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Hetero-dicarbene Complexes of Palladium(II): Syntheses and Catalytic Activities

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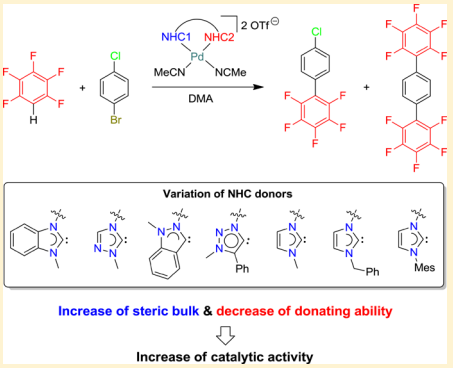
Supporting Information

ABSTRACT: A series of Pd(II) dibromido complexes **2**–**6** bearing *cis*-chelating hetero-dicarbenes, which contain two different types of NHCs linked by a propylene chain, have been synthesized. In most cases, the *N*-methylbenzimidazolin-2-ylidene moiety was kept as one NHC donor, while the other one varies with different heterocyclic backbones. As an exception, the hetero-diNHC in complex **8** is derived by combining 1,2,4-triazole and indazole precursors instead. Analogous complexes **9**–**17**, carrying more labile $CF_3CO_2^-$ or CH_3CN ligands, were synthesized by reacting the aforementioned bromido complexes with AgO_2CCF_3 or AgOTf in CH_3CN. A systematic catalytic comparison of **9**–**17** in the direct arylation of pentafluorobenzene with 4-chlorobromobenzene was carried out, and complexes that contain bulkier and less electron-donating ligands were found to be more active. Complex **12**, carrying the mesitylimidazolin-2-ylidene unit, proved to be the most efficient, and its activity was also tested in the direct arylation of tetrafluorobenzenes.



INTRODUCTION

N-Heterocyclic carbenes (NHCs) are ubiquitous ligands in contemporary organometallic chemistry, as they generally form complexes that possess high stabilities and diverse structures.[1] More important, they have found widespread applications in catalysis.[2] Both steric and electronic properties of NHCs are easily tunable by introducing different substituents at the nitrogen atoms, including alkyl, aryl, and various donor groups.[3] Moreover, two NHC moieties can be linked by alkyl/aryl bridges to form chelating ligands, the complexes of which usually feature enhanced stabilities and structural diversities.[4]

Another important way to modify NHCs is through changes in the backbones.[5] In addition to classical NHCs, which are derived from imidazole (**a**), benzimidazole (**b**), imidazoline (**c**), and 1,2,4-triazole (**d**), carbenes from many other heterocycles have been studied, such as indazole (**e**),[6] 1,2,3-triazole (**f**),[7] and pyrazole (**g**)[8] (Figure 1). The carbene donor atom of these nonclassical carbenes is not adjacent to two nitrogen atoms, and therefore they have different topologies and electronic features, which have been demonstrated to influence the properties and applications of the resulting complexes to a large extent.[5] Several studies on the comparison of different carbenes, mainly between imidazolin-2-ylidenes (**a**) and mesoionic imidazolin-4-ylidenes (**h**),[9] or mesoionic 1,2,3-triazolin-5-ylidenes[7] have been reported. Nevertheless, such systematic studies[6,8,10] are worth extending in particular to the direct comparison of various carbenes within the same complex.[8a−e,11]

Previously, we have reported the first two *cis*-chelating hetero-dicarbene complexes, which feature an imidazolin-2-ylidene unit linked to a benzimidazolin-2-ylidene moiety via a propylene linker.[12] Surprisingly, these were found to be more active in catalyzing Mizoroki–Heck reactions than their respective homo-dicarbene analogues bearing two of the same NHCs. The increased activity was ascribed to an electronic asymmetry in the complex as a result of two different NHC donors. In an extension of this research, we herein report the preparation of an extensive series of new hetero-diNHC complexes, in which one carbene is generally kept constant (i.e., benzimidazolin-2-ylidene), while the other carbene is systematically changed ranging from classical to nonclassical NHCs. Their catalytic activities in the direct arylation of polyfluorobenzene are compared in terms of sterics and electronics as well.

RESULTS AND DISCUSSION

Syntheses of Ligand Precursors. The syntheses of various hetero-diazolium salts containing two different heterocycles bridged by a propylene chain from the common electrophile **A** are summarized in Scheme 1. Alkylation of benzyl- and mesitylimidazole with **A** gives rise to dicationic salts **B**·2HBr and **C**·2HBr in yields of 88% and 85%, respectively. Similarly, the reaction of **A** with the less electron-rich 1-methyl-1,2,4-triazole yielded **D**·2HBr in 35% yield. The synthesis of **F**·$2HBF_4$, bearing both benzimidazolium and 1,2,3-triazolium moieties, was achieved by a two-step sequence. Salt **A** underwent a click reaction[13] when treated with NaN_3, copper powder, and phenyl acetylene to form **E**, which was subsequently alkylated with Me_3OBF_4, resulting in the dicationic salt **F**·$2HBF_4$ in a nonoptimized overall yield of 55%.

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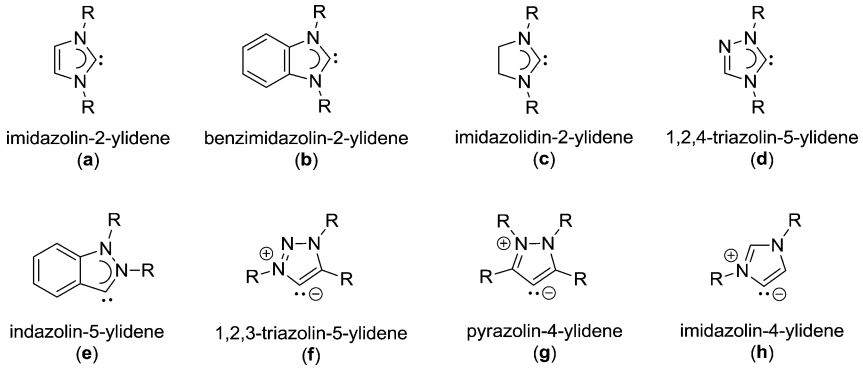
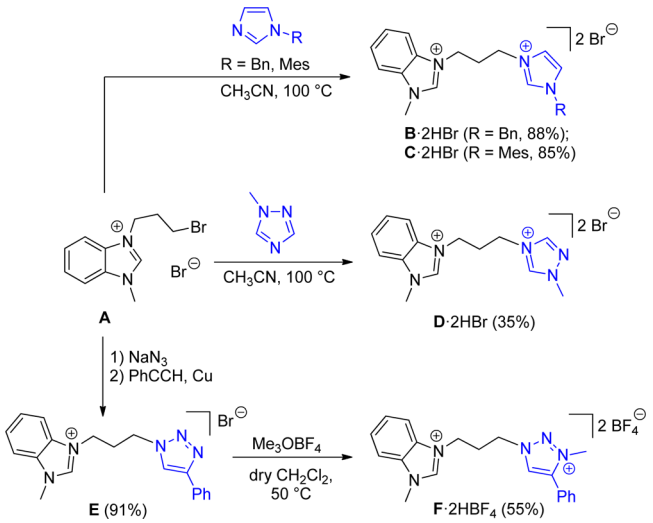


Figure 1. Selected different types of classical, nonclassical, and mesoionic NHCs.

Scheme 1. Syntheses of Propylene-Bridged Diazolium Salts (B–D)·2HBr and F·2HBF$_4$



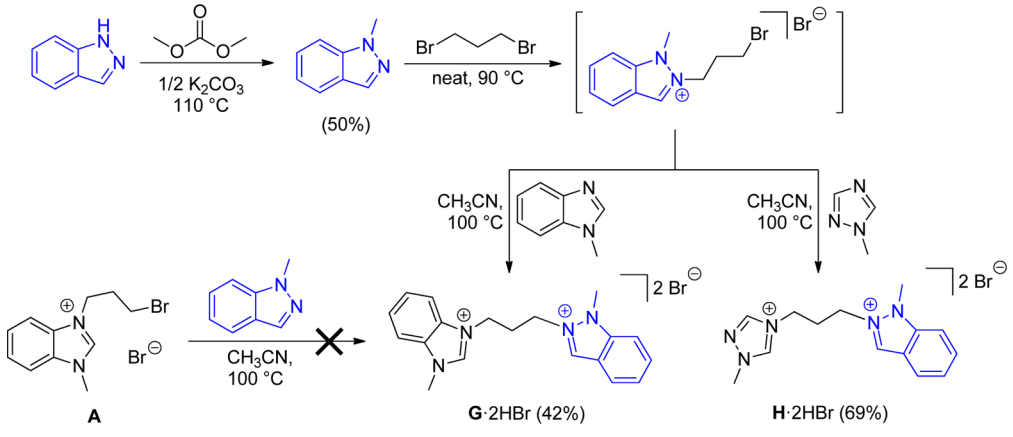
To synthesize the indazolium analogue **G**·2HBr, 1-methylindazole was prepared first by treating commercially available indazole with K_2CO_3 in neat dimethyl carbonate (Scheme 2). This reaction avoids the handling of alkyl halides or Me_2SO_4 and represents a greener and environmentally friendlier method to methylate indazole.

However, no reaction occurred when salt **A** was treated with 1-methylindazole, which is a rather weak nucleophile. The $-I$ effect of the neighboring nitrogen atom and the benzannulation lowers the electron density, which hampers the alkylation process. **G**·2HBr was finally synthesized from a different approach. 1-Methylindazole was treated with excess 1,3-dibromopropane to yield 2-(3-bromopropyl)-1-methylindazolium bromide, which further reacted with the stronger nucleophile 1-methylbenzimidazole to give the desired product in 42% yield. In analogy, salt **H**·2HBr, bearing both 1,2,4-triazolium and indazolium moieties, was prepared in 69% yield.

All salts were characterized by multinuclear NMR spectroscopies and ESI mass spectrometry. In their ^{1}H NMR spectra, two downfield signals in the range 10.32 to 9.16 ppm were observed for the acidic protons of both heterocycles. Three resonances in the range 5.04–2.55 ppm for the propylene bridge confirm the unsymmetrical nature of these compounds. In addition, signals assignable to the $[M - 2X]^{2+}$ and $[M - X]^+$ fragments supporting the formation of the expected salts were found in their positive mode ESI mass spectra.

Syntheses of Pd(II) Complexes. Following the procedure reported for the synthesis of hetero-diNHC complex **1** and homo-diNHC **7**,[12] palladium(II) complexes **2**–**6** and **8**, bearing chelating hetero-dicarbene ligands, were synthesized by reacting the respective diazolium salts with $Pd(OAc)_2$ in wet DMSO at an elevated temperature of 100 °C (Scheme 3). It is noteworthy that a dilute solution (0.3 mmol of staring materials in ~40 mL of DMSO) facilitates the formation of expected *cis*-chelate complexes. When the synthesis of **3** was carried out in a more concentrated solution (0.3 mmol of starting materials in 5 mL of DMSO), large amounts of a white powder insoluble in any organic solvent and water was observed, which may be attributed to the formation of polymeric products. Under

Scheme 2. Syntheses of Propylene-Bridged Diazolium Salts G·2HBr and H·2HBr



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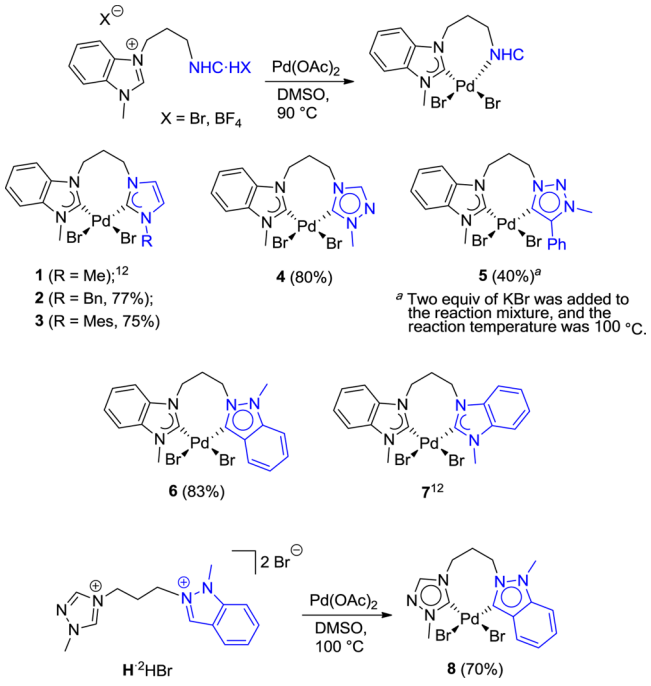
Scheme 3. Syntheses of Dibromido-Pd(II) Hetero-dicarbene Complexes 1−8



optimized conditions, all complexes, with the exception of **5**, were isolated in good yields of >70% as off-white to yellow powders. The lower yield of complex **5** can be ascribed to the more difficult deprotonation of the 1,2,3-triazolium moiety. In general, they are moderately soluble in DMSO and DMF, sparingly soluble in CH_3CN, and insoluble in chlorinated solvents, hydrocarbons, and diethyl ether.

Successful complexation was corroborated by the absence of the two downfield signals characteristic for the hetero-diazolium salts in the ^{1}H NMR spectra of most complexes. However, well-resolved NMR spectra for complexes **3**, **6**, and **8** could not be obtained due to their poor solubility. Generally, the ^{1}H NMR spectra show line-broadening due to the dynamic ring-flipping of the metallacyle, which is commonly observed in diNHC Pd(II) complexes, and further complicated by the unsymmetrical nature of hetero-diNHC ligands in particular.[12] In addition, all methylene protons of the bridges become diastereotopic upon complexation and give rise to a complicated pattern of signals in the range 5.58−1.86 ppm as a consequence of diastereotopy in the propylene bridge, which is evidence for the rigid chelating bonding mode of the hetero-diNHC ligands. In the ^{13}C NMR spectrum of **2**, two resonances at 174.6 and 161.0 ppm are assigned to the two carbene carbon atoms. However, the carbene signals of complexes **3**−**6** and **8** could not be resolved despite prolonged acquisition times.

Another proof for the complex formation comes from the ESI mass spectra of **2**−**4** and **6**, where signals assignable to the $[M - Br]^+$ fragments were observed. In the case of complex **5**, a signal at m/z 559 for the $[M - Br + CH_3CN]^+$ fragment was detected instead. Similarly, formation of complex **8** is supported by a signal at m/z 519, which can be assigned to the $[M - Br + DMSO]^+$ solvate.

Single crystals suitable for X-ray diffraction analysis of complex **4** were obtained by slow evaporation of a CH_3CN solution. The solid-state structure depicted in Figure 2 confirms the formation of **4** as a hetero-dicarbene Pd(II) complex. The

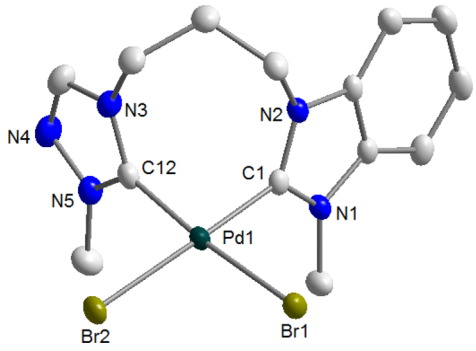


Figure 2. Molecular structure of **4** showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Pd1−C1 1.978(2), Pd1−C12 1.973(3), Pd1−Br2 2.4842(3), Pd1−Br1 2.4654(3); C12−Pd1−C1 86.21(10), C1−Pd1−Br1 90.64(7), Br1−Pd1−Br2 93.22(1), Br2−Pd1−C12 90.20(7), C12−Pd1−Br1 174.62(7), C1−Pd1−Br2 174.74(7).

square-planar Pd(II) center is coordinated by two bromido ligands and one bridging hetero-diNHC ligand in a *cis*-chelating manner. The lengths of the two Pd−C bonds are essentially equal within 3σ [1.978(2) and 1.973(3) Å, respectively], which are within the same range as reported data for the homoanalogues.[12,14] However, the Pd1−Br2 bond *trans* to the benzimidazole-derived carbene [2.4842(3) Å] is markedly longer than that *trans* to the 1,2,4-triazolin-5-ylidene [2.4654(3) Å], indicating a stronger *trans* influence of the benzimidazolin-2-ylidene, which is also in line with its stronger electron-donating ability previously determined by our ^{13}C NMR-based electronic parameter.[15,16] The bite angle amounts to 86.21(10)°, which is in the same range as those reported for other homo- and hetero-dicarbene systems.[12,14] The dihedral angles between the coordination plane and the carbene planes are 76° and 77°, respectively, which are also in the expected range.[12]

Previous studies have shown that more labile co-ligands can enhance the catalytic activities of pertinent complexes.[16] Thus, the bromido ligands of **1**−**8** were replaced with weaker ones by reacting with AgOTf in acetonitrile (Scheme 4). Despite having a triple bond, the acetonitrile ligand is not a suitable spectroscopic probe for the evaluation of ligands' donating abilities. In contrast to the commonly used and strongly π-accepting carbonyl ligand, acetonitrile is a poor π-acceptor. This is also evidenced from its position in the general spectrochemical series.[17] In combination with a Lewis acidic Pd(II) center, significant π-back-bonding can be excluded, and the resulting labile metal bonding can readily free up coordination sites for incoming substrates. To compare the influence of different co-ligands, the trifluoroacetato complex **9** was also synthesized by salt metathesis reaction of **3** with AgO_2CCF_3. In general, all complexes of **9**−**17** show improved solubilities, which is consistent with previous findings,[16] facilitating solution NMR data collection. In their ^{1}H NMR spectra, signals with similar splitting patterns to those of their respective precursors are found. In the ^{19}F NMR spectrum of **9**, the signal for the O_2CCF_3 groups is detected at 1.39 ppm. Similarly, the presence of OTf in **10**−**17** is supported by a resonance at around −3.00 ppm.

Moreover, a quartet at 122.1 ppm with a coupling constant of around 320 Hz is observed in the ^{13}C NMR spectra of **10**−**17**, which is characteristic for the CF_3 group. $^{13}C_{carbene}$ signals could be resolved only for complexes **10**, **12**, **13**, and **16**. Of the two

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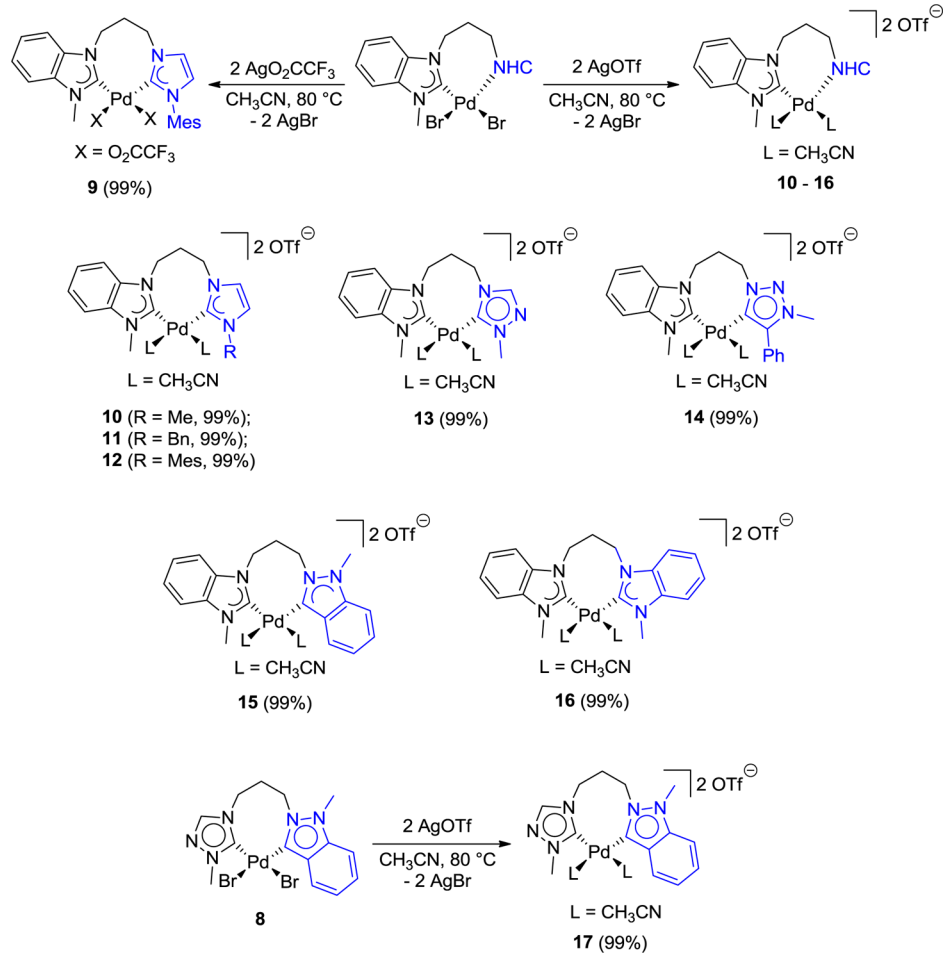
Scheme 4. Syntheses of Pd(II) Hetero-dicarbene Complexes Bearing Labile Co-ligands



carbene resonances observed in the hetero-diNHC complexes **10**, **12**, and **13**, the relatively more downfield one in the range 158.1−160.5 ppm is assigned to the constant benzimidazole-derived carbene, while signals for the other carbenes are found more upfield in the range 146.6−153.8 ppm. Expectedly, for the symmetrical homo-diNHC complex **16**, only one carbene signal is detected at 159.7 ppm.

In the ESI mass spectrum of the dicarboxylato complex **9**, two signals at *m*/*z* 578 and 1269 are observed, which are attributable to the $[M - O_2CCF_3]^+$ and $[2\ M - O_2CCF_3]^+$ fragments, respectively, lending support for the successful replacement of bromido with trifluoroacetato ligands. Similarly, signals assignable to the $[M - 2OTf]^{2+}$, $[M - OTf - 2CH_3CN]^+$, and $[M - OTf - CH_3CN]^+$ fragments in the mass spectra of **10**−**17** also provide evidence for the successful salt metathesis reactions.

The solid-state structures of complexes **9** and **12A** have been determined by X-ray diffraction analysis on single crystals obtained from solutions in CH_2Cl_2 (for **9**) and CH_2Cl_2 with adventitious DMSO (for **12A**), respectively. The molecular structures depicted in Figures 3 and 4 show that the bromido ligands have successfully been removed in both complexes. In the neutral complex **9**, two new trifluoroacetato ligands can be found. The Pd1−C12 bond [1.962(2) Å] is longer than the Pd1−C1 bond [1.950(2) Å], which may be due to the presence of the bulky mesityl group of the imidazole-derived carbene. The Pd1−O3 bond [2.075(1) Å] *trans* to benzimidazolin-2-ylidene is slightly longer than the Pd1−O1 bond [2.064(1) Å].

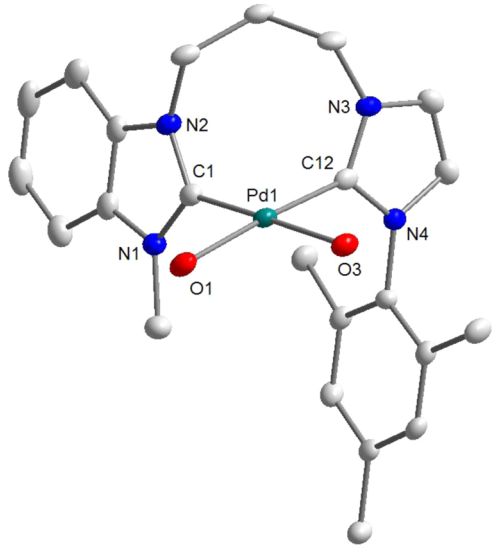


Figure 3. Molecular structure of **9**·CH_2Cl_2 showing 50% probability ellipsoids. Hydrogen atoms, the CH_2Cl_2 molecule, and the $[CF_3CO]$ fragments are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Pd1−C1 1.950(2), Pd1−C12 1.962(2), Pd1−O3 2.075(1), Pd1−O1 2.064(1); C1−Pd1−C12 88.93(8), C12−Pd1−O3 90.54(7), O3−Pd1−O1 87.31(6), O1−Pd1−C1 93.15(7), C1−Pd1−O3 178.41(7), C12−Pd1−O1 176.48(6).

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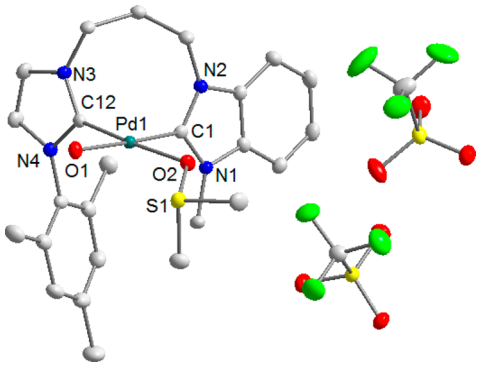

Figure 4. Molecular structure of **12A** showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Pd1−C12 1.957(2), Pd1−C1 1.932(2), Pd1−O2 2.092(1), Pd1−O1 2.094(1); C12−Pd1−C1 87.27(7), C1−Pd1−O2 88.32(6), O2−Pd1−O1 90.58(5), O1−Pd1−C12 93.77(6), C12−Pd1−O2 175.43(6), C1−Pd1−O1 177.13(6).

This elongation may be the result of steric interactions with the more bulky mesitylimidazolin-2-ylidene in close proximity. The bite angle amounts to 88.96(8)°, while the dihedral angles between the [PdC_2O_2] coordination plane and the carbene planes are 71° and 82°, respectively. The relatively large difference between the latter may be ascribed to cystal packing effects.

In the structure of complex **12A**, the initial acetonitrile ligands in **12** have been replaced by H_2O and DMSO molecules during crystallization. As a result of steric reasons and possibly of antisymbiosis,[18] the ambidentate DMSO ligand prefers to coordinate to the palladium center via the harder oxygen atom instead of the softer sulfur donor.[19] Two triflate counteranions balance the overall charge. The Pd1−C12 bond [1.957(2) Å] *trans* to DMSO is found to be longer than Pd1−C1 [1.932(2) Å], which may be again ascribed to the bulkiness of mesitylimidazolin-2-ylidene. The lengths of the two Pd−O bonds are the same within 3σ [2.092(1) and 2.094(1) Å]. The average Pd−C bonds in **12A** are shorter as compared to those in **9**. The Pd−O bonds, on the other hand, are elongated as a result of the coordination of weaker donating H_2O/DMSO ligands. The bite angle amounts to 87.27(7)°, which is comparable to the one determined for complex **9**. The dihedral angles between the [PdC_2O_2] coordination plane and the carbene planes are 89° and 79°.

Catalysis. The direct arylation of pentafluorobenzene straightforwardly functionalizes C−H bonds and avoids possible byproducts generated by classical C−C coupling reactions, and has gained increasing interest.[20,21] The catalytic cycle for this reaction, proposed with the help of computational studies, involves a series of steps including (i) oxidative addition of the aryl halide, (ii) ligand exchange reactions with the carbonate base, (iii) metal-assisted deprotonation and coordination of the pentafluorobenzene, and finally (iv) reductive elimination of the unsymmetrical biaryl.[20,21a,22] The order of these steps in this concerted metalation−deprotonation (CMD) pathway could not be ascertained, and multiple simultaneous mechanisms may be involved under certain conditions. Nevertheless, it is conceivable that a fine-tuning of the stereoelectronic properties of the catalyst will have some effect on these individual steps. A well-balanced electron donation from the ligands can influence oxidative addition and ligand exchange reactions, while increased steric bulk should favor reductive eliminations, which are all crucial steps in the proposed CMD mechanism.

Since a previous study has also revealed that bromido complexes perform poorly in this reaction, only complexes **9**−**17** were considered in this study.[16] To compare the catalytic performances, which considers both the activity and stability of hetero-dicarbene complexes, and to study the influence of different co-ligands and types of NHCs on this reaction, these complexes were screened in the reaction between 4-chlorobromobenzene and 3 equiv of pentafluorobenzene (Table 1).

For practicality reasons and to provide a simple and general procedure, drying of the solvent was not required for this catalytic study, and the more challenging 4-chlorobromobenzene substrate was chosen to discern differences in the activation of Cl versus Br in this reaction. Furthermore, the reactions were carried out without additives or cocatalysts, which are often required in the palladium-catalyzed direct arylation of polyfluorobenzenes.[20,22]

When the reaction was catalyzed by 1 mol % precatalyst **9** in 1 mL of DMA at 120 °C, the Br-activated monocoupled product **I** was isolated in a yield of 60%, while the doubly coupled product **II** was obtained in only 3% yield. In comparison, the reaction catalyzed by **12** under identical conditions yielded **I** in a higher yield of 64% and **II** in a yield of 5%, suggesting that the complex with an even more labile acetonitrile ligand slightly outperformed the trifluoroacetato analogue.

The catalytic activities of the other triflate complexes **10**, **11**, and **13**−**17** were then tested in this model reaction and compared (Scheme 5). Surprisingly, only 4% of **I** was obtained when the reaction was catalyzed by complex **10**, carrying a methylimidazole-derived carbene. In contrast, the electronically similar, but more bulky benzylimidazolin-2-ylidene complex **11** catalyzed the reaction better and gave 49% of **I** along with 2% of **II**. Comparing these results with those obtained for the mesitylimidazolin-2-ylidene complex **12**, it may be concluded that the activity increases as the ligand becomes bulkier and less electron-donating, possibly facilitating the reductive elimination of the product.[15] Precatalyst **13**, which bears a weaker donating methyl-1,2,4-triazole-derived carbene, afforded 49% of **I** and 3% of **II**. When the carbene was changed to the strongly donating 1,2,3-triazolin-5-ylidene, the reaction catalyzed by **14** gave rise to only 32% of **I**, while no doubly coupled product **II** was detected at all. The most electron-rich indazolin-3-ylidene complex **15** yielded only 6% of **I**, while the comparatively less electron-rich homo-dicarbene complex **16** produced 34% of **I**. Complex **17**, combining the weakest donating 1,2,4-triazolin-5-ylidene and the strongest donating indazolin-3-ylidene, catalyzed the reaction and afforded a 44% yield of **I**.

The stepwise decreasing catalytic activities of complexes **13**, **16**, and **10**, which have similar coordination environments around the Pd(II) center, may be linked to the increasing donating abilities of their NHCs. Notably, the same trend was observed with the hetero-bis(carbene) complexes bearing two different monodentate NHCs.[16] Despite being more electron-rich, complex **14** performed better than **10**, which may be due to the presence of the Ph group at the C-4 position of 1,2,3-triazolin-5-ylidene, which makes the coordination environment more congested compared to the smaller methyl group in **10**.

Complex **12**, bearing the bulkiest NHC, is the best precatalyst for the direct arylation of pentafluorobenzene in

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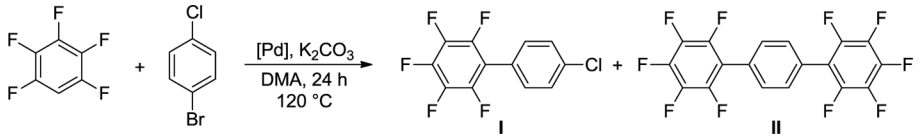
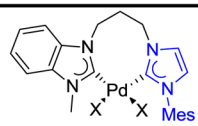
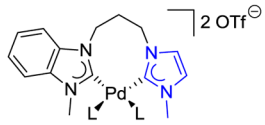
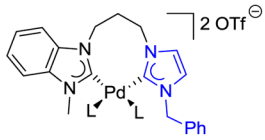
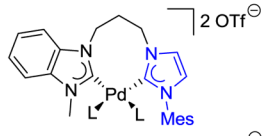
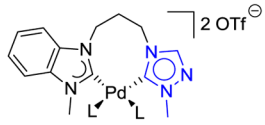
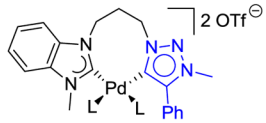
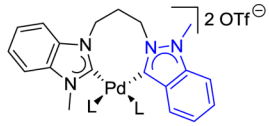
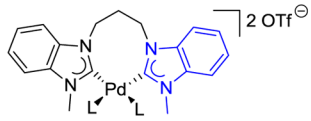
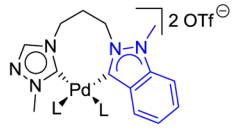
Table 1. Direct Arylation of Pentafluorobenzene Catalyzed by Pd(II) Hetero-dicarbene Complexes[a]



Entry	[Cat] No.	[Cat] structure	Yield of I %(mg)	Yield of II %(mg)
1	**9**		60(50)	3(4)
2	**10**		4(3)	0(0)
3	**11**		49(41)	2(3)
4	**12**		64(54)	5(6)
5	**13**		49(41)	3(3)
6	**14**		32(27)	0(0)
7	**15**		6(5)	0(0)
8	**16**		34(28)	0(0)
9	**17**		44(37)	0(0)

[a]Reaction conditions: precatalyst (1 mol %), K_2CO_3 (0.66 mmol, 91.2 mg), pentafluorobenzene (0.9 mmol, 100 μL), 4-chlorobromobenzene (0.3 mmol, 57.4 mg), DMA (1 mL), 120 °C, 24 h. All the yields are isolated yields and an average of two runs and are given in percentage and mg. X = $CF_3CO_2^-$; L = CH_3CN.

this series. Therefore, it was subsequently employed to catalyze the arylation between tetrafluorobenzene and 4-bromotoluene (Scheme 5). Due to the absence of the fifth fluorine atom, the C−H activation is believed to be more challenging.[20,21a,e−h,j,22] Reaction of 1,2,3,5-tetrafluorobenzene and 4-bromotoluene catalyzed by 1 mol % **12** produced 60% of the monocoupled product and 40% of the doubly coupled product, which implies that **12** is efficient in activating relatively less reactive C−H bonds. 1,2,4,5-Tetrafluorobenzene reacted with 4-bromotoluene and yielded 40% of monocoupled product as well as 17% of doubly coupled product. In 1,2,3,4-tetrafluorobenzene, the C−H bonds are adjacent to only one C−F bond, which makes the C−H activation even more challenging. As expected, the yield of the monocoupled product decreased to 10%, while only 8% of the doubly coupled product was isolated.

Overall, these findings reveal that the hetero-dicarbene Pd(II) complexes perform better than hetero-bis(carbene) complexes bearing two nonlinked, monodentate carbene

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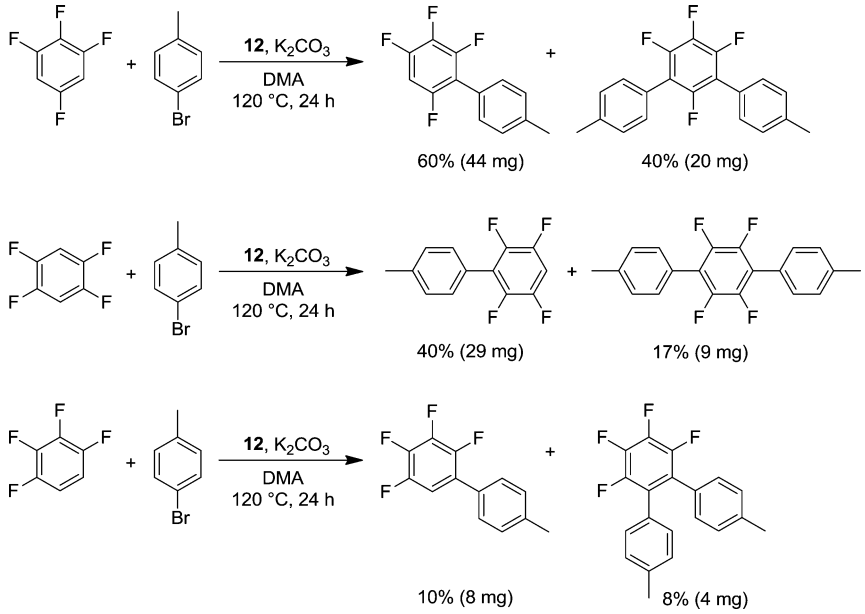
Scheme 5. Direct Arylation of Tetrafluorobenzene Catalyzed by Complex 12[a]



[a]Reaction conditions: precatalyst (1 mol %), K_2CO_3 (0.33 mmol, 45.6 mg), tetrafluorobenzene (0.9 mmol), 4-bromotoluene (0.3 mmol, 37 μL), DMA (1 mL), 120 °C, 24 h. All the yields are isolated yields and an average of two runs.

ligands in catalyzing this particular reaction.[16,23] Furthermore, hetero-diNHC Pd(II) complexes compare well to Pd(II)/phosphine systems commonly used in the literature for different but similar transformations.[20,21] The latter require a higher catalyst loading of 5 mol %, excess of phosphine ligands, and substoichiometric amounts of cocatalysts, such as pivalic acid, for decent to good yields with aromatic monohalides,[20,21a,b,e,f,j,22] while our well-defined hetero-diNHC systems are already operative at only 1 mol % with aromatic dihalides without the need for additives or additional ligands.

CONCLUSION

We have reported the preparation and characterization of a series of Pd(II) complexes **2**–**6** and **8** bearing rare chelating hetero-dicarbene ligands, which allow stereoelectronic tuning on a finer level. The bromido ligands of these complexes were replaced by reacting with AgO_2CCF_3 or AgOTf to give more active complexes **9**–**17**, carrying labile O_2CCF_3/CH_3CN ligands. All complexes have been fully characterized, and some of their molecular structures have been determined by X-ray diffraction analyses. The catalytic activities of **9**–**17** were studied and compared in the direct arylation of pentafluorobenzene with 4-chlorobromobenzene. Results of this comparison indicate that more active catalysts are obtained when the second NHC is weaker donating but more bulky. Complex **12**, bearing the bulkiest and relatively weakly electron-donating mesityl-imidazolin-2-ylidene unit, proved to be the most active precatalyst in this series. It was also found to be efficient in catalyzing the arylation of tetrafluorobenzenes. By stepwise variation of the two different NHC moieties a more suitable stereoelectronic situation could be potentially achieved at the metal center, possibly allowing for more balanced oxidative addition and reductive elimination steps. With this indication, research in our lab is currently ongoing to further fine-tune the stereoelectronic properties of hetero-dicarbene complexes to provide further support and also to explore potential applications of these complexes in catalyzing other organic transformations.

EXPERIMENTAL SECTION

General Considerations. Unless otherwise noted, all operations were performed without taking precautions to exclude air and moisture, and all solvents and chemicals were used as received. 1-Methylbenzimidazole,[24] 1-mesitylimidazole,[25] 1-(3-bromopropyl)-3-methylbenzimidazolium bromide (**A**),[12] 1-(3-(1-methylimidazolium-3-yl)propyl)-3-methylbenzimidazolium dibromide (**A1**·2HBr),[12] 1,3-di(1-methylbenzimidazolium-3-yl)propyl dibromide (**A2**·2HBr),[12] complex **1**,[12] and complex **7**[12] were synthesized according to reported procedures. 1-Methyl-1,2,4-triazole was purchased and used as received. ^1H, ^{13}C, and ^{19}F NMR chemical shifts (δ) were internally referenced to the residual solvent signals relative to tetramethylsilane (^1H, ^{13}C) or externally to CF_3CO_2H (^{19}F).

1-Methylindazole. A mixture of 1*H*-indazole (0.591 g, 6 mmol), dimethyl carbonate (4 mL), and K_2CO_3 (0.346 g, 3 mmol) in DMF (5 mL) was heated at 130 °C for 2 days. H_2O (20 mL) was added, and the resulting mixture was extracted with CH_2Cl_2 (10 mL). The organic phase was then washed with H_2O (3 × 5 mL) and dried over Na_2SO_4. After the solvent was removed in vacuo, a 1:1 mixture of methylindazole isomers was obtained. 1-Methylindazole was purified by column chromatography (eluent: ethyl acetate/hexane = 3:7) (0.396 g, 3 mmol, 50%). The ^1H NMR spectrum is consistent with literature data.[26]

1-(3-(1-Benzylimidazolium-3-yl)propyl)-3-methylbenzimidazolium Dibromide (B·2HBr). A mixture of salt **A** (1.002 g, 3 mmol) and 1-benzylimidazole (0.618 g, 3.9 mmol) in CH_3CN (10 mL) was heated at 85 °C for 2 days. The mixture was cooled to ambient temperature, and all the volatiles were removed in vacuo. The resulting solid was dissolved in MeOH (3 mL) and added dropwise into diethyl ether (20 mL). The resulting mixture was stirred and filtered to get a white solid, which was again dissolved in MeOH (3 mL), added into diethyl ether (20 mL), and filtered. This process was repeated and monitored by TLC until the starting material was fully removed. The product was obtained as a white solid (1.304 g, 2.65 mmol, 88%). ^1H NMR (500 MHz, DMSO-d_6): δ 9.76 (s, 1 H, $NCH_{bimi}N$), 9.50 (s, 1 H, $NCH_{imi}N$), 8.10–8.04 (m, 2 H, Ar-H), 7.88–7.84 (m, 2 H, Ar-H), 7.72–7.69 (m, 2 H, Ar-H), 7.43–7.38 (m, 5 H, Ar-H), 5.45 (s, 2 H, NCH_2Ph), 4.62 (t, ^3J(H,H) = 7.0 Hz, 2 H,

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NCH_2), 4.37 (t, ^3J(H,H) = 7.0 Hz, 2 H, NCH_2), 4.08 (s, 3 H, NMe), 2.55 (m, 2 H, CH_2). $^{13}C\{^1H\}$ NMR (125.76 MHz, DMSO-d_6): δ 143.4 ($NCH_{bimi}N$), 136.9 ($NCH_{imi}N$), 135.2, 132.3, 131.4, 129.5, 129.3, 128.9, 127.1, 127.0, 123.3, 123.2, 114.1, 114.0 (Ar-C), 52.5 (NCH_2Ph), 46.6, 44.1 (NCH_2), 33.8 (NMe), 29.3 (CH_2). MS (ESI): m/z = 166 $[M - 2Br]^{2+}$, 412 $[M - Br]^+$.

1-(3-(1-Mesitylimidazolium-3-yl)propyl)-3-methylbenzimidazolium Dibromide (C·2HBr). This compound was synthesized in analogy to **B**·2HBr from salt **A** (0.668 g, 2 mmol) and 1-mesitylimidazole (0.550 g, 3 mmol) in 85% yield (0.885 g, 1.7 mmol). ^1H NMR (300 MHz, DMSO-d_6): δ 9.98 (s, 1 H, NCHN), 9.64 (s, 1 H, NCHN), 8.23 (s, 1 H, Ar-H), 8.19−8.15 (m, 1 H, Ar-H), 8.09−8.06 (m, 1 H, Ar-H), 7.99 (s, 1 H, Ar-H), 7.75−7.72 (m, 2 H, Ar-H), 7.15 (s, 2 H, Ar-H), 4.67 (t, ^3J(H,H) = 7.0 Hz, 2 H, NCH_2), 4.53 (t, ^3J(H,H) = 7.0 Hz, 2 H, NCH_2), 4.13 (s, 3 H, NMe), 2.65 (m, 2 H, CH_2), 2.33 (s, 3 H, p-CH_3), 2.04 (s, 6 H, o-CH_3). $^{13}C\{^1H\}$ NMR (75.47 MHz, DMSO-d_6): δ 143.5 ($NCH_{bimi}N$), 140.8 ($NCH_{imi}N$), 138.0, 134.8, 132.4, 131.6, 131.4, 129.8, 127.1, 124.5, 123.6, 114.2, 114.1 (Ar-C), 47.1, 44.1 (NCH_2), 33.8 (NMe), 29.4 (CH_2), 21.1 (p-Me), 17.2 (o-Me). MS (ESI): m/z = 180 $[M - 2Br]^{2+}$, 440 $[M - Br]^+$.

1-(3-(1-Methyl-1,2,4-triazolium-4-yl)propyl)-3-methylbenzimidazolium Dibromide (D·2HBr). This compound was synthesized in analogy to **B**·2HBr from salt **A** (0.668 g, 2 mmol) and 1-methyl-1,2,4-triazole (0.374 g, 4.5 mmol) in 35% yield (0.309 g, 0.74 mmol). ^1H NMR (300 MHz, DMSO-d_6): δ 10.32 (s, 1 H, NCHN), 9.96 (s, 1 H, NCHN), 9.35 (s, 1 H, NCHN), 8.18−8.15 (m, 1 H, Ar-H), 8.07−8.05 (m, 1 H, Ar-H), 7.74−7.70 (m, 2 H, Ar-H), 4.67 (t, ^3J(H,H) = 7.0 Hz, 2 H, NCH_2), 4.47 (t, ^3J(H,H) = 7.0 Hz, 2 H, NCH_2), 4.12 (s, 3 H, NMe), 4.09 (s, 3 H, NMe), 2.56 (m, 2 H, CH_2). $^{13}C\{^1H\}$ NMR (75.47 MHz, DMSO-d_6): δ 144.9 (NCHN), 143.5 (NCHN), 143.4 (NCHN), 132.4, 131.3, 127.0, 126.99, 114.1 (Ar-C), 45.0, 44.0 (NCH_2), 39.2, 33.9 (NMe), 28.9 (CH_2). MS (ESI): m/z = 337 $[M - Br]^+$.

1-(3-(4-Phenyl-1,2,3-triazolyl)propyl)-3-methylbenzimidazolium Bromide (E). A mixture of salt **A** (1.002 g, 3 mmol) and NaN_3 (0.215 g, 3.3 mmol) was heated in CH_3CN (10 mL) at 75 °C overnight. The resulting mixture was cooled to ambient temperature and filtered over Celite. The solvent of the filtrate was removed in vacuo to give a brown oil, which was treated with phenylacetylene (0.362 mL, 3.3 mmol), copper powder (0.230 g, 3.6 mmol), in H_2O/^{t}BuOH (10 mL, v/v 1:1) at 80 °C overnight. The resulting mixture was filtered, and the remaining solid was dissolved in MeOH (15 mL). The solvent of the combined filtrate was removed in vacuo, and the residual solid was washed with THF (3 × 5 mL) to yield the product as a pale yellow solid (1.085 g, 2.72 mmol, 91%). ^1H NMR (300 MHz, DMSO-d_6): δ 9.89 (s, 1 H, NCHN), 8.69 (s, 1 H, NCHCPh), 8.13−8.10 (m, 1 H, Ar-H), 8.02−7.99 (m, 1 H, Ar-H), 7.82−7.79 (m, 2 H, Ar-H), 7.70−7.67 (m, 2 H, Ar-H), 7.47−7.42 (m, 2 H, Ar-H), 7.35−7.31 (m, 1 H, Ar-H), 4.67−4.60 (m, 4 H, NCH_2), 4.07 (s, 3 H, NMe), 2.60 (m, 2 H, CH_2). $^{13}C\{^1H\}$ NMR (75.47 MHz, DMSO-d_6): δ 146.8 (NCHN), 143.5 (NCHCPh), 132.3, 131.3, 131.1, 129.4, 128.4, 127.0, 125.6, 122.2, 114.04, 114.00 (Ar-C), 47.3, 44.7 (NCH_2), 33.8 (NMe), 29.4 (CH_2). MS (ESI): m/z = 318 $[M - Br]^+$.

1-(3-(3-Methyl-4-phenyl-1,2,3-triazolium-1-yl)propyl)-3-methylbenzimidazolium Bis(tetrafluoroborate) (F·2HBF$_4$). Compound **E** (0.398 g, 1 mmol) and Me_3OBF_4 (0.444 g, 3 mmol) were suspended in dry CH_2Cl_2 (10 mL) and heated under reflux for 2 days. After filtration, the resulting white solid was washed with CH_2Cl_2 (3 × 3 mL), dissolved in MeOH (3 mL), and filtered over Celite. The solvent of the filtrate was removed in vacuo, and the residual solid was washed with THF (3 × 3 mL) followed by ethyl acetate (3 × 3 mL). The product was obtained as a white powder (0.280 g, 0.55 mmol, 55%). ^1H NMR (300 MHz, DMSO-d_6): δ 9.68 (s, 1 H, NCHN), 9.16 (s, 1 H, NCHCPh), 8.10−8.06 (m, 2 H, Ar-H), 7.74−7.71 (m, 7 H, Ar-H), 4.81 (t, ^3J(H,H) = 6.8 Hz, 2 H, NCH_2), 4.67 (t, ^3J(H,H) = 6.8 Hz, 2 H, NCH_2), 4.30 (s, 3 H, NMe), 4.12 (s, 3 H, NMe), 2.68 (m, 2 H, CH_2). $^{13}C\{^1H\}$ NMR (75.47 MHz, DMSO-d_6): δ 143.5 (NCHN), 142.9 (NCHCPh), 132.4, 132.1, 131.4, 130.0, 129.7, 129.5, 127.14, 127.11, 123.1, 114.2, 114.0 (Ar-C), 50.6, 43.9 (NCH_2), 39.3, 33.8 (NMe), 28.5 (CH_2). MS (ESI): m/z = 167 $[M - 2BF_4]^{2+}$, 420 $[M - BF_4]^+$, 927 $[2\ M - BF_4]^+$.

1-Methyl-2-(3-(1-methylbenzimidazolium-3-yl)propyl)-indazolium Dibromide (G·2HBr). 1-Methylindazole (0.522 g, 3.9 mmol) reacted with 1,3-dibromopropane (3 mL) neat at 90 °C for 2 days. Having cooled to ambient temperature, the reaction mixture was washed with diethyl ether (3 × 15 mL) to remove starting materials. The resulting solid was stirred with 1-methylbenzimidazole (0.515 g, 3.9 mmol) in CH_3CN (10 mL) at 85 °C for 2 days. The reaction mixture was cooled to ambient temperature, and all the volatiles were removed in vacuo. The residual solid was washed with CH_2Cl_2 (3 × 5 mL) to yield the product as a white powder (0.764 g, 1.64 mmol, 42%). ^1H NMR (300 MHz, DMSO-d_6): δ 9.90 (s, 1 H, NCHN), 9.46 (s, 1 H, NCH), 8.19−8.04 (m, 4 H, Ar-H), 7.93−7.88 (m, 1 H, Ar-H), 7.74−7.71 (m, 2 H, Ar-H), 7.56−7.51 (m, 1 H, Ar-H), 5.04−5.02 (m, 2 H, NCH_2), 4.74−4.72 (m, 2 H, NCH_2), 4.35 (s, 3 H, NMe), 4.11 (s, 3 H, NMe), 2.69 (m, 2 H, CH_2). $^{13}C\{^1H\}$ NMR (75.47 MHz, DMSO-d_6): δ 143.5 (NCHN), 140.9 (NCH), 133.5, 133.1, 132.3, 131.4, 127.0, 125.5, 123.4, 119.3, 114.1, 111.9 (Ar-C), 48.3, 44.0 (NCH_2), 34.3, 33.8 (NMe), 28.3 (CH_2). MS (ESI): m/z = 153 $[M - 2Br]^{2+}$.

1-Methyl-2-(3-(1-methyl-1,2,4-triazolium-4-yl)propyl)-indazolium Dibromide (H·2HBr). This compound was synthesized in analogy to **G**·2HBr from 1-methylindazole (0.250 g, 1.9 mmol), 1,3-dibromopropane (1.5 mL), and 1-methyl-1,2,4-triazole (0.158 g, 1.9 mmol) in 69% yield (0.072 g, 0.17 mmol). ^1H NMR (300 MHz, DMSO-d_6): δ 10.23 (s, 1 H, NCHN), 9.40 (s, 1 H, NCHN), 9.28 (s, 1 H, Ar-H), 8.14 (d, 1 H, Ar-H), 8.07 (d, 1 H, Ar-H), 7.92 (t, 1 H, Ar-H), 7.55 (t, 1 H, Ar-H), 4.94 (br s, 2 H, NCH_2), 4.43 (br s, 2 H, NCH_2), 4.35 (s, 3 H, NMe), 4.09 (s, 3 H, NMe), 2.65−2.60 (m, 2 H, CH_2). $^{13}C\{^1H\}$ NMR (75.47 MHz, DMSO-d_6): δ 145.0 (NCHN), 143.6 (NCH), 141.0, 133.6, 133.1, 125.6, 123.4, 119.4, 111.8 (Ar-C), 48.0, 44.8 (NCH_2), 34.2 (NMe), 28.3 (CH_2). One NMe signal overlaps with the signals of DMSO-d_6. MS (ESI): m/z = 337 $[M - Br]^+$.

***cis*-[PdBr$_2$(B-κ^2*C*)] (2).** A mixture of **B**·2HBr (0.246 g, 0.5 mmol) and $Pd(OAc)_2$ was heated in DMSO (40 mL) at 90 °C overnight. The color of the reaction mixture turned from red to yellow. After filtration, the solvent of the filtrate was removed by vacuum distillation. The resulting solid was washed with H_2O (3 × 10 mL), diethyl ether (3 × 10 mL), and CH_3CN (3 × 2 mL). The product was isolated as an off-white powder (0.230 g, 0.36 mmol, 77%). ^1H NMR (500 MHz, DMSO-d_6): δ 7.76−7.75 (m, 1 H, Ar-H), 7.55−7.54 (m, 1 H, Ar-H), 7.38−7.27 (m, 6 H, Ar-H), 7.18−7.16 (m, 1 H, Ar-H), 6.99 (s, 1 H, Ar-H), 5.92 (d, ^2J(H,H) = 15.2 Hz, 1 H, NC*H*HPh), 5.57 (d, ^2J(H,H) = 15.2 Hz, 1 H, NCH*H*Ph), 5.20 (ps-t, 1 H, NC*H*H), 5.04 (ps-t, 1 H, NCH*H*), 4.87 (ps-d, 1 H, NC*H*H), 4.49 (ps-d, 1 H, NCH*H*), 3.84 (s, 3 H, NMe), 2.52−2.49 (m, 1 H, C*H*H), 1.97−1.94 (m, 1 H, CH*H*). $^{13}C\{^1H\}$ NMR (125.76 MHz, DMSO-d_6): δ 174.6 ($NC_{bimi}N$), 161.0 ($NC_{imi}N$), 136.8, 134.3, 134.0, 129.0, 128.4, 128.1, 124.6, 124.0, 123.9, 122.2, 111.4, 111.0 (Ar-C), 53.7 (NCH_2Ph), 52.2, 49.0 (NCH_2), 35.0 (NMe), 30.8 (CH_2). Anal. Calcd for $C_{21}H_{22}Br_2N_4Pd$: C, 42.27; H, 3.72; N, 9.39. Found: C, 42.15; H, 3.83; N, 9.67. MS (ESI): m/z = 517 $[M - Br]^+$.

***cis*-[PdBr$_2$(C-κ^2*C*)] (3).** This compound was synthesized in analogy to **2** from **C**·2HBr (0.260 g, 0.5 mmol) and $Pd(OAc)_2$ (0.112 g, 0.5 mmol) in 75% yield (0.234 g, 0.38 mmol). The ^1H and ^{13}C NMR spectra could not be obtained due to poor solubility. Anal. Calcd for $C_{23}H_{26}Br_2N_4Pd$: C, 44.22; H, 4.19; N, 8.97. Found: C, 44.50; H, 4.50; N, 8.66. MS (ESI): m/z = 545 $[M - Br]^+$.

***cis*-[PdBr$_2$(D-κ^2*C*)] (4).** A mixture of **D**·2HBr (0.125 g, 0.3 mmol) and $Pd(OAc)_2$ (0.067 g, 0.3 mmol) in DMSO (25 mL) was heated at 90 °C overnight. After filtration, the solvent of the filtrate was removed by vacuum distillation. The resulting solid was washed with H_2O (3 × 10 mL) and diethyl ether (3 × 10 mL) to give the product as a yellow solid (0.125 g, 0.24 mmol, 80%). ^1H NMR (300 MHz, DMSO-d_6): δ 8.64 (s, 1 H, NCHN), 7.76−7.73 (m, 1 H, Ar-H), 7.67−7.64 (m, 1 H, Ar-H), 7.38−7.35 (m, 2 H, Ar-H), 5.18 (ps-t, 1 H, NC*H*H), 4.90−4.78 (m, 2 H, NCH_2), 4.61−4.55 (m, 1 H, NCH*H*), 4.20 (s, 3 H, NMe), 4.12 (s, 3 H, NMe), 2.50 (br s, 1 H, C*H*H), 1.98−1.86 (m, 1 H, CH*H*). $^{13}C\{^1H\}$ NMR (75.47 MHz, DMSO-d_6): δ 145.4 (NCHN),

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134.6, 133.9, 124.0, 123.9, 111.6, 111.1 (Ar-C), 49.8, 48.6 (NCH_2), 35.3 (NMe), 30.4 (CH_2). One NMe signal overlaps with DMSO-d_6 signals. Carbene signals were not detected. Anal. Calcd for $C_{14}H_{17}Br_2N_5Pd$: C, 32.24; H, 3.29; N, 13.43. Found: C, 32.42; H, 3.59; N, 13.06. MS (ESI): m/z = 442 $[M - Br]^+$.

***cis*-[PdBr$_2$(F-κ^2*C*)] (5).** A mixture of **F**·2HBF$_4$ (0.145 g, 0.3 mmol), $Pd(OAc)_2$ (0.067 g, 0.3 mmol), and KBr (0.068 g, 0.6 mmol) was heated at 100 °C overnight. After filtration, the solvent of the filtrate was removed by vacuum distillation. The resulting solid was washed with DMSO (3 × 2 mL), H_2O (3 × 10 mL), and diethyl ether (3 × 10 mL) to give the product as a yellow solid (0.072 g, 0.12 mmol, 40%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.14−8.12 (m, 2 H, Ar-H), 7.70−7.64 (m, 4 H, Ar-H), 7.50−7.47 (m, 1 H, Ar-H), 7.34−7.25 (m, 2 H, Ar-H), 5.40−5.30 (m, 2 H, NCH_2), 5.00−4.82 (m, 2 H, NCH_2), 3.98 (s, 3 H, NMe), 3.19 (s, 3 H, NMe), 2.73−2.67 (m, 1 H, C*H*H), 1.98−1.86 (m, 1 H, CH*H*). ^{13}C{^{1}H} NMR (75.47 MHz, DMSO-d_6): 134.4, 133.9, 130.5, 130.3, 129.5, 129.3, 127.2, 123.8, 123.7, 111.2, 110.9 (Ar-C), 56.0, 48.2 (NCH_2), 38.3, 33.5 (NMe), 30.7 (CH_2). Carbene signals were not detected. Anal. Calcd for $C_{20}H_{21}Br_2N_5Pd$: C, 40.19; H, 3.54; N, 11.72. Found: C, 40.50; H, 3.58; N, 11.86. MS (ESI): m/z = 559 $[M - Br + CH_3CN]^+$.

***cis*-[PdBr$_2$(G-κ^2*C*)] (6).** This compound was synthesized in analogy to **2** from **G**·2HBr (0.140 g, 0.3 mmol) and $Pd(OAc)_2$ (0.067 g, 0.3 mmol) in 83% yield (0.142 g, 0.25 mmol). Decent quality NMR spectra could not be obtained due to poor solubility. Anal. Calcd for $C_{19}H_{20}Br_2N_4Pd$: C, 39.99; H, 3.53; N, 9.82. Found: C, 39.65; H, 3.06; N, 9.26. MS (ESI): m/z = 569 $[M - Br + DMSO]^+$, 1061 $[2\ M - Br]^+$, 1139 $[2\ M - Br + DMSO]^+$.

***cis*-[PdBr$_2$(H-κ^2*C*)] (8).** This compound was synthesized in analogy to **2** from **H**·2HBr (0.072 g, 0.17 mmol) and $Pd(OAc)_2$ (0.039 g, 0.17 mmol) in 70% yield (0.062 g, 0.12 mmol). Decent quality NMR spectra could not be obtained due to poor solubility. Anal. Calcd for $C_{14}H_{17}Br_2N_5Pd$: C, 32.24; H, 3.29; N, 13.43. Found: C, 32.54; H, 3.50; N, 13.46. MS (ESI): m/z = 520 $[M - Br + DMSO]^+$.

***cis*-[Pd(O$_2$CCF$_3$)$_2$(C-κ^2*C*)] (9).** Complex **3** (0.0312 g, 0.05 mmol) and AgO_2CCF_3 (0.0221 g, 0.1 mmol) were suspended in CH_3CN (5 mL) and heated at 80 °C overnight. The mixture was cooled to ambient temperature and filtered over Celite. The solvent of the filtrate was removed in vacuo to give the product as an off-white solid (0.0345 g, 0.05 mmol, 99%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37−7.32 (m, 4 H, Ar-H), 7.12 (d, 2 H, Ar-H), 6.93 (s, 1 H, Ar-H), 6.77 (s, 1 H, Ar-H), 6.35 (ps-t, 1 H, NC*H*H), 5.94 (ps-t, 1 H, NCH*H*), 4.70−4.63 (m, 1 H, NC*H*H), 4.52−4.48 (m, 1 H, NCH*H*), 3.63 (s, 3 H, NMe), 2.63 (s, 4 H, *o*-Me + C*H*H), 2.41 (s, 3 H, *o*-Me), 2.12 (s, 4 H, *p*-Me + CH*H*). ^{19}F{^{1}H} NMR (282.37 MHz, $CDCl_3$): δ 1.39 (CF_3). Anal. Calcd for $C_{27}H_{26}F_6N_4O_4Pd$: C, 46.94; H, 3.79; N, 8.11. Found: C, 46.50; H, 3.59; N, 8.06. Better values could not be obtained despite several trials. MS (ESI): m/z = 578 $[M - O_2CCF_3]^+$, 1269 $[2\ M - O_2CCF_3]^+$.

***cis*-[Pd(A1-κ^2*C*)(CH$_3$CN)$_2$](OTf)$_2$ (10).** Complex **1** (0.013 g, 0.025 mmol) and AgOTf (0.0128 g, 0.050 mmol) were suspended in CH_3CN (5 mL). The resulting mixture was filtered over Celite. A yellow powder was obtaind after the solvent of the filtrate was removed in vacuo, which was dissolved in CH_2Cl_2 (3 mL). The suspension was filtered over Celite, and the solvent of the filtrate was removed under vacuum. The resulting solid was dissolved in CH_3CN (3 mL), and the solvent was removed to give the product as a yellow solid (0.0185 g, 0.025 mmol, 99%). ^{1}H NMR (300 MHz, CD_3CN): δ 7.64−7.58 (m, 2 H, Ar-H), 7.45−7.42 (m, 2 H, Ar-H), 7.14−7.09 (m, 2 H, Ar-H), 5.13 (ps-t, 1 H, NC*H*H), 4.94 (ps-t, 1 H, NCH*H*), 4.85−4.78 (m, 1 H, NC*H*H), 4.48−4.41 (m, 1 H, NCH*H*), 4.24 (s, 3 H, NMe), 3.99 (s, 3 H, NMe), 1.95 (s, CH_3CN, correct integration is not possible due to ligand exchange with the solvent). Signals for the other two methylene protons were not observed due to overlap with solvent signals. ^{13}C{^{1}H} NMR (75.47 MHz, CD_3CN): δ 160.3 ($NC_{bimi}N$), 146.6 ($NC_{imi}N$), 135.7, 135.1, 125.9, 125.8, 125.6, 125.5 (Ar-C), 122.1 (q, ^1J(C,F) = 320.8 Hz, CF_3), 118.3 (CN), 112.5, 111.8 (Ar-C), 53.1, 49.9 (NCH_2), 38.9, 36.3 (NMe), 30.5 (CH_2), 1.32 (m, CH_3CN, assignment is tentative due to overlap with solvent signals). ^{19}F{^{1}H} NMR (282.37 MHz, CD_3CN): −2.98 (O_3SCF_3). Anal. Calcd for $C_{21}H_{24}F_6N_6O_6PdS_2$: C, 34.04; H, 3.26; N, 11.34. Found: C, 34.44; H, 3.50; N, 11.06. MS (ESI): m/z = 221 $[M - 2OTf]^{2+}$, 551 $[M - OTf - CH_3CN]^+$.

***cis*-[Pd(B-κ^2*C*)(CH$_3$CN)$_2$](OTf)$_2$ (11).** This compound was synthesized in analogy to **10** from complex **2** (0.0180 g, 0.03 mmol) and AgOTf (0.0154 g, 0.06 mmol) in 99% yield (0.0245 g, 0.03 mmol). ^{1}H NMR (500 MHz, CD_3CN): δ 7.67−7.34 (m, 8 H, Ar-H), 7.24 (s, 1 H, Ar-H), 7.07−7.05 (m, 2 H, Ar-H), 5.84 (d, ^2J(H,H) = 15.6 Hz, 1 H, NC*H*HPh), 5.54 (d, ^2J(H,H) = 15.6 Hz, 1 H, NCH*H*Ph), 5.18 (ps-t, 1 H, NC*H*H), 5.03 (ps-t, 1 H, NCH*H*), 4.88−4.82 (m, 1 H, NC*H*H), 4.55−4.49 (m, 1 H, NCH*H*), 4.02 (s, 3 H, NMe), 1.95 (s, CH_3CN, correct integration is not possible due to ligand exchange with the solvent). Signals for the other two methylene protons were not observed due to overlap with solvent signals. ^{13}C{^{1}H} NMR (125.76 MHz, CD_3CN): δ 136.6, 135.5, 135.4, 130.0, 129.5, 128.0, 126.6, 125.6, 124.9 (Ar-C), 122.1 (q, ^1J(C, F) = 319.9 Hz, CF_3), 118.3 (CN), 112.5, 112.0 (Ar-C), 55.2 (NCH_2Ph), 53.5, 50.0 (NCH_2), 35.9 (NMe), 30.5 (CH_2), 1.32 (m, CH_3CN, assignment is tentative due to overlap with solvent signals). Carbene signals were not detected. ^{19}F{^{1}H} NMR (282.37 MHz, CD_3CN): δ −2.98 (O_3SCF_3). Anal. Calcd for $C_{27}H_{28}F_6N_6O_6PdS_2$: C, 39.69; H, 3.45; N, 10.29. Found: C, 39.83; H, 3.79; N, 10.06. MS (ESI): m/z = 259 $[M - 2OTf]^{2+}$, 586 $[M - OTf - 2CH_3CN]^+$.

***cis*-[Pd(C-κ^2*C*)(CH$_3$CN)$_2$](OTf)$_2$ (12).** This compound was synthesized in analogy to **10** from complex **3** (0.0187 g, 0.03 mmol) and AgOTf (0.015 g, 0.06 mmol) in 99% yield (0.0254 g, 0.03 mmol). ^{1}H NMR (500 MHz, CD_3CN): δ 7.66−7.61 (m, 2 H, Ar-H), 7.48−7.46 (m, 3 H, Ar-H), 7.25 (s, 1 H, Ar-H), 7.13−7.11 (m, 2 H, Ar-H), 5.22−5.13 (m, 2 H, NCH_2), 4.85 (br-s, 1 H, NC*H*H), 4.68−4.66 (m, 1 H, NCH*H*), 3.49 (s, 3 H, NMe), 2.41 (s, 3 H, *o*-Me), 2.22 (s, 3 H, *o*-Me), 2.15 (s, 3 H, *p*-Me), 1.95 (s, CH_3CN, correct integration is not possible due to ligand exchange with the solvent). Signals for the other two methylene protons were not observed due to overlap with solvent signals. ^{13}C{^{1}H} NMR (125.76 MHz, CD_3CN): δ 160.5, 147.9 (NCN), 141.8, 136.4, 136.2, 136.1, 135.0, 134.5, 130.9, 130.6, 127.3, 126.2, 125.9, 125.8 (Ar-C), 122.1 (q, ^1J(C,F) = 320.8 Hz, CF_3), 118.3 (CN), 112.4, 112.3 (Ar-C), 53.8, 50.5 (NCH_2), 35.8, 31.2 (NMe), 21.2 (*o*-Me), 18.1 (*p*-Me), 16.9 (CH_2), 1.32 (m, CH_3CN, assignment is tentative due to overlap with solvent signals). ^{19}F{^{1}H} NMR (282.37 MHz, CD_3CN): δ −2.98 (O_3SCF_3). Anal. Calcd for $C_{29}H_{32}F_6N_6O_6PdS_2$: C, 41.21; H, 3.82; N, 9.94. Found: C, 41.59; H, 3.49; N, 9.77. MS (ESI): m/z = 614 $[M - OTf - 2CH_3CN]^+$.

***cis*-[Pd(CH$_3$CN)$_2$(D-κ^2*C*)](OTf)$_2$ (13).** This compound was synthesized in analogy to **10** from complex **4** (0.0156 g, 0.03 mmol) and AgOTf (0.0154 g, 0.06 mmol) in 99% yield (0.0222 g, 0.03 mmol). ^{1}H NMR (500 MHz, CD_3CN): δ 8.30 (s, 1 H, NCHN), 7.64−7.60 (m, 2 H, Ar-H), 7.45−7.43 (m, 2 H, Ar-H), 5.20 (ps-t, 1 H, NC*H*H), 4.90−4.82 (m, 2 H, NCH_2), 4.59−4.56 (m, 1 H, NCH*H*), 4.23 (s, 3 H, NMe), 4.19 (s, 3 H, NMe), 1.95 (s, CH_3CN, correct integration is not possible due to ligand exchange with the solvent). Signals for the other two methylene protons were not observed due to overlap with solvent signals. ^{13}C{^{1}H} NMR (125.76 MHz, CD_3CN): δ 158.1, 153.8 (NCN), 146.7 (NCHN), 136.0, 135.1, 125.64, 125.60 (Ar-C), 122.1 (q, ^1J(C,F) = 320.8 Hz, CF_3), 118.3 (CN), 112.5, 111.9 (Ar-C), 50.8, 49.5 (NCH_2), 41.1, 36.0 (NMe), 30.2 (CH_2), 1.32 (m, CH_3CN, assignment is tentative due to overlap with solvent signals). ^{19}F{^{1}H} NMR (282.37 MHz, CD_3CN): δ −2.98 (O_3SCF_3). Anal. Calcd for $C_{20}H_{23}F_6N_7O_6PdS_2$: C, 32.37; H, 3.12; N, 13.21. Found: C, 32.43; H, 3.50; N, 13.74. Better values could not be obtained despite several trials. MS (ESI): m/z = 222 $[M - 2OTf]^{2+}$, 552 $[M - OTf - CH_3CN]^+$.

***cis*-[Pd(CH$_3$CN)$_2$(F-κ^2*C*)](OTf)$_2$ (14).** This compound was synthesized in analogy to **10** from complex **5** (0.0180 g, 0.03 mmol) and AgOTf (0.0154 g, 0.06 mmol) in 99% yield (0.0245 g, 0.03 mmol). ^{1}H NMR (500 MHz, CD_3CN): δ 7.72−7.68 (m, 3 H, Ar-H), 7.61−7.58 (m, 3 H, Ar-H), 7.43−7.36 (m, 3 H, Ar-H), 5.27−5.19 (ps-t, 2 H, NCH_2), 5.00−4.94 (m, 1 H, NC*H*H), 4.87−4.80 (m, 1 H, NCH*H*), 3.85 (s, 3 H, NMe), 3.24 (s, 3 H, NMe), 2.69−2.64 (m, 1 H, C*H*H), 1.95 (s, CH_3CN, correct integration is not possible due to ligand exchange with the solvent). The signal for one methylene proton was

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not detected due to overlap with solvent signals. $^{13}C\{^1H\}$ NMR (125.76 MHz, CD_3CN): δ 132.1, 130.9, 130.6, 125.5, 125.3 (Ar-C), 118.3 (CN), 112.2, 111.7 (Ar-C), 57.0, 49.3 (NCH_2), 41.4, 38.5 (NMe), 34.6 (CH_2), 1.32 (m, CH_3CN, assignment is tentative due to overlap with solvent signals). Carbene signals were not detected. $^{19}F\{^1H\}$ NMR (282.37 MHz, CD_3CN): δ −3.00 (O_3SCF_3). Anal. Calcd for $C_{26}H_{27}F_6N_7O_6PdS_2$: C, 38.17; H, 3.33; N, 11.99. Found: C, 38.50; H, 3.53; N, 11.76. MS (ESI): m/z = 260 $[M - 2OTf]^{2+}$, 587 $[M - OTf - 2CH_3CN]^+$, 628 $[M - OTf - CH_3CN]^+$.

***cis*-[Pd(CH_3CN)$_2$(G-κ^2*C*)](OTf)$_2$ (15).** This compound was synthesized in analogy to **10** from complex **6** (0.0171 g, 0.03 mmol) and AgOTf (0.0154 g, 0.06 mmol) in 99% yield (0.0237 g, 0.03 mmol). ^1H NMR (500 MHz, CD_3CN): δ 8.36−8.34 (d, 1 H, Ar-H), 7.67−7.57 (m, 2 H, Ar-H), 7.46−7.32 (m, 5 H, Ar-H), 5.53 (ps-t, 1 H, NC*H*H), 5.32 (ps-t, 1 H, NCH*H*), 5.11−5.04 (m, 1 H, NC*H*H), 4.94−4.86 (m, 1 H, NCH*H*), 4.18 (s, 3 H, NMe), 3.93 (s, 3 H, NMe), 2.58−2.50 (m, 1 H, C*H*H), 1.95 (s, CH_3CN, correct integration is not possible due to ligand exchange with the solvent). The signal for one methylene proton was not observed due to overlap with solvent signals. $^{13}C\{^1H\}$ NMR (125.76 MHz, CD_3CN): δ 146.6, 141.1, 133.8, 128.1, 126.2, 124.6 (Ar-C), 122.1 (q, ^1J(C,F) = 320.8 Hz, CF_3), 118.3 (CN), 111.5 (Ar-C), 53.6, 50.3 (NCH_2), 40.8, 34.5 (NMe), 29.3 (CH_2), 1.32 (m, CH_3CN, assignment is tentative due to overlap with solvent signals). Carbene signals were not detected. $^{19}F\{^1H\}$ NMR (282.37 MHz, CD_3CN): −2.94 (O_3SCF_3). Anal. Calcd for $C_{25}H_{26}F_6N_6O_6PdS_2$: C, 37.96; H, 3.31; N, 10.62. Found: C, 37.50; H, 3.51; N, 10.08. Better values could not be obtained despite several trials. MS (ESI): m/z = 246 $[M - 2OTf]^{2+}$, 601 $[M - OTf - CH_3CN]^+$.

***cis*-[Pd(A2-κ^2*C*)(CH_3CN)$_2$](OTf)$_2$ (16).** This compound was synthesized in analogy to **10** from complex **7** (0.0171 g, 0.03 mmol) and AgOTf (0.0154 g, 0.06 mmol) in 99% yield (0.0237 g, 0.03 mmol). ^1H NMR (300 MHz, CD_3CN): δ 7.60−7.54 (m, 4 H, Ar-H), 7.40−7.37 (m, 4 H, Ar-H), 5.21 (ps-t, 2 H, NC*H*H), 4.91−4.85 (m, 2 H, NCH*H*), 4.26 (s, 6 H, NMe), 2.66−2.60 (m, 1 H, C*H*H), 1.95 (s, CH_3CN, correct integration is not possible due to ligand exchange with the solvent). The signal for one methylene proton was not observed due to overlap with solvent signals. $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_3CN): δ 159.7 (NCN), 135.7, 135.3, 125.5, 125.4 (Ar-H), 122.1 (q, ^1J(C,F) = 321.1 Hz, CF_3), 118.3 (CN), 112.4, 111.8 (Ar-H), 50.0 (NCH_2), 36.3 (NMe), 29.5 (CH_2), 1.32 (m, CH_3CN, assignment is tentative due to overlap with solvent signals). $^{19}F\{^1H\}$ NMR (282.37 MHz, CD_3CN): δ −2.95 (O_3SCF_3). Anal. Calcd for $C_{25}H_{26}F_6N_6O_6PdS_2$: C, 37.96; H, 3.31; N, 10.62. Found: C, 37.56; H, 3.61; N, 10.26. MS (ESI): m/z = 246 $[M - 2OTf]^{2+}$, 601 $[M - OTf - CH_3CN]^+$.

***cis*-[Pd(CH_3CN)$_2$(H-κ^2*C*)](OTf)$_2$ (17).** This compound was synthesized in analogy to **10** from complex **8** (0.0156 g, 0.03 mmol) and AgOTf (0.0154 g, 0.06 mmol) in 99% yield (0.0222 g, 0.03 mmol). ^1H NMR (500 MHz, CD_3CN): δ 8.30 (d, ^3J(H, H) = 8.0 Hz, 1 H, Ar-H), 8.26 (s, 1 H, NCHN), 7.73 (t, ^3J(H, H) = 8.0 Hz, 1 H, Ar-H), 7.49 (d, ^3J(H, H) = 8.0 Hz, 1 H, Ar-H), 7.40 (t, ^3J(H, H) = 8.0 Hz, 1 H, Ar-H), 5.20−5.50 (m, 1 H, NC*H*H), 5.03−4.92 (m, 2 H, NCH_2), 4.58−4.55 (m, 1 H, NCH*H*), 4.09 (s, 3 H, NMe), 3.99 (s, 3 H, NMe), 1.95 (s, CH_3CN, correct integration is not possible due to ligand exchange with the solvent). Signals for the other two methylene protons were not observed due to overlap with solvent signals. $^{13}C\{^1H\}$ NMR (125.76 MHz, CD_3CN): δ 146.4 (NCHN), 141.0, 133.7, 127.9, 126.0, 124.4 (Ar-C), 122.1 (q, ^1J(C,F) = 320.8 Hz, CF_3), 118.3 (CN), 111.4 (Ar-C), 50.2, 47.8 (NCH_2), 40.6, 34.4 (NMe), 29.2 (CH_2), 1.32 (m, CH_3CN, assignment is tentative due to overlap with solvent signals). Carbene signals were not detected. $^{19}F\{^1H\}$ NMR (282.37 MHz, CD_3CN): δ −2.98 (O_3SCF_3). Anal. Calcd for $C_{20}H_{23}F_6N_7O_6PdS_2$: C, 32.37; H, 3.12; N, 13.21. Found: C, 32.68; H, 3.52; N, 13.06. MS (ESI): m/z = 222 $[M - 2OTf]^{2+}$, 552 $[M - OTf - CH_3CN]^+$.

Direct Arylation of Polyfluorobenzene. In a typical run, a Schlenk tube was charged with precatalyst (1 mol %), K_2CO_3 (0.66 mmol, 0.33 mmol in the case of tetrafluorobenzene), and aryl halide (0.3 mmol) if it is a solid. The reaction vessel was evacuated and refilled with nitrogen three times. Aryl halide (0.3 mmol, if it is a liquid), pentafluorobenzene (0.9 mmol) or tetrafluorobenzene (0.9 mmol), and DMA (1.0 mL) were added, and the reaction was placed in a preheated oil bath and stirred. After 24 h at 120 °C, the mixture was cooled to ambient temperature, and dichloromethane (2 mL) was added. The suspension was filtered through Celite, and the residue was washed with dichloromethane (2 × 2 mL). The solvent of the filtrate was removed, and the crude product was loaded onto silica gel using hexane or a hexane/ether mixture as eluent to purify the compound. The yields indicated were calculated as an average of two runs.

X-ray Diffraction Studies. X-ray data for **4**, **9**·CH_2Cl_2, and **12A** (CCDC 997220−997222) were collected with a Bruker AXS SMART APEX diffractometer, using Mo Kα radiation at 223(2) K with the SMART suite of programs.[27] Data were processed and corrected for Lorentz and polarization effects with SAINT,[28] and for absorption effect with SADABS.[29] Structural solution and refinement were carried out with the SHELXTL suite of programs.[30] 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 S1 in the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data for **4**, **9**·CH_2Cl_2, and **12A** as CIF files, and ^1H and ^{13}C NMR spectra of salts and complexes. 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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■ REFERENCES

(1) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122.
(2) (a) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290. (b) Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Angew. Chem., Int. Ed.* **2007**, *46*, 2768. (c) Díez-González, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612. (d) Mata, J. A.; Hahn, F. E.; Peris, E. *Chem. Sci.* **2014**, *5*, 1723.
(3) (a) Normand, A. T.; Cavell, K. J. *Eur. J. Inorg. Chem.* **2008**, 2781. (b) John, A.; Ghosh, P. *Dalton Trans.* **2010**, *39*, 7183. (c) Bierenstiel, M.; Cross, E. D. *Coord. Chem. Rev.* **2011**, *255*, 574. (d) Yuan, D.; Huynh, H. V. *Molecules* **2012**, *17*, 2491. (e) Fliedel, C.; Braunstein, P. *J. Organomet. Chem.* **2014**, *751*, 286.
(4) (a) Simpson, P. V.; Skelton, B. W.; Brown, D. H.; Baker, M. V. *Eur. J. Inorg. Chem.* **2011**, 1937. (b) Baker, M. V.; Brown, D. H.; Simpson, P. V.; Skelton, B. W.; White, A. H. *Dalton Trans.* **2009**, 7294. (c) Scherg, T.; Schneider, S. K.; Frey, G. D.; Schwarz, J.; Herdtweck, E.; Herrmann, W. A. *Synlett* **2006**, *18*, 2894. (d) Baker, M. V.; Brown, D. H.; Simpson, P. V.; Skelton, B. W.; White, A. H.; Williams, C. C. *J. Organomet. Chem.* **2006**, *691*, 5845. (e) Lee, H. M.; Lu, C. Y.; Chen, C. Y.; Chen, W. L.; Lin, H. C.; Chiu, P. L.; Cheng, P. Y. *Tetrahedron* **2004**, *60*, 5807. (f) Han, Y.; Lee, L. J.; Huynh, H. V. *Chem.—Eur. J.* **2010**, *16*, 771. (g) Maity, R.; Rit, A.; Schulte to Brinke, C.; Kösters, J.;

Hahn, F. E. *Organometallics* **2013**, *32*, 6174. (h) Sabater, S.; Mata, J. A.; Peris, E. *Nat. Commun.* **2013**, *4*, 2553.
(5) Crabtree, R. H. *Coord. Chem. Rev.* **2013**, *257*, 755 and references therein.
(6) (a) Guo, S.; Sivaram, H.; Yuan, D.; Huynh, H. V. *Organometallics* **2013**, *32*, 3685. (b) Zhou, Y.; Liu, Q.; Lv, W.; Pang, Q.; Ben, R.; Qian, Y.; Zhao, J. *Organometallics* **2013**, *32*, 3753.
(7) (a) Donnelly, K. F.; Petronilho, A.; Albrecht, M. *Chem. Commun.* **2013**, *49*, 1145. (b) Crowley, J. D.; Lee, A.-L.; Kilpin, K. J. *Aust. J. Chem.* **2011**, *64*, 1118. (c) Mathew, P.; Neels, A.; Albrecht, M. *J. Am. Chem. Soc.* **2008**, *130*, 13534.
(8) (a) Han, Y.; Huynh, H. V. *Dalton Trans.* **2011**, *40*, 2141. (b) Lavallo, V.; Dyker, C. A.; Donnadieu, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 5411. (c) Fernández, I.; Dyker, C. A.; DeHope, A.; Donnadieu, B.; Frenking, G.; Bertrand, G. *J. Am. Chem. Soc.* **2009**, *131*, 11875. (d) Martin, D.; Melaimi, M.; Soleilhavoup, M.; Bertrand, G. *Organometallics* **2011**, *30*, 5304.
(9) (a) Lebel, H.; Janes, M. K.; Charette, A. B.; Nolan, S. P. *J. Am. Chem. Soc.* **2004**, *126*, 5046. (b) Yang, L.; Krüger, A.; Neels, A.; Albrecht, M. *Organometallics* **2008**, *27*, 3161. (c) Kong, Y.; Ren, H.; Xu, S.; Song, H.; Liu, B.; Wang, B. *Organometallics* **2009**, *28*, 5934. (d) Heckenroth, M.; Kluser, E.; Neels, A.; Albrecht, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 6293. (e) Bacciu, D.; Cavell, K. J.; Fallis, I. A.; Ooi, L. *Angew. Chem., Int. Ed.* **2005**, *44*, 5282. (f) Heckenroth, M.; Neels, A.; Garnier, M. G.; Aebi, P.; Ehlers, A. W.; Albrecht, M. *Chem.—Eur. J.* **2009**, *15*, 9375. (g) Zuo, W.; Braunstein, P. *Organometallics* **2012**, *31*, 2606. (h) Gong, X.; Zhang, H.; Li, X. *Tetrahedron Lett.* **2011**, *52*, 5596. (i) Xu, X.; Kim, S. H.; Zhang, X.; Das, A. K.; Hirao, H.; Hong, S. H. *Organometallics* **2013**, *32*, 164.
(10) (a) Han, Y.; Yuan, D.; Teng, Q.; Huynh, H. V. *Organometallics* **2011**, *30*, 1224. (b) Prades, A.; Viciano, M.; Sanaú, M.; Peris, E. *Organometallics* **2008**, *27*, 4254. (c) Stander-Grobler, E.; Schuster, O.; Heydenrych, G.; Cronje, S.; Tosh, E.; Albrecht, M.; Frenking, G.; Raubenheimer, H. G. *Organometallics* **2010**, *29*, 5821. (d) Raubenheimer, H. G.; Cronje, S. *Dalton Trans.* **2008**, 1265. (e) Schneider, S. K.; Julius, G. R.; Loschen, C.; Raubenheimer, H. G.; Frenking, G.; Herrmann, W. A. *Dalton Trans.* **2006**, 1226. (f) Iglesias, M.; Albrecht, M. *Dalton Trans.* **2010**, *39*, 5213. (g) Zhang, Y.; Clavadetscher, J.; Bachmann, M.; Blacque, O.; Venkatesan, K. *Inorg. Chem.* **2014**, *53*, 756. (h) Ng, C.-O.; Yiu, S.-M.; Ko, C.-C. *Inorg. Chem.* **2014**, *53*, 3022. (i) Zanardi, A.; Mata, J. A.; Peris, E. *Organometallics* **2009**, *28*, 4335. (j) Leigh, V.; Ghattas, W.; Lalrempuia, R.; Müller-Bunz, H.; Pryce, M. T.; Albrecht, M. *Inorg. Chem.* **2013**, *52*, 5395. (k) Ciancaleoni, G.; Biasiolo, L.; Bistoni, G.; Macchioni, A.; Tarantelli, F.; Zuccaccia, D.; Belpassi, L. *Organometallics* **2013**, *32*, 4444. (l) Chung, L.-H.; Cho, K.-S.; England, J.; Chan, S.-C.; Wieghardt, K.; Wong, C.-Y. *Inorg. Chem.* **2013**, *52*, 9885.
(11) (a) Yuan, D.; Huynh, H. V. *Dalton Trans.* **2011**, *40*, 11698. (b) Tan, K. V.; Dutton, J. L.; Skelton, B. W.; Wilson, D. J. D.; Bernard, P. J. *Organometallics* **2013**, *32*, 1913.
(12) Huynh, H. V.; Jothibasu, R. *J. Organomet. Chem.* **2011**, *696*, 3369.
(13) (a) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004. (b) Bock, V. D.; Hiemstra, H.; van Maarseveen, J. H. *Eur. J. Org. Chem.* **2006**, 51. (c) Meldal, M.; Tornøe, C. W. *Chem. Rev.* **2008**, *108*, 2952.
(14) Chen, Q.; Lv, L.; Yu, M.; Shi, Y.; Li, Y.; Pang, G.; Cao, C. *RSC Adv.* **2013**, *3*, 18359.
(15) Huynh, H. V.; Han, Y.; Jothibasu, R.; Yang, J. A. *Organometallics* **2009**, *28*, 5395.
(16) Yuan, D.; Huynh, H. V. *Organometallics* **2012**, *31*, 405.
(17) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; HarperCollins College Publishers: New York, 1993; pp 405−408.
(18) Pearson, R. G. *Inorg. Chem.* **1973**, *12*, 712.
(19) (a) Wayland, B. B.; Schramm, R. F. *Inorg. Chem.* **1969**, *8*, 971. (b) Annibale, G.; Cattalini, L.; Bertolasi, V.; Ferretti, V.; Gilli, G.; Tobe, M. L. *J. Chem. Soc., Dalton Trans.* **1989**, 1265.
(20) He, M.; Soulé, J.-F.; Doucet, H. *ChemCatChem* **2014**, *6*, 1824 and references therein.
(21) (a) Lafrance, M.; Rowley, C. N.; Woo, T. K.; Fagnou, K. *J. Am. Chem. Soc.* **2006**, *128*, 8754. (b) Lafrance, M.; Shore, D.; Fagnou, K. *Org. Lett.* **2006**, *8*, 5097. (c) Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev.* **2007**, *107*, 174. (d) Ackermann, L.; Vicente, R.; Kapdi, A. R. *Angew. Chem., Int. Ed.* **2009**, *48*, 9792. (e) René, O.; Fagnou, K. *Org. Lett.* **2010**, *12*, 2116. (f) Chen, F.; Min, Q.-Q.; Zhang, X. *J. Org. Chem.* **2012**, *77*, 2992. (g) Do, H.-Q.; Daugulis, O. *J. Am. Chem. Soc.* **2008**, *130*, 1128. (h) Do, H.-Q.; Khan, R. M. K.; Dangulis, O. *J. Am. Chem. Soc.* **2008**, *130*, 15185. (i) Zhao, D.; Wang, W.; Lian, S.; Yang, F.; Lan, J.; You, J. *Chem.—Eur. J.* **2009**, *15*, 1337. (j) Zhang, H.-H.; Dong, J.; Hu, Q.-S. *Eur. J. Org. Chem.* **2014**, *6*, 1327.
(22) Lapointe, D.; Fagnou, K. *Chem. Lett.* **2010**, *39*, 1118.
(23) Bernhammer, J. C.; Huynh, H. V. *Organometallics* **2012**, *31*, 5121.
(24) Shieh, W.-C.; Dell, S.; Repic, O. *Org. Lett.* **2001**, *3*, 4279.
(25) Liu, J.; Chen, J.; Zhao, J.; Zhao, Y.; Li, L.; Zhang, H. *Synthesis* **2003**, *17*, 2661.
(26) Wheeler, R. C.; Baxter, E.; Campbell, I. B.; Macdonald, S. J. F. *Org. Process Res. Dev.* **2011**, *15*, 565.
(27) *SMART* version 5.628; Bruker AXS Inc.: Madison, WI, 2001.
(28) *SAINT+* version 6.22a; Bruker AXS Inc.: Madison, WI, 2001.
(29) Sheldrick, G. W. *SADABS* version 2.10; University of Göttingen, 2001.
(30) *SHELXTL* version 6.14; Bruker AXS Inc.: Madison, WI, 2000.