrum displays only one set of signals, suggesting the free rotation of Pd−$C_{carbene}$ bonds. The three *N*-methyl groups of the triazolidine-diylidene bridge give two singlets at 3.89 and 3.16 ppm with an intensity ratio of 1:2. The carbene signal is found at 178.4 ppm in the ^{13}C NMR spectrum of complex **3**. ESI-MS spectrometry further supports the formation of **3**, by dominant peaks at *m*/*z* 658 and 1389, arising from the dicationic species $[M - 2Br]^{2+}$ and the monocationic species $[M - Br]^+$, respectively.

Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a concentrated solution of **3** in CH_2Cl_2. The molecular structure is depicted in Figure 4. The dinuclear complex contains two *anti*-oriented [PdBr(DPPP)] fragments, which are linked by a triazolidine-3,5-diylidene ligand. Two $PdCBrP_2$ coordination planes are almost perpendicular to the dicarbene ring with an average dihedral angle of ∼82°. The average P−Pd−P angle (91.84°) in the six-membered

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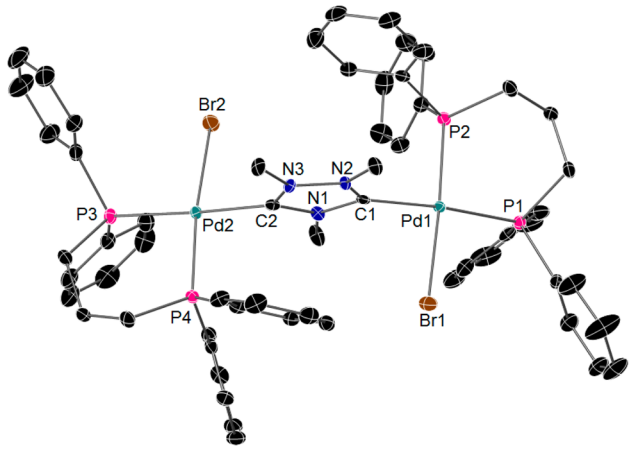


Figure 4. Molecular structure of **3** showing 50% probability ellipsoids. Hydrogen atoms, solvent molecules, and bromide anions are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Pd1−C1 2.038(5), Pd1−P2 2.2670(13), Pd1−P1 2.3074(13), Pd1−Br1 2.4795(6), Pd2−C2 2.023(5), Pd2−P4 2.2646(13), Pd2−P3 2.3032(13), Pd2−Br2 2.4608(6); C1−Pd1−P2 92.53(13), C1−Pd1−P1 170.87(14), P2−Pd1−P1 90.36(5), C1−Pd1−Br1 84.99(13), P2−Pd1−Br1 176.05(4), P1−Pd1−Br1 91.63(4), C2−Pd2−P4 90.35(13), C2−Pd2−P3 176.17(14), P4−Pd2−P3 93.31(5), C2−Pd2−Br2 84.36(13), P4−Pd2−Br2 173.67(4), P3−Pd2−Br2 91.92(4).

palladacycles falls in the range of diphosphine bite angles typically observed in Pd(II) DPPP complexes.[11] As expected, the bond lengths of Pd1−P1 and Pd2−P3 are markedly longer than those of Pd1−P2 and Pd2−P4, respectively, due to the *trans*-influence of dicarbene ligand. Lastly, the interpalladium distance of 6.080 Å is longer than that in complex *all-cis*-**2**, probably due to the repulsion of the two bulky diphosphine ligands.

Our previous study has revealed that palladium carbene complexes with labile acetato coligands are superior catalyst precursors compared to those with halido coligands.[4a,12] Thus, tetrabromido complex *all-cis*-**2** was treated with four equivalents of silver acetate, affording the tetra-acetato complex *all-cis*-[Pd(O$_2$CCH$_3$)$_2$(PPh$_3$)]$_2$(μ-ditz) (*all-cis*-**4**) as the major product along with minor amounts of another inseparable isomer, *cis-trans*-[Pd(O$_2$CCH$_3$)$_2$(PPh$_3$)]$_2$(μ-ditz) (*cis-trans*-**4**) in a ratio of ∼3:1, as indicated by ^{1}H NMR spectroscopy (Scheme 4).

The ^{1}H NMR spectrum of the major product *all-cis*-**4** shows two singlets at 1.69 and 1.42 ppm for the four CH$_3$ groups of the acetato ligands. The two sets of *N*-CH$_3$ groups of the dicarbene ligand resonate at 4.27 and 3.10 ppm in an intensity ratio of 1:2, respectively. As expected, the two *cis*-standing PPh$_3$ ligands give only one singlet at 25.2 ppm in the ^{31}P NMR spectrum of *all-cis*-**4**.

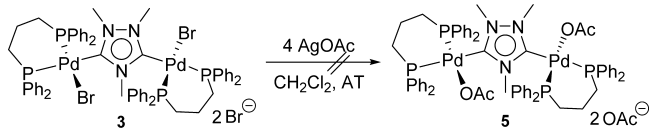
The formation of the *cis*−*trans* isomer, as the minor product, was clearly verified by the three singlets at 4.14, 3.32, and 2.97 ppm of equal intensity observed for the inequivalent *N*-CH$_3$ groups of the dicarbene ligand. The absence of the 2-fold symmetry for this isomer is further corroborated by ^{31}P NMR spectroscopy, which displays two singlets at 25.3 and 23.9 ppm for the two inequivalent phosphine ligands. The ^{13}C NMR signals due to the carbene donors and the carbonyl groups of *all-cis*- and *cis-trans*-**4** fall in a narrow range (171.8−178.0 ppm) and have not been assigned further.

The formation of complex **4** bearing acetato ligands is also supported by ESI mass spectrometry with dominant peaks at m/z 1026 for [M − CH$_3$COO]$^+$ species.

^{1}H NMR spectroscopy monitoring of **4** reveals insignificant change of the isomeric ratio. Due to the more labile nature of acetato coligands, complex **4** is less stable in contrast to the bromido precursor *all-cis*-**2**. Slow decomposition of **4** to palladium black was observed in solution upon standing for 1 d.

Attempts to prepare the diphosphine-acetato complex [Pd(OAc)(DPPP)]$_2$(μ-ditz)(OAc)$_2$ (**5**) using complex **3** as the precursor failed (Scheme 5). Instead, fast decomposition to palladium black was observed. The increased steric repulsion brought about by more bulky acetato versus bromido coligands in an already crowded complex may account for the instability of complex **5**.

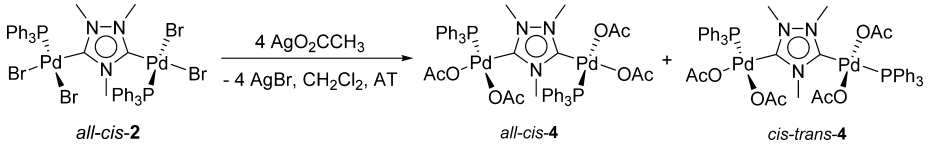
Scheme 5. Attempt to Synthesize Diphosphine-acetato Complex 5



Synthesis of Mononuclear Equivalents. Previous work[3,4a] has suggested that the catalytic performance could be enhanced as a result of synergistic effects between two catalytically active metal centers linked by a triazolidine-diylidene ligand. To examine the potential cooperativity exerted by the two linked Pd(II) centers in the ditz complexes described herein, their corresponding mononuclear equivalents were synthesized. It should be noted that an earlier study on the electronic communication across triazolidine-diylidene employed 1,3-dibutylimidazolin-2-ylidene as the supporting ligand in the mononuclear counterparts.[3h] However, this imidazole-based carbene is not a suitable monocarbene equivalent due to its much stronger donating ability and different sterical demand compared to trimethyltriazolidine-diylidene studied herein, which is known to be a rather weak donor.[4a,7c] In contrast, triazolin-5-ylidene, as one of the weakest NHCs[7c] and therefore closest to the ditz, was selected as a monocarbene equivalent.

As shown in Scheme 6, the triazolium precursor salt tazy·H$^+$I$^-$ (**B**, tazy = 1,4-dimethyl-1,2,4-triazolin-5-ylidene) was prepared via a slightly modified approach[13] by methylation of 1-methyltriazole with iodomethane. To avoid ligand scrambling in the subsequent metalation step, salt **B** was subjected to an anion metathesis reaction with NaBF$_4$. Similar to bis(acetonitrile) complex *all-trans*-**1**, the monopalladium complex *trans*-[PdBr$_2$(CH$_3$CN)(tazy)] (**6**) was prepared in a good yield

Scheme 4. Synthesis of Dipalladium(II) Tetra-acetato Complex 4



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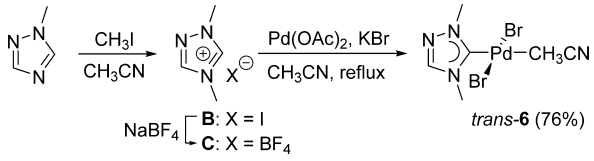
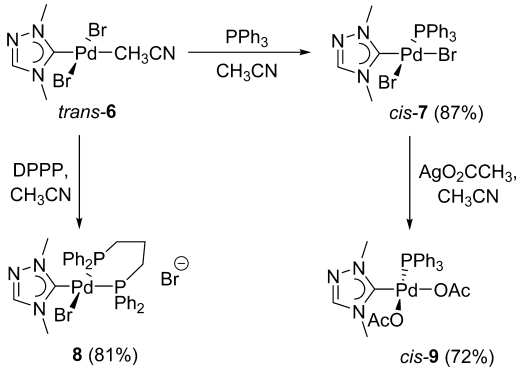
Scheme 6. Synthesis of Pd(II) Triazolin-5-ylidene Acetonitrile Complex *trans*-6



of 76% by reaction of salt **C**, $Pd(OAc)_2$, and excess KBr in CH_3CN.

Complex *trans*-**6** can be exploited as a precursor, and ligand replacement reactions employing PPh_3 and DPPP ligands gave the complexes *cis*-$[PdBr_2(PPh_3)(tazy)]$ (**7**) and $[PdBr(DPPP)(tazy)]Br$ (**8**) in decent yields of 87% and 81%, respectively (Scheme 7). Bromido abstraction of *cis*-**7** was achieved by using

Scheme 7. Synthesis of Mono-Pd(II) Triazolin-5-ylidene Complexes *cis*-7, 8, and *cis*-9



2 equiv of AgO_2CCH_3, affording the desired mixed phosphine/acetato complex *cis*-**9**.

All the newly synthesized mono-Pd(II) triazolin-5-ylidene complexes **6**–**9** were identified by multinuclei NMR spectroscopy and further corroborated by ESI-mass spectrometry. In addition, the formation of *cis*-**7** was confirmed by X-ray diffraction analysis on the single crystals obtained by slow evaporation of a concentrated CH_2Cl_2/*n*-hexane solution. The solid-state molecular structure is depicted in Figure 5. As expected, it exhibits square planar geometry with the palladium center surrounded by PPh_3, one triazolin-5-ylidene ligand, and two *cis*-oriented bromido coligands. Comparison of *cis*-**7** with its dinuclear counterpart *all-cis*-**2** revealed that all the key bond parameters are essentially equal within 3σ.

Catalytic Study. Arylated imidazoles are known to exhibit a variety of interesting biological properties,[14] and they can be accessed via transition metal-catalyzed arylation from imidazoles and aryl halides. In this regard, a few well-defined precatalysts[15] have been reported, but surprisingly NHCs have rarely been exploited as ancillary ligands in such arylation catalysis.[15a,b] In a preliminary study, direct C5-arylation of 1-methylimidazoles was attempted using all the triazolidine-3,5-diylidene and triazolin-5-ylidene complexes described herein as catalyst precursors.

The arylation of 1-methylimidazole with 4-bromoacetophenone at 2.5 mol % catalyst loading (based on Pd) and a reaction time of 18 h at 140 °C was chosen as a standard test reaction to compare the performance of different precatalysts (Table 1).

All the newly synthesized complexes proved to be catalytically active in this regioselective arylation reaction. It should be

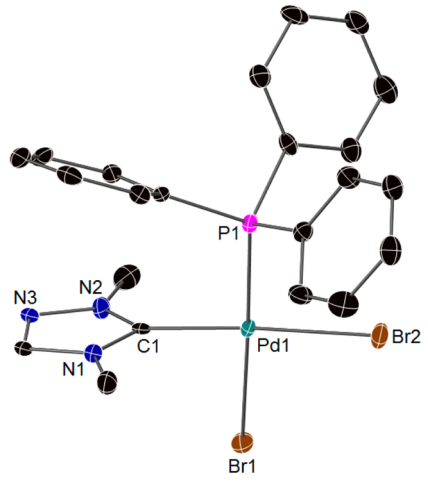


Figure 5. Molecular structure of *cis*-**7** showing 50% probability ellipsoids. Hydrogen atoms, solvent molecules, and bromide anions are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Pd1–C1 1.988(5), Pd1–P1, 2.2686(14), Pd1–Br2 2.4510(7), Pd1–Br1 2.4758(7); C1–Pd1–P1 93.19(14), C1–Pd1–Br2 176.18(14), P1–Pd1–Br2 90.36(4), C1–Pd1–Br1 85.26(14), P1–Pd1–Br1 178.32(4), Br2–Pd1–Br1 91.16(2), N2–C1–N1 104.5(4).

noted that a previous computational study reported that the free energy of activation for C–H functionalization of 1-methylimidazoles follows the order C4 ≫ C2 ≥ C5.[16] Due to the comparable energy for C2–H and C5–H activation, the formation of C2,C5-diarylated imidazoles was commonly observed in the previously reported catalytic systems. Interestingly, in all the entries of Table 1, C5-monoarylated imidazole was afforded as the predominant product and only a negligible amount of C2,C5-diarylated product was found.

Dipalladium(II) triazolidine-3,5-diylidene complexes are found to be generally superior compared to their mononuclear equivalents (entries 1–8), which supports a potential synergistic effect by the two palladium centers linked by the triazolidine-diylidene ligand. To quantify and compare the cooperative effects, the cooperativity index (a) proposed by Jones and James[17] was calculated using eqs 1 and 2 and is listed in Table 1. In our cases, A_O and A_P were taken as the yields obtained in the dinuclear and mononuclear systems, respectively. The highest index value a = 0.67 obtained from entries 3 and 4 revealed the strongest synergistic effect in mixed dicarbene/bis(phosphine) complex *all-cis*-**2**. However, the relationship between the cooperativity effect and the ancillary ligands remains to be explored in the future.

$$\bar{A} = \frac{A_P}{n} \quad (1)$$

$$a = \frac{A_O - A_P}{\bar{A}} \quad (2)$$

Among all the precatalysts, mixed dicarbene/diphosphine complex **3** and mixed dicarbene/monophosphine complex **4** with acetato coligands are found to be the two best catalytic performers. Nevertheless, when a more challenging substrate, 4-chloroacetophenone, was used, a dramatic decrease of the yield was observed (entry 3 vs 9, entry 4 vs 10). The yields, however, can be slightly improved by using TBAB (TBAB = tetrabutylammonium bromide) as an additive (entries 9 and 10 vs entries 11 and 12). Here, complex **3** performs slightly better compared to acetato complex **4** (entry 11 vs entry 12).

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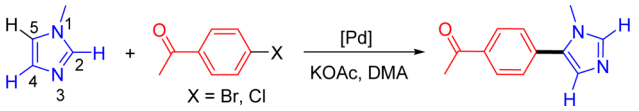
Table 1. Direct C5-Arylation Reaction of 1-Methylimidazole Catalyzed by Complexes 1−4 and 6−9[a]

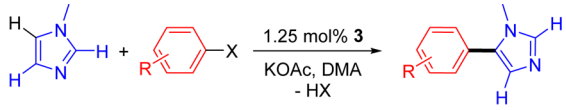


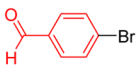
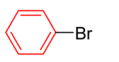
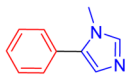
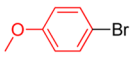
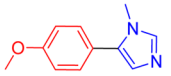
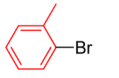
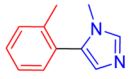
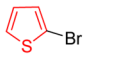
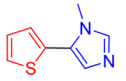
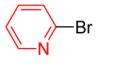
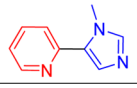
entry	catalyst	aryl halide	yield [%][b]	cooperativity index (a)
1	*all-trans*-**1**	4-bromoacetophenone	51	0.43
2	*trans*-**6**	4-bromoacetophenone	42	
3	*all-cis*-**2**	4-bromoacetophenone	60	0.67
4	*cis*-**7**	4-bromoacetophenone	45	
5	**3**	4-bromoacetophenone	70	0.37
6	**8**	4-bromoacetophenone	59	
7	**4**	4-bromoacetophenone	72	0.53
8	*cis*-**9**	4-bromoacetophenone	57	
9	**3**	4-chloroacetophenone	11	
10	**4**	4-chloroacetophenone	2	
11[c]	**3**	4-chloroacetophenone	32	
12[c]	**4**	4-chloroacetophenone	20	

[a]Reaction conditions generally not optimized. Reaction conditions: 0.5 mmol of aryl halide, 0.75 mmol (1.5 equiv) of 1-methylimidazole, 1.25 mol % of dipalladium precatalysts or 2.5 mol % of monopalladium precatalysts, 1.0 mmol (2.0 equiv) of KOAc, DMA (1 mL), 140 °C, 18 h. [b]GC yields using naphthalene as internal standards in an average of two runs. [c]With addition of 0.1 mmol (20% equiv) of $[N(n\text{-}C_4H_9)_4]Br$.

Using complex **3** as the best performer, a selection of electronically and sterically varied aryl halides as well as heteroaryl halides were examined in a small substrate scope study. The results are summarized in Table 2. Moderate yields can be achieved in nearly all the entries. Electron-deficient aryl halides seem to be more suitable compared to the electron-rich ones (entries 1−3). The S-donor of 2-bromothiophene does not undermine the catalytic activity (entry 5). The reaction in entry 6 is rather sluggish where the more challenging substrate 2-bromopyridine with a stronger N-donor was exploited.

Table 2. Direct C5-Arylation Reaction Catalyzed by Complexes 3[a]



Entry	Catalyst	Aryl halide	Product	Yield [%][b]
1	**3**			54
2	**3**			53
3[c]	**3**			42
4[c]	**3**			35
5[c]	**3**			62
6[c]	**3**			trace

[a]Reaction conditions: 0.5 mmol of aryl halide, 0.75 mmol (1.5 equiv) of 1-methylimidazole, 1.25 mol % of **3**, 1.0 mmol (2.0 equiv) of KOAc, 140 °C, 18 h. [b]Isolated yields in an average of two runs. [c]With addition of 0.1 mmol (20% equiv) of $[N(n\text{-}C_4H_9)_4]Br$.

CONCLUSION

We have synthesized a series of new dipalladium(II) complexes (**1−4**) with a Janus-type triazolidine-diylidene linker and mono/diphosphines as ancillary ligands. It has been demonstrated that CH_3CN-coordinated complex *all-trans*-$[PdBr_2(CH_3CN)]_2(\mu\text{-ditz})$ (**1**) is a suitable precursor for the further ligand replacement reactions. In the case of mixed dicarbene/bis(phosphine) complex $[PdBr_2(PPh_3)]_2(\mu\text{-ditz})$ (**2**), the *all-cis* isomer is found to be thermodynamically favorable, which has been confirmed by NMR spectroscopy and X-ray diffraction analysis. Bromido substitution of *all-cis*-**2** with AgO_2CCH_3 furnished the tetra-acetato complex $[Pd(CH_3COO)_2(PPh_3)]_2(\mu\text{-ditz})$ (**4**), with the *all-cis* isomer as the predominant product, but the *cis−trans* form was also detected in small amounts. All the dipalladium triazolidine-diylidene complexes proved to be active in direct catalytic C5-arylation of 1-methylimidazoles and show superior performance in comparison to their mononuclear equivalents, indicating a cooperativity effect of the two bridged Pd centers. Current work in our laboratory is focused on broadening the ancillary ligand diversity of dipalladium triazolidine-diylidene complexes and extending their scope to metallo-supramolecular carbene chemistry.

EXPERIMENTAL SECTION

General Considerations. Unless otherwise stated, all manipulations were carried out without taking precautions to exclude air and moisture. All chemicals and solvents were used as received without further purification if not mentioned otherwise. Precursor salts 1,2,4-trimethyl-1,2,4-triazolium tetrafluoroborate (**A**) and 1,4-dimethyl-1,2,4-triazolium iodide (**B**) were synthesized as reported.[4a,13] Triazolium iodide salt **B** was converted to its tetrafluoroborate analogue **C** via salt metathesis reaction by stirring with $NaBF_4$ in acetone overnight at ambient temperature. ^1H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on 300 and 500 MHz spectrometers, and the chemical shifts (δ) were internally referenced to the residual solvent signals relative to tetramethylsilane (^1H and ^{13}C) or externally to 85% H_3PO_4 (^{31}P) and CF_3CO_2H (^{19}F). ESI mass spectra were measured using a LCQ spectrometer. Elemental analyses were performed on a Vario Micro Cube elemental analyzer at the Department of Chemistry, National University of Singapore.

Synthesis of *all-trans*-$[PdBr_2(CH_3CN)]_2(\mu\text{-ditz})$ (1). 1,2,4-Trimethyl-1,2,4-triazolium tetrafluoroborate (**A**) (77 mg, 0.27 mmol), $Pd(OAc)_2$ (124 mg, 0.55 mmol), and KBr (297 mg, 2.5 mmol) were mixed in CH_3CN (10 mL). The reaction mixture was stirred and heated at 60 °C for 6 h. The resulting suspension was cooled and filtered through Celite. The filtrate was collected and concentrated. Column chromatography (SiO_2) followed by *n*-hexane precipitation gave the product as a yellow solid (141 mg, 0.194 mmol, 72%). ^1H NMR (500 MHz, CD_3CN): δ 4.31 (s, 3 H, NCH_3), 4.25 (s, 6 H, NCH_3), 1.94 (s, CH_3CN). $^{13}C\{^1H\}$ NMR (125.76 MHz, CD_3CN): δ 160.6 (NCN), 118.3 (CH_3CN), 41.6 (NCH_3), 38.8 (NCH_3), 1.38 (CH_3CN). Anal. Calcd for $C_9H_{15}Br_4N_5Pd_2$: C, 14.90; H, 2.08; N, 9.65. Found: C, 14.74; H, 2.14; N, 9.57. MS(ESI): m/z 749 $[M + Na]^+$.

Synthesis of *all-cis*-$[PdBr_2(PPh_3)]_2(\mu\text{-ditz})$ (2). Complex *all-trans*-$[PdBr_2(CH_3CN)]_2(\mu\text{-ditz})$ (**1**) (73 mg, 0.1 mmol) and PPh_3 (53 mg, 0.2 mmol) were mixed in CH_3CN (10 mL). The reaction mixture was stirred and heated at 80 °C overnight. All the volatiles were removed *in vacuo*, and the yellow residue was washed with diethyl ether (3 × 5 mL). Column chromatography (SiO_2) gave the product as a yellow solid (110 mg, 0.094 mmol, 94%). ^1H NMR (300 MHz,

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CD_2Cl_2): δ 7.52−7.49 (m, 30 H, Ar−H), 4.08 (s, 3 H, NCH_3), 2.96 (s, 6 H, NCH_3). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2): δ 176.7 (NCN), 134.8 (d, Ar−C, ^2J(P,C) = 19 Hz), 132.0 (d, Ar−C, ^4J(P,C) = 3 Hz), 129.4 (d, Ar−C, ^1J(P,C) = 54 Hz), 129.3 (d, Ar−C, ^3J(P,C) = 11 Hz), 41.4 (NCH_3), 36.5 (NCH_3). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2): δ 28.0 (s, PPh_3). Anal. Calcd for $C_{41}H_{39}Br_4N_3P_2Pd_2$: C, 42.15; H, 3.37; N, 3.60. Found: C, 42.37; H, 3.77; N, 3.42. MS(ESI): *m/z* 1121 $[M - Br + CH_3OH]^+$.

Synthesis of [PdBr(DPPP)]$_2$(μ-ditz)Br$_2$ (3). Complex *all-trans*-$[PdBr_2(CH_3CN)]_2$(μ-ditz) (**1**) (73 mg, 0.1 mmol) and 1,3-bis(diphenylphosphino)propane (83 mg, 0.2 mmol) were mixed, and CH_3CN (10 mL) was added. The reaction mixture was stirred overnight at ambient temperature, yielding a pale yellow suspension. All the volatiles were removed *in vacuo*, and the residue was washed with diethyl ether (3 × 5 mL) followed by ice-cold acetone (2 × 3 mL). The residue was dried *in vacuo*, yielding an off-white solid. Crystallization from a concentrated CH_2Cl_2 solution afforded the analytically pure product (125 mg, 0.085 mmol, 85%). ^1H NMR (500 MHz, DMSO-d_6): δ 8.09 (br, s, 4 H, Ar−H), 7.73−7.69 (m, 6 H, Ar−H), 7.56−7.35 (m, 21 H, Ar−H), 7.21 (br, s, 9 H, Ar−H), 3.89 (s, 3 H, NCH_3), 3.18 (s, 6 H, NCH_3), 2.82, 2.58, 1.21 (br m, 12 H, PCH_2 and PCH_2CH_2). ^{13}C NMR (125.76 MHz, DMSO-d_6): 178.4 (d, NCN, ^2J(P,C) = 151 Hz), 134.4, 134.3, 134.0, 133.9, 132.8, 132.6, 132.2, 131.9, 131.5, 131.4, 130.9, 130.5, 129.8, 129.7, 129.1, 129.0, 128.3, 128.0, 127.8, 125.9, 125.5 (Ar−C), 36.9, 30.7 (NCH_3), 23.8, 23.5, 22.2, 21.9, 17.6 (PCH_2 and PCH_2CH_2). $^{31}P\{^1H\}$ NMR (202.45 MHz, DMSO-d_6): δ 9.7, −1.9 (d, $PPh_2(CH_2)_3PPh_2$, ^2J(P,P) = 35 Hz). Anal. Calcd for $C_{59}H_{61}Br_4N_3P_4Pd_2$: C, 48.26; H, 4.19; N, 2.86. Found: C, 48.42; H, 4,24; N, 2.93. MS(ESI): *m/z* 654 $[M - 2Br]^{2+}$, 1389 $[M - Br]^+$.

Synthesis of [Pd(CH$_3$COO)$_2$(PPh$_3$)]$_2$(μ-ditz) (4). Complex *all-cis*-**2** (58 mg, 0.05 mmol) and AgO_2CCH_3 (35 mg, 0.21 mmol) were mixed in CH_2Cl_2 (10 mL). The reaction mixture was stirred at ambient temperature for 6 h in the dark. The precipitate was filtered off via Celite, and the filtrate was evaporated *in vacuo* to yield the product as an off-white solid (37 mg, 0.034 mmol, 68%). Overlapping and signals that cannot be unambiguously assigned are indicated with an asterisk (*). *all-cis*-**4**: ^1H NMR (300 MHz, $CDCl_3$): δ 7.49−7.38 (m, 30 H, Ar−H*), 4.27 (s, 3 H, NCH_3), 3.10 (s, 6 H, NCH_3), 1.69, 1.42 (s, 12 H, CH_3COO*). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 178.0, 177.6, 177.5, 177.4, 177.3, 172.0, 171.8 (NCN* and CH_3COO*), 134.7 (d, Ar−C, *J*(P,C) = 11 Hz), 132.6 (d, Ar−C, ^4J(P,C) = 2 Hz), 129.7 (d, Ar−C*, *J*(P,C) = 11 Hz), 127.5 (d, Ar−C, ^1J(P,C) = 55 Hz), 40.4 (NCH_3), 36.9 (NCH_3), 23.8, 23.3 (CH_3COO*). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): δ 25.2 (s, PPh_3). *cis-trans*-**4**: ^1H NMR (300 MHz, $CDCl_3$): δ 7.49−7.38 (m, 30 H, Ar−H*), 4.14, 3.32, 2.97 (s, 9 H, NCH_3), 1.69, 1.47, 1.45, 1.42 (s, 12 H, CH_3COO*). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 178.0, 177.6, 177.5, 177.4, 177.3, 172.0, 171.8 (NCN* and CH_3COO*), 132.7 (d, Ar−C, ^3J(P,C) = 10 Hz), 130.0 (Ar−C*), 129.2 (d, Ar−C, ^2J(P,C) = 12 Hz), 127.6 (d, Ar−C, ^1J(P,C) = 55 Hz), 40.7. 37.2, 36.2 (NCH_3), 24.0, 23.8, 23.3 (CH_3COO*). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): δ 25.3, 23.9 (s, PPh_3). Anal. Calcd for $C_{49}H_{51}N_3O_8P_2Pd_2 \cdot 1.25CH_2Cl_2$: C, 50.68; H, 4.53; N, 3.53. Found: C, 50.77; H, 4.87; N, 3.88. MS(ESI): *m/z* 1026 $[M - CH_3COO]^+$.

Synthesis of *trans*-[PdBr$_2$(CH$_3$CN)(tazy)] (6). 1,4-Dimethyl-1,2,4-triazolium tetrafluoroborate (**C**) (255 mg, 1.38 mmol), $Pd(OAc)_2$ (310 mg, 1.38 mmol), and KBr (820 mg, 6.89 mmol) were mixed in CH_3CN (10 mL). The reaction mixture was stirred and heated at 70 °C overnight. The resulting suspension was cooled and filtered through Celite. The filtrate was collected and concentrated. Column chromatography (SiO_2) followed by *n*-hexane precipitation gives the product as a brown-yellow solid (424 mg, 1.05 mmol, 76%). ^1H NMR (300 MHz, CD_3CN): δ 8.20 (s, 1 H, NCHN), 4.10 (s, 3 H, NCH_3), 3.94 (s, 3 H, NCH_3), 1.94 (s, CH_3CN). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_3CN): δ 163.1 (NCN), 145.3 (NCHN), 40.4 (NCH_3), 36.1 (NCH_3). No correct elemental analysis could be obtained for this compound, despite several attempts. MS(ESI): *m/z* 1009 $[3\ M - Br - 3CH_3CN]^+$, 688 $[2\ M - Br - CH_3CN]^+$.

Synthesis of *cis*-[PdBr$_2$(PPh$_3$)(tazy)] (7). Complex *trans*-**6** (40 mg, 0.1 mmol) and PPh_3 (27 mg, 0.1 mmol) were mixed and heated in CH_3CN at 80 °C overnight. All the volatiles were removed, and the residue was washed with diethyl ether (3 × 5 mL), affording the product as a yellow solid (54 mg, 0.087 mmol, 87%). ^1H NMR (300 MHz, CD_2Cl_2): δ 7.69−7.37 (m, 16 H, Ar−H), 3.77 (s, 3 H, NCH_3), 3.58 (s, 3 H, NCH_3). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2): δ 169.1 (NCN), 143.4 (NCHN), 134.3 (d, *J*(P,C) = 11 Hz, Ar−C), 131.7 (d, ^4J(P,C) = 2 Hz, Ar−C), 130.3 (d, ^1J(P,C) = 54 Hz, Ar−C), 128.9 (d, *J*(P,C) = 11 Hz, Ar−C), 39.8 (NCH_3), 35.4 (NCH_3). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2): δ 26.9 (s, PPh_3). Anal. Calcd for $C_{22}H_{22}Br_2N_3PPd$: C, 42.24; H, 3.54; N, 6.72. Found: C, 42.01; H, 3.42; N, 6.42. MS(ESI): *m/z* 577 $[M - Br + CH_3OH]^+$.

Synthesis of [PdBr(DPPP)(tazy)]Br (8). Complex *trans*-**6** (40 mg, 0.1 mmol) and 1,3-bis(diphenylphosphino)propane (42 mg, 0.1 mmol) were mixed and stirred in CH_3CN at ambient temperature overnight. All the volatiles were removed *in vacuo*, and the residue was washed with diethyl ether (3 × 5 mL), affording the product as an off-white solid (63 mg, 0.081 mmol, 81%). ^1H NMR (500 MHz, DMSO-d_6): δ 8.38 (s, 1 H, NCHN), 7.84−7.27 (m, 20 H, Ar−H), 3.63 (s, 3 H, NCH_3), 3.58 (s, 3 H, NCH_3), 3.19−3.01 (m, 2 H, CH_2), 2.76−2.67 (m, 2 H, CH_2), 1.95−1.76 (m, 2 H, CH_2). $^{13}C\{^1H\}$ NMR (125.76 MHz, DMSO-d_6): δ 172.4 (d, NCN, ^2J(C,P) = 154 Hz), 144.7 (NCHN), 133.4, 133.3, 133.2, 133.1, 132.6, 132.3, 132.2, 132.0, 131.8, 131.4, 131.2, 130.0, 129.8, 129.8, 129.4, 129.3, 129.1, 129.0, 128.9, 128.8, 128.7 (Ar−C), 34.9 (NCH_3), 23.6, 23.4, 22.8, 22.7, 22.6, 22.5, 17.9 (PCH_2 and PCH_2CH_2). The ^{13}C NMR resonance due to the second NCH_3 group accidentally overlaps with the DMSO-d_6 solvent residual signal. $^{31}P\{^1H\}$ NMR (202.45 MHz, DMSO-d_6): δ 11.4, −2.2 (d, $PPh_2(CH_2)_3PPh_2$, ^2J(P,P) = 40 Hz). Anal. Calcd for $C_{31}H_{33}Br_2N_3P_2Pd \cdot 0.75CH_2Cl_2$: C, 45.43; H, 4.14; N, 5.01. Found: C, 45.31; H, 3.64; N, 5.09. MS(ESI): *m/z* 696 $[M - Br]^+$.

Synthesis of *cis*-[Pd(CH$_3$COO)$_2$(PPh$_3$)(tazy)] (9). Complex *cis*-**7** (63 mg, 0.1 mmol) and AgO_2CCH_3 (35 mg, 0.21 mmol) were mixed, and CH_2Cl_2 (10 mL) was added. The reaction mixture was stirred at ambient temperature for 6 h in the dark. The precipitate was filtered off via Celite, and the filtrate was evaporated *in vacuo* to yield the product as an off-white solid (42 mg, 0.072 mmol, 72%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.61−7.38 (m, 16 H, Ar−H), 3.88 (s, 3 H, NCH_3), 3.63 (s, 3 H, NCH_3), 2.51, 1.87 (s, 6 H, CH_3COO). Overlapping and signals that cannot be unambiguously assigned are indicated with an asterisk (*). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$): δ 177.9 (NCN or CH_3COO*), 143.7 (NCHN), 134.6 (d, ^2J(P,C) = 12 Hz, Ar−C), 132.2 (br s, Ar−C), 129.4 (d, ^3J(P,C) = 11 Hz, Ar−C), 128.8 (d, ^1J(P,C) = 54 Hz, Ar−C), 40.2, 35.6 (NCH_3), 24.1, 23.3 (s, CH_3COO). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): δ 24.9 (PPh_3). No correct elemental analysis could be obtained for this compound, despite several recrystallization attempts. MS(ESI): *m/z* 525 $[M - OAc]^+$.

General Procedure for Regioselective C5 Arylation of 1-Methylimidazoles. In a typical run, a 25 mL Schlenk tube was charged with 1-methylimidazole (60 μL, 0.75 mmol), KOAc (98.2 mg, 1.0 mmol), aryl halide (0.5 mmol), 1.25 mol % of dipalladium precatalysts or 2.5 mol % of monopalladium precatalysts, and DMA (1 mL). The reaction mixture was sealed and heated at 140 °C for 18 h. The reaction mixture was cooled to ambient temperature, and H_2O (5 mL) was added, followed by extraction with ethyl acetate (3 × 10 mL). The organic phases were collected and dried over Na_2SO_4. All the volatiles were removed *in vacuo*, and the product was isolated by column chromatography and analyzed by ^1H NMR spectroscopy.

X-ray Diffraction Studies. X-ray data for *all-cis*-**2**·1.5CH_2Cl_2, **3**·3CH_2Cl_2·H_2O, and *cis*-**7** were collected with a Bruker AXS SMART APEX diffractometer, using Mo Kα radiation at 100(2) K with the SMART suite of programs.[18] Data were processed and corrected for Lorentz and polarization effects with SAINT[19] and for absorption effects with SADABS.[20] Structural solution and refinement were carried out with the SHELXTL suite of programs.[21] The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. All non-hydrogen atoms were generally given anisotropic displacement parameters in the

final model. All H atoms were put at calculated positions. A summary of the most important crystallographic data is given in Table SI-1.

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic data for *all-cis*-**2**·1.5CH_2Cl_2, **3**·3CH_2Cl_2·H_2O, and *cis*-**7** as CIF files and a summary of the most important crystallographic data. 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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