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1,2,3-Triazolin-5-ylidenes: Synthesis of Hetero-bis(carbene) Pd(II) Complexes, Determination of Donor Strengths, and Catalysis

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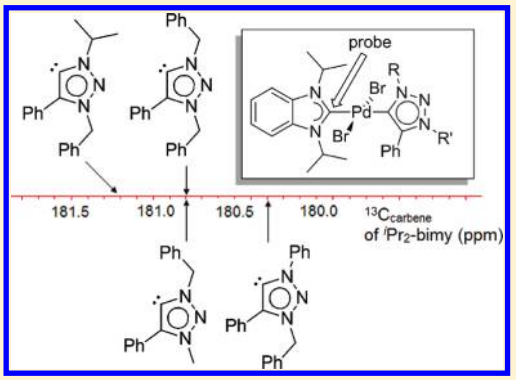
Supporting Information

ABSTRACT: A series of hetero-bis(carbene) complexes *trans*-[$PdBr_2$(^{i}Pr_2-bimy)(trz)] **1**−**4** (^{i}Pr_2-bimy = 1,3-diisopropylbenzimidazolin-2-ylidene; trz = 1,2,3-triazolin-5-ylidene) bearing the constant ^{i}Pr_2-bimy and varying mesoionic 1,2,3-triazolin-5-ylidenes with different N-substituents has been synthesized as complex probes. Their ^{13}C NMR spectroscopic evaluation shows that mesoionic 1,2,3-triazolin-5-ylidenes are, in general, stronger donors than classical NHCs, while weaker than some nonclassical NHCs, such as pyrazolin-3-ylidenes and mesoionic imidazolin-4-ylidenes. More importantly and for the first time, this methodology proves useful in establishing substituent effects in the donating abilities of 1,2,3-triazolin-5-ylidenes on a finer level. In addition, the trifluoroacetato analogues [$Pd(O_2CCF_3)_2$(^{i}Pr_2-bimy)(trz)] **5**−**7** have been synthesized through salt metathesis of **1**, **2**, and **4** with AgO_2CCF_3. The catalytic activities of complexes **1**, **2**, and **4**−**7** were examined in the direct arylation of pentafluorobenzene. Complexes bearing less donating trz ligands perform better in this catalysis, and trifluoroacetato complexes outperformed their bromido analogues.



INTRODUCTION

N-heterocyclic carbenes (NHCs) have become standard ligands in organometallic chemistry[1] and have found wide application in catalysis[2] and many other fields.[3] Recent NHC research has gone beyond classical Arduengo-type carbenes,[4] and more and more emphasis has been put on the development of new carbene types, which possess different topologies and electronic properties.[5] Numerous studies have been carried out to examine their donating abilities, which influence the properties of pertinent transition-metal complexes to a great extent. Thus, the knowledge of donating capacities may pave the way for catalyst design. Although Tolman's electronic parameter (TEP)[6] and related carbonyl-based methods are widely used to determine the donor strengths of certain ligands, they suffer from some limitations. For instance, the preparation of the respective complexes {[$Ni(CO)_3L$] or [$MX(CO)_2L$] (L = ligand in study, M = Ir(I) or Rh(I), X = halide)} requires the handling of highly toxic starting materials, such as [$Ni(CO)_4$] or CO gases, or expensive Ir or Rh precursors. Furthermore, their application for the study of NHCs gave inconsistent results in certain cases,[7] mainly due to the wrong assumption that the π back-donation from metal centers to NHCs or other ligands competing with that to the CO ligands is negligible.[8] Indeed, caution must be taken when donating abilities of ligands, and, in particular, those of similar ligands, are compared based on wavenumbers.[9] Another major approach known as Lever's electronic parameter (LEP) is based on electrochemical E_0 values of a redox couple of complexes bearing the ligands of interest. Limitations to that method lie in the requirement for less-common electrochemical apparatus and the nonreversible redox behavior of many complexes due to either decomposition or noninnocent ligand properties.[10]

To overcome these problems, we have recently introduced a new, safe, and nondestructive method that employs a ^{13}C NMR spectroscopic evaluation of complexes of the type *trans*-[$PdBr_2$(^{i}Pr_2-bimy)L] (^{i}Pr_2-bimy = 1,3-diisopropylbenzimidazolin-2-ylidene), in which L represents the ligand of interest.[11] It was empirically found that the ^{13}C carbenoid signal of the constant [$PdBr_2$(^{i}Pr_2-bimy)] probe was sensitive to the transoid ligand L, whereby stronger donating ligands would lead to a more downfield shift.[12] The donor strengths of 25 Werner-type and organometallic ligands have been compared on a unified scale in the previous study.[11]

An extension of this methodology to other ligand systems, especially to newly emerging and nonclassical carbenes, such as 1,2,3-triazolin-5-ylidenes (trz), is desirable. Following the first report on complexes of this new type of mesoionic carbenes by Albrecht et al,[13] a number of studies have appeared on the syntheses of related transition-metal complexes and of their catalytic activities.[14] Furthermore, the isolation and structural characterization of the free trz ligand by Bertrand et al.[15] provided more insights into the understanding of its mesoionic nature. IR spectroscopic evaluation of their Ir(I) and Rh(I) carbonyl complexes revealed that trz ligands are stronger donors than classical NHCs, but weaker than mesoionic imidazolin-4-ylidenes or pyrazolin-4-ylidenes. However, none of these systems were capable in discerning any substituent effects, since

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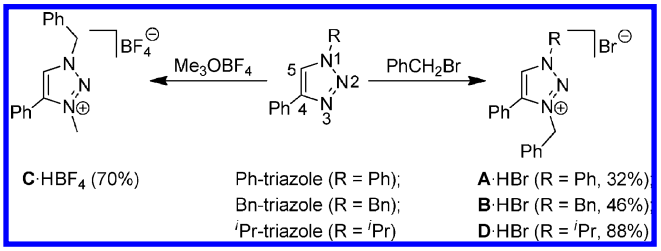
complexes of different carbenes with either alkyl or phenyl substituents gave essentially the same CO stretching frequencies, highlighting the above-mentioned limitations of carbonyl-based methodologies.[14b,15b]

As our contribution to a more detailed understanding of mesoionic trz ligands and in extension of our ^{13}C NMR-based electronic parameter, a series of Pd(II) hetero-bis(carbene) complexes of the type *trans*-[$PdBr_2$($^iPr_2$-bimy)(trz)] have been synthesized as spectroscopic probes for the donor strength evaluation and comparison of 1,2,3-triazolin-5-ylidenes. The preparation of trifluoroacetato analogues [$Pd(O_2CCF_3)_2$($^iPr_2$-bimy)(trz)] and their catalytic activities in the direct arylation of pentafluorobenzene are reported as well.

RESULTS AND DISCUSSION

Synthesis of the Ligand Precursors. Triazolium salts with phenyl (**A**·HBr), benzyl (**B**·HBr, **C**·HBF_4), or isopropyl (**D**·HBr) N1 substituents were synthesized via two-step reactions (Scheme 1). 1-Substituted 1,2,3-triazoles were first

Scheme 1. Preparation of Ligand Precursors A·HBr–D·HBr

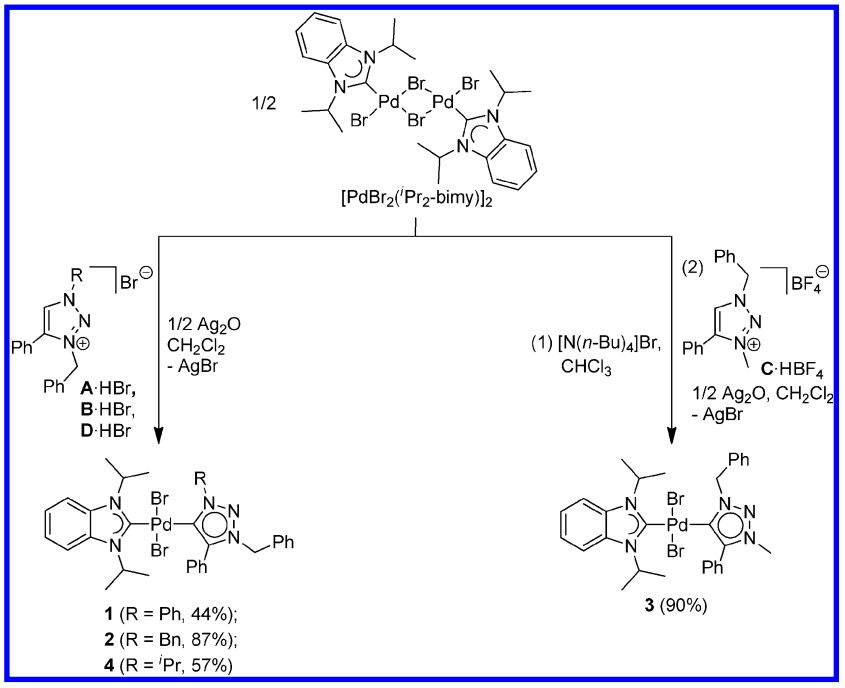


synthesized by a "click reaction"[16] involving a copper-catalyzed [3 + 2] cycloaddition of azides and alkynes. Alkylation of these 1,2,3-triazoles with benzyl bromide or Meerwein's salt[14c] gave rise to 1,3-disubstituted triazolium salts (**A**·HBr–**D**·HBr) in moderate to good yields, which served as ligand precursors for 1,2,3-triazolin-5-ylidenes (Scheme 1). The yields for the alkylation step depend largely on the N1 substituent. The reaction with ^{i}Pr-triazole gave a good yield of 88% after heating in neat benzyl bromide overnight, whereas the yield dropped to 46% when the same reaction condition was applied to Bn-triazole. Alkylation of Ph-triazole gave only 32% yield even though the reaction time was prolonged to 3 days. Apparently, the yields dropped as the inductive effect of the N1 substituent decreases. In the ^1H NMR spectra of salts **A**·HBr–**D**·HBr, downfield signals ranging from 9.75 to 10.18 ppm were assigned to the protons attached to the procarbene carbon atoms, supporting the successful alkylations. Moreover, a base peak assignable to the triazolium cation in each ESI mass spectrum also corroborates the formation of the expected salts.

Synthesis of Pd(II) Complexes. To determine and compare the donor strengths of 1,2,3-triazolin-5-ylidenes, hetero-bis(carbene) complexes *trans*-[$PdBr_2$($^iPr_2$-bimy)(trz)] bearing the constant $^iPr_2$-bimy probe and the trz ligands in question were synthesized. One-pot bridge-cleavage reactions of dimeric [$PdBr_2$($^iPr_2$-bimy)]$_2$ with 2 equiv of ligand precursors **A**·HBr, **B**·HBr, or **D**·HBr and 1.2 equiv of Ag_2O in CH_2Cl_2 yielded the desired hetero-bis(carbene) complexes *trans*-[$PdBr_2$($^iPr_2$-bimy)(**A**)] (**1**), *trans*-[$PdBr_2$($^iPr_2$-bimy)(**B**)] (**2**) and *trans*-[$PdBr_2$($^iPr_2$-bimy)(**D**)] (**4**) suitable for measuring the donor strengths of mesoionic 1,2,3-triazole-derived carbenes (Scheme 2). Because ligand precursor **C**·HBF_4 bears BF_4^- as the counteranion, complex *trans*-[$PdBr_2$($^iPr_2$-bimy)(**C**)] (**3**) was prepared by reacting it with a tribromido complex, generated in situ by addition of [N(*n*-Bu)$_4$]Br to [$PdBr_2$($^iPr_2$-bimy)]$_2$, in order to compensate for the absence of halide in **C**·HBF_4 (Scheme 2).

Complexes **1**–**4** were isolated as yellow solids in moderate to good yields, which are soluble in most organic solvents, such as CH_2Cl_2, $CHCl_3$, MeOH, and CH_3CN, with the exception of nonpolar ones, such as hexane and diethyl ether. Their formation is supported by ESI mass spectra, where a base peak corresponding to the $[M - Br]^+$ fragment and a smaller signal assignable to $[2M - Br]^+$ are present in all cases. In the ^1H NMR spectra, the absence of downfield signals for the

Scheme 2. Syntheses of Complexes 1–4



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triazolium salts and the presence of peaks from both $^{i}Pr_2$-bimy and the trz ligands also corroborate the formation of the expected hetero-bis(carbene) complexes. The characteristic multiplets for the C−H protons of the isopropyl groups of the $^{i}Pr_2$-bimy ligand range from 6.05 to 5.73 ppm, which are shifted upfield in comparison to those of the precursor $[PdBr_2(^{i}Pr_2\text{-bimy})]_2$ (cf. 6.54 ppm). Moreover, due to the loss of symmetry upon complex formation, two C−H proton signals are observed in the ^{1}H NMR spectrum of complex **1**. One additional septet appears at 6.05 ppm for complex **4**, which is assigned to the isopropyl group of trz ligands. For complexes **2** and **3**, however, only one multiplet integrating to 2 is observed in each spectrum due to accidental overlap.

In the ^{13}C NMR spectra of complexes **1**−**4**, two carbene signals are observed as expected. The downfield signals ranging from 180.3 to 181.2 ppm are assigned to $^{i}Pr_2$-bimy, whereas those ranging from 157.9 to 160.6 ppm are attributed to the 1,2,3-triazole-derived carbenes. In comparison to the donor strengths of other carbene ligands previously determined on the ^{13}C NMR spectroscopic scale,[11] 1,2,3-triazolin-5-ylidenes prove to be stronger donors than classical NHCs of types **I**−**III** (Figure 1), which can be explained by a reduced electron-withdrawing effect of only one nitrogen atom adjacent to the carbene centers. Moreover, they are weaker than some non-classical carbenes, such as pyrazolin-3-ylidenes **IV** and meso-ionic imidazolin-4-ylidenes **V** (Figure 1), which is attributable to the presence of a third electron-withdrawing nitrogen atom in the triazole-derived systems. Furthermore, they show similar donating abilities with indazolin-3-ylidenes **VI**.[11]

A closer inspection of the $^{i}Pr_2$-bimy chemical shifts among the four trz complexes **1**−**4** revealed increasing downfield shifts in the order **1** (180.3 ppm) < **2**/**3** (180.8 ppm) < **4** (181.2 ppm), reflecting a stepwise increase of the trz ligand's donor ability.[17] Because complexes **1**, **2**, and **4** differ only in the N1 substituent of the trz ligand, the determined order also correctly reflects the increasing positive inductive effects of the groups Ph < Bn < ^{i}Pr. This result demonstrates that substituent effects are indeed present and that they can be efficiently measured using our new ^{13}C NMR-based electronic parameter. It must be highlighted that the lower sensitivity of common IR-based methodologies is not sufficient to discern electronic influences brought about by different substituents.[14b,15b] Notably, the electronic properties of carbene ligands in complexes **2** and **3** that differ only in their N3 substituents cannot be further separated even on our ^{13}C NMR scale. Apparently, it is difficult to discern remote and minute variations six bonds away from the carbene probe.

Trifluoroacetato Complexes. Changing halido to trifluoroacetato ligands is a common practice to improve the solubilities and catalytic activities of transition-metal complexes.[19] Reactions of complexes **1**, **2**, and **4** with 2 equiv of AgO_2CCF_3 gave rise to new hetero-bis(carbene) complexes $[Pd(O_2CCF_3)_2(^{i}Pr_2\text{-bimy})(trz)]$ (**5**−**7**) bearing labile trifluoroacetato ligands with the precipitation of AgBr (Scheme 3).

Compared with their precursors, the newly formed complexes **5**−**7** are, in general, more soluble in common organic solvents, which is a common feature of trifluoroacetato complexes.[19] All three compounds are mixtures of cis and trans isomers, as evidenced by two sets of signals observed in their ^{1}H NMR spectra. In their ^{13}C NMR spectra, all the carbene signals are shifted upfield by 4−5 ppm, due to the replacement of bromido with less electron-donating trifluoroacetato ligands, resulting in generally more Lewis acidic Pd centers. The signals of other carbon atoms of triazole rings are shifted downfield by 0.7−1 ppm.

Single crystals of **7** suitable for X-ray diffraction analysis were grown from a concentrated CH_2Cl_2 solution as a representative. Its molecular structure depicted in Figure 2 shows that both

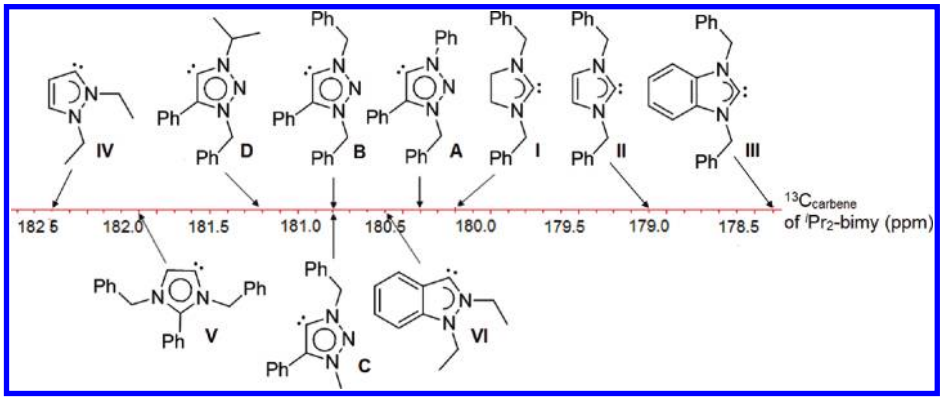
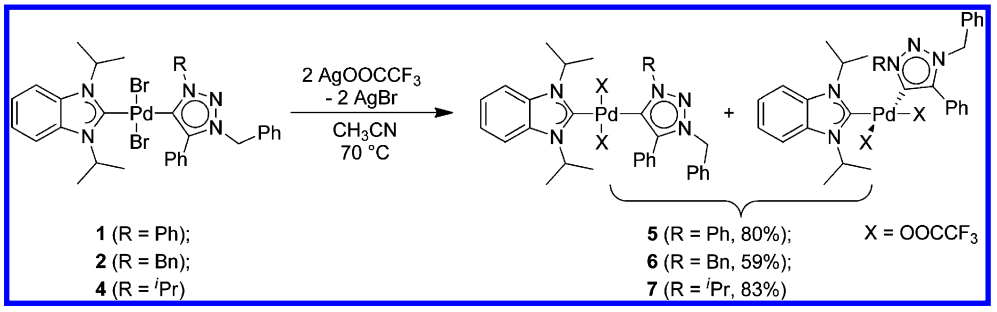


Figure 1. Donor abilities of NHCs on the ^{13}C NMR scale.[18]

Scheme 3. Syntheses of Complexes 5−7



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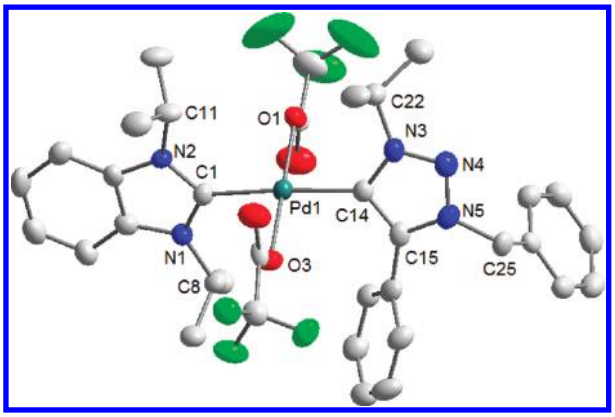


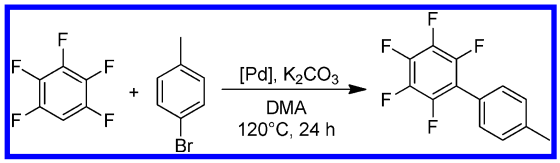
Figure 2. Molecular structure of **7** showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Pd1–C1 2.025(5), Pd1–O1 2.055(4), Pd1–C14 2.031(5), Pd1–O3 2.028(4); C1–Pd1–O1 91.74(17), O1–Pd1–C14 90.36(18), C14–Pd1–O3 89.15(18), O3–Pd1–C1 88.84(18), C1–Pd1–C14 175.6(2), O1–Pd1–O3 178.71(16).

bromido ligands have been replaced with trifluoroacetato ligands, which bind to the Pd center in a monodentate manner. In addition, they are arranged trans to each other. The two remaining coordination sites are taken by one benzimidazole- and one triazole-derived carbene. The two Pd–$C_{carbene}$ bond lengths [2.025(5) and 2.031(5) Å] are essentially the same. The dihedral angles between the carbene planes and the [PdC_2O_2] coordination plane are 64.6(1)° and 51.1(2)°, which deviate substantially from the ideal 90°, probably due to the steric congestion around the metal center. The angle between the two carbene planes amounts to 13.4(2)°.

Catalysis. Although Pd–NHC complexes have been widely used in C–C coupling reactions (vide supra), not much attention has been paid to the direct arylation via direct C–H bond functionalization. Although both reactions may lead to biaryls, direct arylation is superior to Suzuki coupling in the sense that no boronic acid waste will be produced. Direct arylation of pentafluorobenzene with aryl halides has been studied with $Pd(OAc)_2$ and phosphine ligands.[20] Because NHCs are widely recognized as phosphine mimics, it is worth studying and comparing the performance of Pd–NHC complexes in such reactions.

A preliminary test was carried out with 4-bromotoluene and 1.1 equiv of pentafluorobenzene catalyzed by 5 mol % precatalyst **2** in the presence of 1.1 equiv of K_2CO_3 in DMA at 120 °C for 24 h, which resulted in a moderate 54% yield of the desired product (Table 1, entry 1). Surprisingly, when the catalyst loading was decreased to 1 mol %, the yield increased to 67% (entry 2). It has been proven in the Heck- and Suzuki-type reactions that a higher catalyst loading may result in a decrease in the performance as more catalysts may decompose and aggregate to Pd black, which hampers the catalytic process.[21] A 60% yield was still obtained when the loading was further decreased to 0.5 mol % (entry 3). With 0.5 mol % catalyst, precatalyst **1** was also tested at both 120 and 140 °C. At 120 °C, complex **1** outperformed **2** as the yield increased to 82% (entry 4). At 140 °C, however, the yield dramatically dropped to 48% (entry 5). Pd black was observed under this condition, which shut down the catalysis to some extent.[21] With the optimized reaction condition, precatalysts **4**–**7** were screened (entries 6–9). It was found that the most electron-rich complex **4** was not as efficient as **1** and **2**, which shows that

Table 1. Catalyst Screening of the Direct Arylation of Pentafluorobenzene[a]



entry	catalyst	catalyst loading (mol %)	yield (%)[b]	TON
1	**2**	5	54	11
2	**2**	1	67	67
3	**2**	0.5	60	120
4	**1**	0.5	82	164
5[c]	**1**	0.5	48	96
6	**4**	0.5	44	88
7	**5**	0.5	85	170
8	**6**	0.5	82	164
9	**7**	0.5	70	140

[a]Reaction conditions: precatalyst, K_2CO_3 (1.1 equiv), pentafluorobenzene (1.1 equiv), 4-bromotoluene (0.3 mmol), DMA (0.2 mL), 120 °C, 24 h. [b]Isolated yield. [c]140 °C.

complexes bearing less donating 1,2,3-triazolin-5-ylidenes are better precatalysts for the direct arylation of pentafluorobenzene. The same trend was observed for the trifluoroacetato complexes, as **5** proved to be a better performer than **6** and **7**. As expected, they are, in general, better precatalysts than their bromido analogues. For instance, the reaction with **4** only gave 44% yield, while 70% yield was obtained when catalyzed by the trifluoroacetato analogue **7**. Similarly, **5** performed better than **1**, and **6** outperformed **2**. Overall, **5** gave rise to the best catalyst for the direct arylation of pentafluorobenzene.

The scope of this reaction was studied with the best precatalyst **5**. The reaction proceeded well with aryl halide bearing electron-donating groups. An 88% yield was obtained with 4-bromoanisole (Table 2, entry 1). The results are also good with 3-bromotoluene (80% yield, entry 2) and 3-bromoanisole (95% yield, entry 3).

However, no conversion was detected with 2-bromotoluene (entry 4). Apparently, the steric effect is the key factor in this case. The yields also dropped substantially for the couplings with electron-withdrawing aryl bromides (4-bromochlorobenzene, 54%, entry 5; 4-bromobenzonitrile, 18%, entry 6). It is noteworthy that, in the case of 4-bromochlorobenzene, no doubly coupled product was detected at all, although 3 equiv of pentafluorobenzene was added. In contrast, under the same condition, the reaction with 1,3-dibromobenzene only gave the doubly coupled product, although in a low yield (20%, entry 7).

■ CONCLUSION

We have reported a series of *trans*-[$PdBr_2$(^{i}Pr$_2$-bimy)(trz)] complexes **1**–**4** bearing ^{i}Pr$_2$-bimy and mesoionic 1,2,3-triazolin-5-ylidenes with different substituents. The study of their ^{13}C NMR spectra shows that 1,2,3-triazolin-5-ylidenes are, in general, stronger donors than normal NHCs, while weaker than some nonclassical NHCs, for example, pyrazolin-3-ylidenes and mesoionic imidazolin-4-ylidenes. Moreover, this study clearly shows that the donor strength of 1,2,3-triazolin-5-ylidene decreases with decreasing +*I* effect of the substituent at the N1 position. Previously, such substituent effects on the donor ability of triazolin-5-ylidenes could not be discerned by classical IR-based methods, highlighting the superiority of our ^{13}C NMR-based methodology in detecting particularly fine differences among

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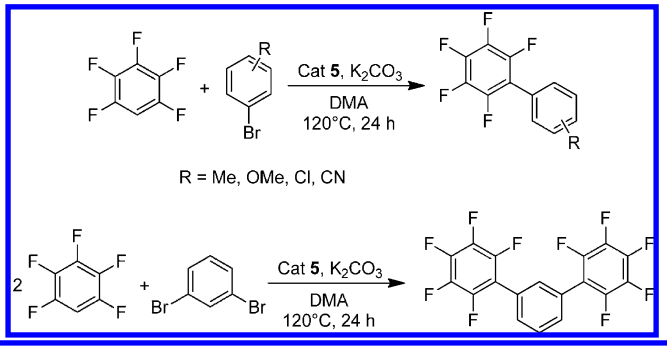
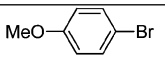
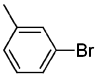
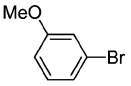
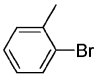
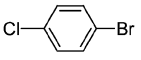
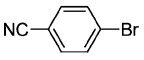
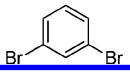
Table 2. Direct Arylation of Pentafluorobenzene[a] Catalyzed by Complex 5[b]



Entry	Aryl halide	Yield [%][b]/TON
1		88
2		80
3		95
4		0
5		54
6		18
7		20

[a]Reaction conditions: precatalyst (1 mol %), K_2CO_3 (1.1 equiv), pentafluorobenzene (1.5 equiv), aryl halide (0.3 mmol, 0.15 mmol in the case of dihalide), DMA (0.2 mL), 120 °C, 24 h. [b]Isolated yields.

ligands. The trifluoroacetato analogues **5**–**7** of complexes **1**, **2**, and **4** have also been synthesized through salt metathesis with AgO_2CCF_3. The catalytic activities of these six complexes were compared in the direct arylation of pentafluorobenzene. Within this series, complexes with less donating ligands perform better in this catalysis and trifluoroacetato complexes outperformed their bromido analogues. Current research in our group is ongoing to extend our donor strength study to a wider range of ligands in an attempt to establish a unified electronic parameter and to explore the catalytic applications of the respective *trans*-[$PdBr_2$(^{i}Pr_2-bimy)L] complex probes.

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. Ph-triazole, Bn-triazole, ^{i}Pr-triazole, and salt **C**·HBF_4[14c] have been synthesized according to reported procedures.[22] ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker ACF 300 spectrometer or AMX 500 spectrophotometer, and the chemical shifts (δ) were internally referenced to the residual solvent signals relative to tetramethylsilane (^{1}H, ^{13}C) or externally to CF_3CO_2H (^{19}F NMR). ESI mass spectra were measured using a Finnigan MAT LCQ spectrometer. Elemental analyses were performed on a PerkinElmer PE 2400 elemental analyzer at the Department of Chemistry, National University of Singapore.

A·HBr. Ph-triazole (86 mg, 0.4 mmol) and benzylbromide (3 mL) were heated in neat at 100 °C for 3 days. After the reaction mixture was cooled to ambient temperature, diethyl ether (20 mL) was added and the resulting suspension was filtered. The precipitate was washed repetitively with copious diethyl ether until the starting materials were fully removed. The product was isolated as a white solid (50 mg, 0.127 mmol, 32%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.18 (s, 1H, NCH), 8.24 (d, 2H, Ar–H), 7.81 (m, 2H, Ar–H), 7.62–7.60 (m, 3H, Ar–H), 7.52 (br-s, 3H, Ar–H), 7.37–7.34 (m, 3H, Ar–H), 7.17 (d, 2H, Ar–H), 5.91 (s, 2H, NCH_2). ^{13}C{^{1}H} NMR (125.76 MHz, $CDCl_3$): 144.7 (s, NCPh), 135.4, 132.7, 132.6, 132.0, 131.1, 130.7, 130.4, 130.3, 130.1, 129.0, 128.8, 122.4, 122.2 (s, Ar–C), 56.8 (s, NCH_2). MS (ESI): m/z = 312 [M − Br]$^+$.

B·HBr. A mixture of Bn-triazole (118 mg, 0.5 mmol) and benzylbromide (1 mL) was heated in neat at 100 °C overnight. Diethyl ether (20 mL) was added, and the resulting suspension was filtered. The precipitate was washed repetitively with diethyl ether until all the starting materials were removed. The compound was isolated as a white solid (93 mg, 0.23 mmol, 46%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.84 (s, 1H, NCH), 7.75–7.06 (m, 15H, Ar–H), 6.25, 5.74 (s, 2H, NCH_2). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): 143.6 (s, NCPh), 132.7, 132.5, 132.1, 131.2, 131.0, 130.5, 130.4, 130.3, 130.1, 129.2, 122.5 (s, Ar–C), 58.4, 56.8 (s, NCH_2). MS (ESI): m/z = 326 [M − Br]$^+$.

D·HBr. ^{i}Pr-triazole (94 mg, 0.5 mmol) and benzylbromide (1 mL) were heated in neat at 100 °C overnight. After reaction, the mixture was allowed to cool to ambient temperature. Diethyl ether (20 mL) was added to the resulting light yellow solution, and some brown oil came out. The mixture was decanted, and the brown oil was redissolved in CH_2Cl_2. The solution was added dropwise into diethyl ether (10 mL), and the suspension was filtered. The precipitate was washed

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repetitively with copious diethyl ether until the starting materials were fully removed. The product was isolated as a brown solid (158 mg, 0.44 mmol, 88%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.75 (s, 1H, NCH), 7.60−7.53 (m, 5H, Ar−H), 7.37−7.35 (m, 3H, Ar−H), 7.09 (d, 2H, Ar−H), 5.71 (s, 2H, NCH_2), 5.55 (m, 1H, ^3J(H, H) = 7.1 Hz, $CH(CH_3)_2$), 1.80 (d, 6H, ^3J(H, H) = 7.1 Hz, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$): 143.6 (s, NCPh), 132.7, 132.2, 131.5, 130.5, 130.3, 130.1, 129.5, 128.6, 122.6 (s, Ar−C), 59.7 (s, NCH_2), 56.1 (s, NCH), 23.1 (s, CH_3). MS (ESI): m/z = 278 $[M - Br]^+$.

***trans*-[PdBr$_2$(^{i}Pr$_2$-bimy)(A)](1).** A mixture of salt **A**·HBr (50 mg, 0.13 mmol), $[PdBr_2(^iPr_2\text{-bimy})]_2$ (60 mg, 0.06 mmol), and Ag_2O (18 mg, 0.08 mmol) was stirred in CH_2Cl_2 (15 mL) at ambient temperature overnight shielded from light. The resulting suspension was filtered over Celite, and the filtrate was removed in vacuo. The residue was subjected to column chromatography (SiO_2, ethyl acetate/hexane, 3:7), and the pure compound was isolated as a yellow solid (44 mg, 0.056 mmol, 44%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.57−8.53 (dd, 2H, Ar−H), 7.99−7.96 (dd, 2H, Ar−H), 7.63−7.56 (m, 6H, Ar−H), 7.47−7.42 (m, 2H, Ar−H), 7.36−7.34 (m, 3H, Ar−H), 7.20−7.10 (m, 4H, Ar−H), 5.90 (m, 1H, ^3J(H, H) = 7.1 Hz, $CH(CH_3)_2$), 5.73 (m, 1H, ^3J(H, H) = 7.1 Hz, $CH(CH_3)_2$), 5.55 (s, 2H, NCH_2), 1.64 (d, 6H, ^3J(H, H) = 7.1 Hz, $CH(CH_3)_2$), 1.53 (d, 6H, ^3J(H, H) = 7.1 Hz, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$): 180.3 (s, NCN−^{i}Pr$_2$-bimy), 160.6 (s, NCCPh), 145.9, 140.6, 134.3, 134.2, 133.7, 132.0, 130.4, 130.3, 129.8, 129.7, 129.4, 129.1, 128.8, 128.6, 126.1, 122.3, 113.0 (s, Ar−C), 54.4, 54.2, 54.0 (s, NCH_2 + NCH), 21.6, 21.5 (s, CH_3). Anal. Calcd for $C_{34}H_{35}Br_2N_5Pd$: C, 52.36; H, 4.52; N, 8.98. Found: C, 52.13; H, 4.61; N, 9.19%. MS (ESI): m/z = 700 $[M - Br]^+$, 1480 $[2M - Br]^+$.

***trans*-[PdBr$_2$(^{i}Pr$_2$-bimy)(B)](2).** A mixture of salt **B**·HBr (93 mg, 0.23 mmol), $[PdBr_2(^iPr_2\text{-bimy})]_2$ (107 mg, 0.11 mmol), and Ag_2O (28 mg, 0.12 mmol) was stirred in CH_2Cl_2 (15 mL) shielded from light. The suspension was filtered over Celite, and the solvent of the filtrate was removed to give the product as a yellow solid (159 mg, 0.20 mmol, 87%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (s, 2H, Ar−H), 7.74−7.73 (m, 2H, Ar−H), 7.52−7.39 (m, 9H, Ar−H), 7.30 (br-s, 2H, Ar−H), 7.14 (s, 2H, Ar−H), 7.03 (s, 2H, Ar−H), 6.16 (s, 2H, NCH_2), 5.96 (m, 2H, $CH(CH_3)_2$), 5.42 (s, 2H, NCH_2), 1.71 (br-s, 6H, $CH(CH_3)_2$), 1.57 (br-s, 6H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$): 180.8 (s, NCN−^{i}Pr$_2$-bimy), 160.4 (s, NCCPh), 146.0, 135.4, 134.3, 133.9, 131.8, 130.1, 129.7, 129.4, 129.35, 129.0, 128.9, 128.2, 122.3, 113.0 (s, Ar−C), 59.0, 54.2, 54.0 (s, NCH_2 + NCH), 21.7, 21.4 (s, CH_3). Anal. Calcd for $C_{35}H_{37}Br_2N_5Pd$: C, 52.95; H, 4.70; N, 8.82. Found: C, 52.54; H, 4.51; N, 8.86%. MS (ESI): m/z = 714 $[M - Br]^+$, 1508 $[2M - Br]^+$.

***trans*-[PdBr$_2$(^{i}Pr$_2$-bimy)(C)](3).** A mixture of $[PdBr_2(^iPr_2\text{-bimy})]_2$ (94 mg, 0.1 mmol) and tetrabutylammonium bromide (64 mg, 0.2 mmol) was heated in $CHCl_3$ (5 mL) at refluxing temperature for 3 h. All the volatiles were removed in vacuo to give an orange solid that was redissolved in CH_2Cl_2 (15 mL). Salt **C**·HBF_4 (67 mg, 0.2 mmol) and Ag_2O (28 mg, 0.12 mmol) were added to the solution, and the resulting mixture was stirred at ambient temperature overnight shielded from light. The suspension was filtered through Celite. The filtrate was extracted with H_2O (3 × 10 mL) and dried over Na_2SO_4. All the volatiles were removed to give the product as a yellow solid (129 mg, 0.18 mmol, 90%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01 (d, 2H, Ar−H), 7.79 (d, 2H, Ar−H), 7.56−7.39 (m, 8H, Ar−H), 7.16−7.14 (m, 2H, Ar−H), 6.13 (s, 2H, NCH_2), 6.05 (m, 2H, ^3J(H, H) = 7.1 Hz, $CH(CH_3)_2$), 1.73 (d, 6H, ^3J(H, H) = 7.1 Hz, $CH(CH_3)_2$), 1.63 (d, 6H, ^3J(H, H) = 7.1 Hz, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$): 180.8 (s, NCN−^{i}Pr$_2$-bimy), 160.0 (s, NCCPh), 145.8, 135.2, 134.2, 131.3, 130.0, 129.9, 129.4, 129.1, 128.9, 128.85, 122.3, 113.0 (s, Ar−C), 59.0, 54.2, 54.0 (s, NCH_2 + NCH), 37.6 (s, NMe_3), 21.6, 21.4 (s, CH_3). Anal. Calcd for $C_{29}H_{33}Br_2N_5Pd$: C, 48.52; H, 4.63; N, 9.76. Found: C, 48.03; H, 4.51; N, 9.84%. MS (ESI): m/z = 638 $[M - Br]^+$, 1356 $[2M - Br]^+$.

***trans*-[PdBr$_2$(^{i}Pr$_2$-bimy)(D)](4).** A mixture of salt **D**·HBr (51 mg, 0.14 mmol), $[PdBr_2(^iPr_2\text{-bimy})]_2$ (67 mg, 0.07 mmol), and Ag_2O (20 mg, 0.09 mmol) was suspended in CH_2Cl_2 (15 mL) and stirred at ambient temperature overnight shielded from light. The resulting suspension was filtered through Celite, and the solvent of the filtrate was removed. The crude product was purified by column chromatography (SiO_2, ethyl acetate/hexane, 3:7) to give the desired compound as a yellow solid (60 mg, 0.08 mmol, 57%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85−7.83 (dd, 2H, Ar−H), 7.53−7.49 (m, 4H, Ar−H), 7.47−7.45 (m, 1H, Ar−H), 7.33−7.31 (m, 3H, Ar−H), 7.15−7.13 (m, 2H, Ar−H), 7.07−7.05 (m, 2H, Ar−H), 6.05 (m, 1H, ^3J(H, H) = 7.1 Hz, $CH(CH_3)_2$), 5.90 (m, 1H, ^3J(H, H) = 7.1 Hz, $CH(CH_3)_2$), 5.74 (m, 2H, ^3J(H, H) = 7.1 Hz, $CH(CH_3)_2$), 5.44 (s, 2H, NCH_2), 1.86 (d, 6H, ^3J(H, H) = 7.1 Hz, $CH(CH_3)_2$), 1.82 (d, 6H, ^3J(H, H) = 7.1 Hz, $CH(CH_3)_2$), 1.53 (d, 6H, ^3J(H, H) = 7.1 Hz, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$): 181.2 (s, NCN−^{i}Pr$_2$-bimy), 157.9 (s, NCCPh), 144.9, 134.3, 134.2, 134.17, 131.7, 129.9, 129.7, 129.3, 129.2, 128.9, 128.1, 122.3, 113.0, 112.9 (s, Ar−C), 58.7, 54.1, 54.0, 53.7 (s, NCH_2 + NCH), 23.5, 21.9, 21.3 (s, CH_3). Anal. Calcd for $C_{31}H_{37}Br_2N_5Pd$: C, 49.92; H, 5.00; N, 9.39. Found: C, 49.64; H, 4.95; N, 9.40%. MS (ESI): m/z = 666 $[M - Br]^+$, 1412 $[2M - Br]^+$.

[Pd(O$_2$CCF$_3$)$_2$(^{i}Pr$_2$-bimy)(A)](5). A mixture of **1** (51 mg, 0.065 mmol) and AgO_2CCF_3 (29 mg, 0.13 mmol) was suspended in CH_3CN (10 mL) and heated at 70 °C overnight shielded from light. The reaction mixture was filtered over Celite, and the solvent of the filtrate was evaporated off. The resulting yellow solid was redissolved in CH_2Cl_2 (5 mL) and passed through silica gel. The solvent of the filtrate was removed to give the product as a yellow solid (44 mg, 0.051 mmol, 80%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.64 (d, 2H, Ar−H), 8.01−7.99 (m, 2H, Ar−H), 7.68−7.63 (m, 3H, Ar−H), 7.59−7.57 (m, 3H, Ar−H), 7.52−7.44 (m, 2H, Ar−H), 7.36−7.31 (m, 3H, Ar−H), 7.19−7.17 (m, 2H, Ar−H), 7.10−7.09 (m, 2H, Ar−H), 6.06−6.01 (m, 2H, ^3J(H, H) = 7.1 Hz, $CH(CH_3)_2$), 5.56 (s, 2H, NCH_2), 1.60 (d, 12H, ^3J(H, H) = 7.1 Hz, $CH(CH_3)_2$). Signals of the minor isomer are not assigned due to overlap. The ratio of the isomeric pair is around 4:1. $^{13}C\{^1H\}$ NMR (125.77 MHz, $CDCl_3$): 176.5 (s, NCN−^{i}Pr$_2$-bimy), 162.2 (q, ^2J(C, F) = 36.7 Hz, COO), 155.2 (s, NCCPh), 146.9, 140.0, 133.8, 133.7, 131.7, 130.9, 130.7, 130.6, 129.9, 129.7, 129.5, 129.4, 129.1, 128.8, 128.6, 128.1, 127.9, 125.9, 123.0 (s, Ar−C), 114.8 (q, ^1J(C, F) = 283.2 Hz, CF_3), 113.4 (s, Ar−C), 54.3, 54.0 (s, NCH_2 + NCH), 22.0, 21.9 (s, CH_3). ^{19}F NMR (282.37 MHz, $CDCl_3$): 1.98 (s, CF_3). Anal. Calcd for $C_{38}H_{35}F_6N_5O_4Pd$: C, 53.94; H, 4.17; N, 8.28. Found: C, 53.71; H, 4.14; N, 8.62%. MS (ESI): m/z = 733 $[M - OOCCF_3]^+$.

[Pd(O$_2$CCF$_3$)$_2$(^{i}Pr$_2$-bimy)(B)](6). This complex was synthesized in analogy to complex **5** from complex **2** (complex **2**: 50 mg, 0.063 mmol; AgOOCCF3: 28 mg, 0.126 mmol; Yield: 32 mg, 0.037 mmol, 59%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85−7.83 (dd, 2H, Ar−H), 7.71 (d, 2H, Ar−H), 7.56−7.52 (m, 5H, Ar−H), 7.47−7.41 (m, 2H, Ar−H), 7.31−7.27 (m, 4H, Ar−H), 7.20−7.18 (dd, 2H, Ar−H), 6.94−6.92 (m, 2H, Ar−H), 6.14−6.10 (m, 4H, NCH_2 + $CH(CH_3)_2$), 5.44 (s, 2H, NCH_2), 1.66 (d, 12H, $CH(CH_3)_2$). Signals of the minor isomer are not assigned due to overlap. The ratio of the isomeric pair is around 6:1. $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$): 176.3 (s, NCN−^{i}Pr$_2$-bimy), 162.0 (q, ^2J(C, F) = 35.8 Hz, COO), 155.5 (s, NCCPh), 146.7, 135.3, 134.0, 133.7, 131.4, 130.5, 129.8, 129.7, 129.6, 129.5, 129.3, 129.2, 128.1, 127.8, 123.3, 123.0 (s, Ar−C), 114.9 (q, ^1J(C, F) = 290.5 Hz, CF_3), 113.7, 113.2 (s, Ar−C), 58.8, 54.5, 54.2, 54.0 (s, NCH_2 + NCH), 22.1, 21.9 (s, CH_3). ^{19}F NMR (282.37 MHz, $CDCl_3$): 2.15 (s, CF_3). Anal. Calcd for $C_{39}H_{37}F_6N_5O_4Pd$: C, 54.46; H, 4.34; N, 8.14. Found: C, 54.26; H, 4.36; N, 8.31%. MS (ESI): m/z = 787 $[M - O_2CCF_3 + CH_3CN]^+$.

[Pd(O$_2$CCF$_3$)$_2$(^{i}Pr$_2$-bimy)(D)](7). This complex was synthesized in analogy to complex **5** from complex **4** (complex **4**: 50 mg, 0.067 mmol; AgOOCCF3: 30 mg, 0.134 mmol; Yield: 45 mg, 0.055 mmol, 83%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87−7.85 (dd, 2H, Ar−H), 7.55−7.52 (m, 5H, Ar−H), 7.33−7.32 (m, 3H, Ar−H), 7.21−7.19 (m, 2H, Ar−H), 6.97−6.95 (m, 2H, Ar−H), 6.16 (m, 2H, ^3J(H, H) = 7.1 Hz, $CH(CH_3)_2$), 5.82 (m, 1H, ^3J(H, H) = 7.1 Hz, $CH(CH_3)_2$), 5.29 (s, 2H, NCH_2), 1.83 (d, 6H, ^3J(H, H) = 7.1 Hz, $CH(CH_3)_2$), 1.69 (d, 6H, ^3J(H, H) = 7.1 Hz, $CH(CH_3)_2$). Signals of the minor isomer are not assigned due to overlap. The ratio of the isomeric pair is around 5:1. $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$): 177.0 (s, NCN−^{i}Pr$_2$-bimy), 162.0 (q, ^2J(C, F) = 35.7 Hz, COO), 153.1 (s, NCCPh), 145.8,

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134.4, 133.8, 131.4, 130.3, 129.8, 129.76, 129.4, 129.1, 128.3, 127.5, 123.3, 123.0 (s, Ar−C), 114.9 (q, ^1J(C, F) = 294.2 Hz, CF_3), 113.4 (s, Ar−C), 58.6, 54.5, 54.1, 53.9 (s, NCH_2 + NCH), 23.6, 22.0, 21.99 (s, CH_3). ^{19}F NMR (282.37 MHz, $CDCl_3$): 2.08 (s, CF_3). Anal. Calcd for $C_{35}H_{37}F_6N_5O_4Pd$: C, 51.76; H, 4.59; N, 8.62. Found: C, 51.52; H, 4.74; N, 8.71%. MS (ESI): m/z = 699 $[M - O_2CCF_3]^+$.

Direct Arylation of Pentafluorobenzene. In a typical run, a Schlenk tube was charged with precatalyst, K_2CO_3 (0.33 mmol), and aryl halide if it is a solid. The reaction vessel was evacuated and refilled with nitrogen three times. Aryl halide (if it is a liquid), pentafluorobenzene (0.3 mmol), and DMA (0.2 mL) were added, and the reaction was placed in a preheated oil bath and stirred. After 24 h, the mixture was cooled to the 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 an eluent to get pure compound.

X-ray Diffraction Studies. X-ray data for **7** were collected with a Bruker AXS SMART APEX diffractometer, using Mo Kα radiation at 100(2) K with the SMART suite of Programs.[23] Data were processed and corrected for Lorentz and polarization effects with SAINT,[24] and for absorption effects with SADABS.[25] Structural solution and refinement were carried out with the SHELXTL suite of programs.[26] 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 ref 27.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data for **7** as a CIF file and ^{1}H and ^{13}C NMR spectra of complexes **1**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(27) Formula, $C_{35}H_{37}F_6N_5O_4Pd$; fw, 812.10; color, yellow; habit, block; cryst size [mm], 0.26 × 0.20 × 0.12; temp [K], 100(2); cryst syst, monoclinic; space group, *P*2(1)/c; *a* [Å], 13.266(5); *b* [Å], 13.365(5); *c* [Å], 20.934(8); α [deg], 90; β [deg], 102.354(12); γ [deg], 90; *V* [Å^3], 3626(2); *Z*, 4; D_c [g cm^{-3}], 1.488; radiation used, Mo Kα; μ [mm^{-1}], 0.587; θ range [deg], 1.82−25.00; no. of unique data, 6381; max., min transm, 0.9329, 0.8623; final *R* indices [$I > 2\sigma(I)$], R_1 = 0.0612, wR_2 = 0.1384; *R* indices (all data), R_1 = 0.0842, wR_2 = 0.1482; goodness-of-fit on F^2, 1.064; peak/hole [e Å^{-3}], 2.272/−0.691.