ORGANOMETALLICS

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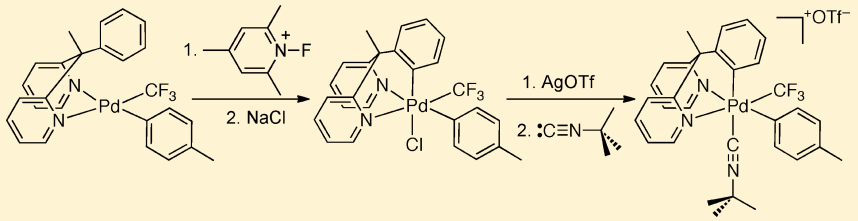
Facial Tridentate Ligands for Stabilizing Palladium(IV) Complexes

Ansis Maleckis and Melanie S. Sanford*

Department of Chemistry, University of Michigan, 930 North University Avenue, Ann Arbor, Michigan 48109, United States

Supporting Information



ABSTRACT: This paper describes the synthesis of a series of Pd^{IV} complexes containing modular monoanionic tridentate facially coordinated NNN and NNC donor ligands. In all cases, these complexes are stable to reductive elimination for a minimum of several days in solution at room temperature. With appropriately designed tridentate ligands, the Pd^{IV} adducts participate in both ligand substitution and C−H activation reactions. Overall, this work shows that unsymmetrical *fac*-L_2X type ligands can serve as versatile and tunable scaffolds for modulating the reactivity of octahedral Pd^{IV} complexes.

INTRODUCTION

Over the past decade, there has been tremendous progress in the development of organic reactions involving high-oxidation-state Pd intermediates.[1] A wide variety of important transformations have been proposed to proceed via such manifolds, including arene and alkane C−H oxidation,[2] alkene difunctionalization,[1d] and Pd/norbornene-catalyzed aromatic alkylation.[3] In all of these cases, carbon−carbon or carbon−heteroatom bond-forming reductive elimination from Pd^{IV} (or closely related dimeric Pd^{III} species) is believed to be a key step of the catalytic cycle. As a result, there has been significant recent interest in the synthesis of Pd^{IV} model complexes[4−8] in order to conduct detailed studies of the mechanism and selectivity of reductive elimination from high-oxidation-state palladium.

In contrast to reductive elimination processes, other organometallic transformations (e.g., ligand substitution,[9] C−H activation,[10] alkene insertion) at Pd^{IV} centers have received considerably less attention. Several recent reports have proposed that these types of reactions serve as key steps in $Pd^{II/IV}$-catalyzed transformations. For example, ligand substitution at Pd^{IV} centers to incorporate solvent and/or halide additives as X-type ligands has been proposed as a key step in catalytic C−H etherification[11] and olefin aminofluorination reactions.[12] C−H activation at Pd^{IV} centers has been implicated in several catalytic reactions, including the dimerization of 2-arylpyridine derivatives,[13e] the carboamination of olefins,[13b] the acetoxylation of allylic C−H bonds,[13c] and direct arylation of naphthalene.[13a,d] In addition, alkene insertion at Pd^{IV} is believed to occur during the Pd-catalyzed olefination of diaryliodonium salts.[14] As such, stoichiometric studies of the feasibility, mechanism, selectivity, and relative rates of such fundamental reactions at Pd^{IV} centers could provide key insights for designing, optimizing, and improving these and related catalytic processes.

With these goals in mind, we sought to identify ligands that would stabilize Pd^{IV} complexes, thereby slowing the relative rate of reductive elimination versus that of these other transformations. Facially coordinated monoanionic tridentate ligands were targeted, because these are known to support a number of isolable organometallic Pd^{IV} complexes.[7,15−17] This paper describes the synthesis of a series of Pd^{IV} compounds containing modular tridentate *fac*-NNN and *fac*-NNC donor ligands. In all cases, these complexes are stable to reductive elimination for at least 2 days in solution at room temperature. With appropriately designed tridentate ligands, the Pd^{IV} adducts participate in both ligand substitution and C−H activation reactions. Overall, this work shows that *fac*-L_2X type ligands can serve as versatile and tunable scaffolds for modulating the reactivity of octahedral Pd^{IV} complexes.

RESULTS AND DISCUSSION

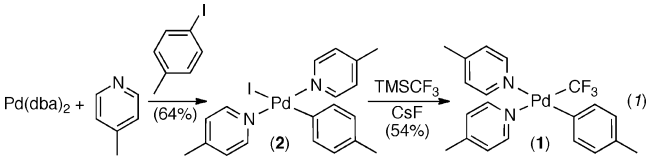
Target Complexes. Our studies targeted complexes of general structure (*fac*-L_2X)$Pd^{IV}(CF_3)$(aryl)(halide). The *fac*-L_2X and trifluoromethyl (CF_3) ligands were selected in order to stabilize the Pd^{IV} center and render competing reductive elimination reactions relatively slow.[5a,7,8,15−17] The halide was anticipated to be a labile ligand that could serve as a site of reactivity at the high-oxidation-state Pd center.

Synthesis of Pd^{II} Precursor. Our initial synthetic efforts focused on identifying a (L)(L′)Pd^{II}(Aryl)(CF_3) precursor that could be used for the synthesis of diverse (*fac*-L_2X)Pd^{II}(Aryl)(CF_3) complexes. It was of particular importance that L and L′ be easily displaced by a wide variety of other ligands. Previous reports have shown that

Received: August 19, 2011
Published: November 18, 2011

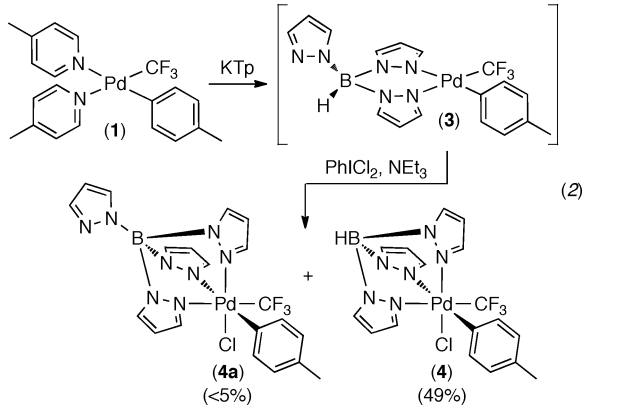
(tmeda)$Pd^{II}(CH_3)_2$ and (tmeda)$Pd^{II}(CH_3)(C_6H_5)$ undergo facile ligand exchange with monophosphines, diphosphines, and bipyridine;[18] as such, we initially hypothesized that (tmeda)-Pd^{II}(Aryl)(CF_3) would be a convenient palladium starting material. While the synthesis of (tmeda)Pd^{II}(Aryl)(CF_3) was straightforward and high yielding, clean ligand exchange was not observed with the *fac*-L_2X ligands investigated in this study. As such, we next targeted the Pd^{II} complex *cis*-(4-Mepy)$_2$Pd(4-MeC_6H_4)(CF_3) (**1**; 4-Mepy = 4-methylpyridine), which contains more labile monodentate 4-Mepy ligands.

As shown in eq 1, complex **1** was prepared in two straightforward steps. First, oxidative addition of 1-iodo-4-

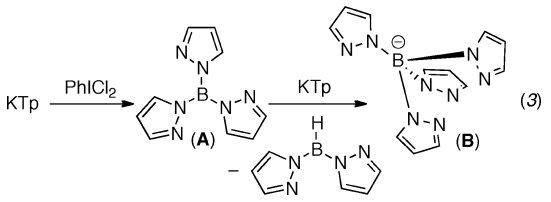


methylbenzene to Pd(dba)$_2$ in the presence of 10 equiv of 4-methylpyridine afforded *trans*-(4-Me-py)$_2$Pd(4-MeC_6H_4)(I) (**2**) in 64% yield.[8a] Since it was not stable in solution, complex **2** was carried forward crude. In the second step, the treatment of **2** with excess CsF/$TMSCF_3$ provided **1** in 54% yield as a white solid.[8a] Notably, the use of dry CsF and anhydrous solvent was essential in order to obtain reproducible yields of **1**. The product was characterized by ^{19}F, ^{13}C, and ^1H NMR spectroscopy. Complex **1** decomposes slowly over 24 h in $CDCl_3$ solution with concomitant release of Pd black; however, it is stable in the solid state for several weeks at room temperature.

Tris(pyrazolyl)borate Ligand. With precursor **1** in hand, we first examined the synthesis of (Tp)Pd^{IV}(4-MeC_6H_4)(CF_3)-(Cl) (Tp = tris(pyrazolyl)borate). Tris(pyrazolyl)borate was selected as the supporting ligand because this tridentate L_2X donor is well-precedented to stabilize a number of other Pd^{IV} complexes.[16] The treatment of **1** with KTp in acetone for 5 min at room temperature afforded the Pd^{II} complex **3**, which was carried forward without further purification (eq 2).[16] The in situ oxidation of **3** with $PhICl_2$[5b] yielded a mixture of **4** and **4a** in an approximately 7:3 ratio.

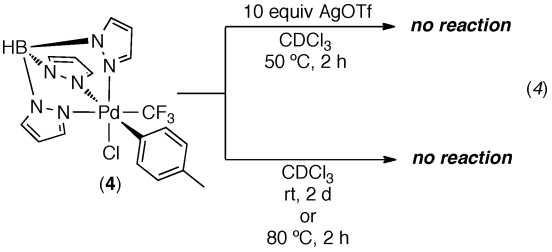


We hypothesized that oxidation of the borohydride ligand to trispyrazolylborane (**A**) and subsequent transfer of a Lewis basic pyrazolyl group formed tetrapyrazolylborate anion (**B**) (eq 3). Subsequent ligand exchange and oxidation could then afford **4a** as a side product to **4**. Consistent with this proposal, the addition of 1 equiv of triethylamine as a sacrificial Lewis



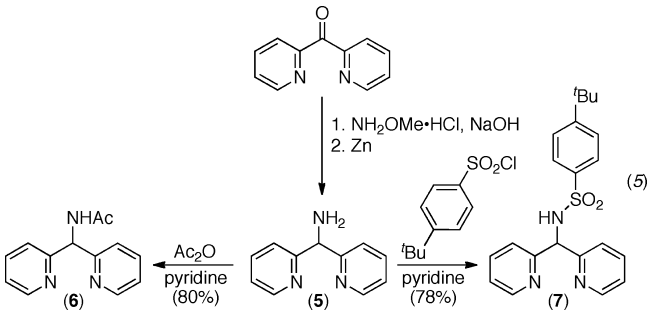
base to scavenge in situ formed trispyrazolylborane decreased the yield of side product **4a** to <5%. Under these conditions, product **4** was obtained in 49% yield after purification by flash chromatography (eq 2). It was characterized by ^1H, ^{13}C, ^{19}F, and ^{11}B NMR spectroscopy.

Reactivity studies of complex **4** revealed that it is highly inert toward both ligand substitution and reductive elimination. For example, the treatment of **4** with 10 equiv of AgOTf or $AgBF_4$ in $CDCl_3$ for 2 h at 50 °C did not afford any substitution of the chloride ligand (eq 4).[19] Complex **4** was also stable in $CHCl_3$



solution for several days at room temperature as well as for up to 2 h at 80 °C.[20] Under these conditions the starting material could be recovered quantitatively from the reaction mixtures. The high thermal stability of **4** is likely tied to the low lability of the Cl ligand, since X-type ligand dissociation is the first step of many reductive elimination reactions from Pd^{IV} centers.[5,6,8]

Bipyridylamide Ligands. We reasoned that unsymmetrical *fac*-tridentate ligands containing a σ donor stronger than pyrazole might enhance the reactivity of Pd^{IV} complexes toward X-type ligand substitution and reductive elimination. Thus, the bipyridylamide ligands **6** (dpaa) and **7** (dpsa) were synthesized. As shown in eq 5, bis(pyridin-2-yl)methylamine (**5**) was



obtained from dipyridyl ketone, as described in the literature.[21] Precursor **5** was then reacted with Ac_2O to form **6** in 80% yield and with (p-$^tBuC_6H_4$)SO_2Cl to afford sulfonamide **7** in 78% yield.

The treatment of complex **1** with 1.15 equiv of ligands **6** and **7** at room temperature afforded Pd^{II} products **8** and **9** in 88% and 78% yields, respectively (eq 6). Complexes **8** and **9** were characterized by ^1H, ^{13}C, and ^{19}F NMR spectroscopy, and all resonances were assigned by 2D $^1H/^1H$ COSY, $^1H/^{13}C$ HSQC, and $^1H/^{13}C$ HMBC NMR spectra.

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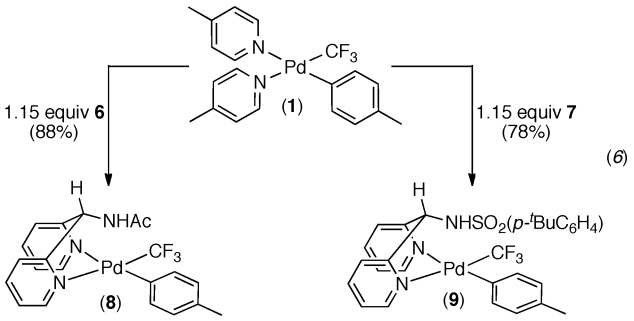


The configurations of complexes **8** and **9** were established using 2D ^{1}H/^{1}H ROESY NMR experiments. Important correlations are shown in Figure 1. For both molecules, the

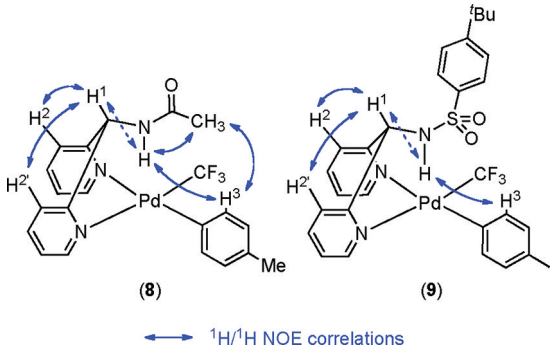
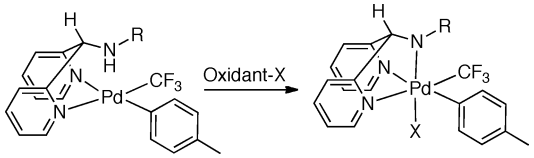


Figure 1. ^{1}H/^{1}H NOE correlations for complexes **8** and **9**.

amide functionality is in the endo position over the square plane of palladium, as evidenced by (1) an NOE correlation between the NH proton of the amide and H^3 and (2) strong correlation between H^1 and H^2/H$^{2'}$ as well as by (3) the lack of NOE correlations between the NH proton and H^2 and H$^{2'}$. The preference for the endo isomer may be a consequence of a noncovalent interaction between the palladium and the NH proton; however, the very weak NOE correlation between the NH proton and H^1 is indicative of some torsional flexibility about the HN−CH^1 bond.

As shown in Table 1, the oxidation of **8** and **9** with $PhICl_2$ at room temperature in CH_2Cl_2 afforded **10** (47% yield) and **11**

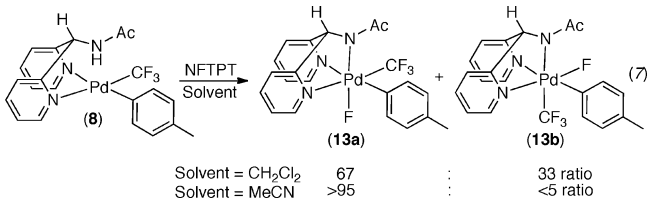
Table 1. Synthesis of NNN-Ligated Palladium(IV) Complexes 10−12



entry	oxidant (X)	R (complex)	yield, % (product)
1	$PhICl_2$ (Cl)	Ac (**8**)	47 (**10**)
2	$PhICl_2$ (Cl)	*p*-^{t}BuC$_6$H$_4$SO$_2$ (**9**)	42 (**11**)
3	NFTPT (F)	*p*-^{t}BuC$_6$H$_4$SO$_2$ (**9**)	68 (**12**)

(42% yield), respectively. Complex **9** also reacted with *N*-fluoro-2,4,6-trimethylpyridinium triflate (NFTPT)[8] to afford the corresponding Pd^{IV} fluoride **12** in 68% yield. In all three of these reactions, a single stereoisomer was detected in both the crude and isolated products. Complexes **10−12** were all purified via column chromatography on silica gel.

In contrast to the reactions in Table 1, the oxidation of **8** with NFTPT in CH_2Cl_2 at room temperature afforded the two different isomeric products **13a** and **13b** (eq 7). ^{1}H NMR



spectroscopic analysis of the crude reaction mixture showed a 67:33 ratio of **13a** and **13b**. These compounds were purified by an aqueous workup followed by chromatography on silica gel and were isolated in 40% and 33% yields, respectively.[22] Interestingly, when the reaction solvent was changed from CH_2Cl_2 to MeCN, product **13a** was obtained as a single detectable stereoisomer in 53% yield.

Complexes **10−13** were characterized by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy, and all resonances were assigned by 2D ^{1}H/^{1}H COSY, ^{1}H/^{13}C HSQC, and ^{1}H/^{13}C HMBC NMR experiments. For amide complexes **11**, **12**, and **13a,b**, the stereochemistry about the Pd^{IV} centers was established via ^{19}F/^{1}H HOESY and ^{1}H/^{1}H ROESY NMR experiments. Significant HOE and NOE correlations are shown in Figure 2.

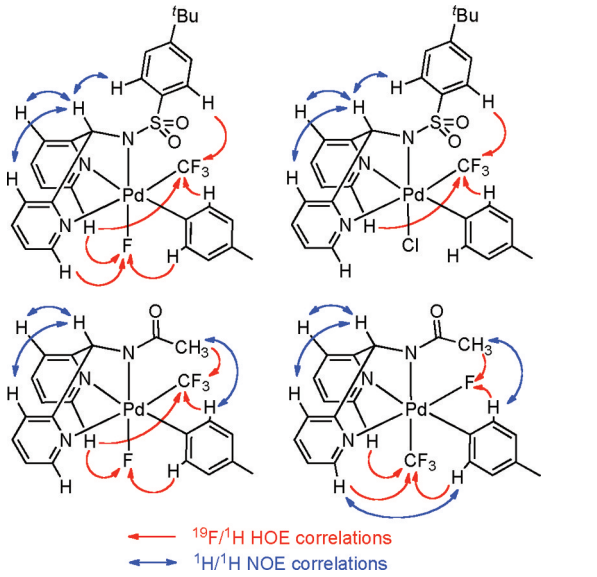


Figure 2. ^{19}F/^{1}H HOE and ^{1}H/^{1}H NOE correlations for complexes **11−13**.

The stereochemistry of complex **10** was assigned on the basis of a pattern of ^{1}H NMR resonances very similar to those of complex **13a**.

The structure and stereochemistry of the Pd^{IV} sulfonamide complexes **11** and **12** were further confirmed by single-crystal X-ray diffraction analysis. Crystals of **11** and **12** were obtained by slow diffusion of MTBE into a MeCN solution at −20 °C. In each case, the solid-state structure was fully consistent with the solution NMR data presented above. Thermal ellipsoid plots of **11** and **12** as well as key bond distances and bond angles are shown in Figures 3 and 4, respectively.

Compounds **10−13** were inert toward carbon−halogen and/or carbon−CF_3 bond-forming reductive elimination. For

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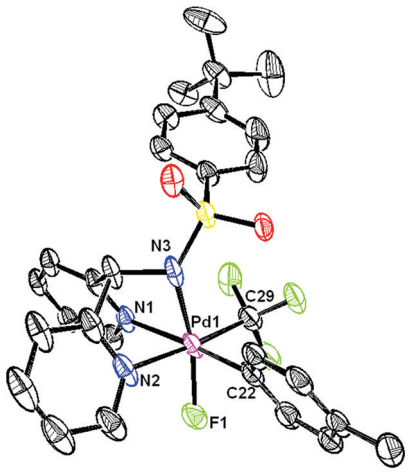


Figure 3. Thermal ellipsoid plot of complex **11**. Thermal ellipsoids are shown at the 50% probability level. H atoms and solvent molecules within the lattice have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd1−C22, 2.027; Pd1−C29, 2.025; Pd1−N1, 2.184; Pd1−N2, 2.128; Pd1−N3, 2.023; Pd1−F1, 1.948; N2−Pd1−N1, 81.2; N2−Pd1−N3, 78.0; N1−Pd1−N3, 79.8; N1−Pd1−C22, 173.4; N2−Pd1−C29, 175.8; N3−Pd1−F1, 168.2, N3−Pd1−C29, 98.6; C29−Pd1−C22, 90.6; C22−Pd1−F1, 88.1.

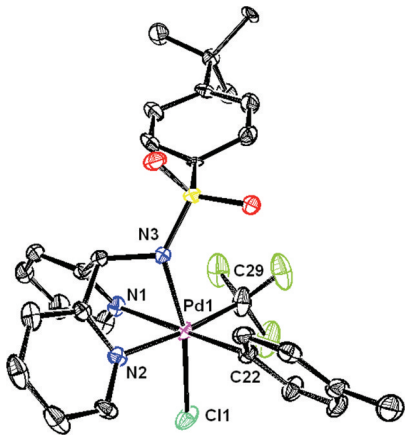
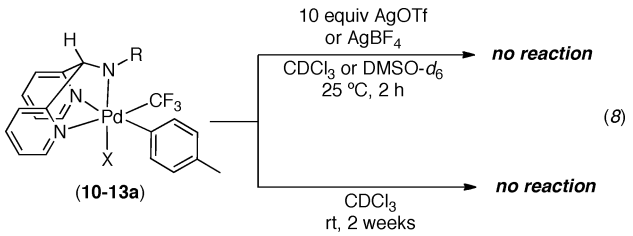


Figure 4. Thermal ellipsoid plot of complex **12**. Thermal ellipsoids are shown at the 50% probability level. H atoms and solvent molecules within the lattice have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd1−C22, 2.043; Pd1−C29, 2.029; Pd1−N1, 2.190; Pd1−N2, 2.137; Pd1−N3, 2.048; Pd1−Cl1, 2.297; N2−Pd1−N1, 83.0; N2−Pd1−N3, 77.5; N1−Pd1−N3, 78.5; N1−Pd1−C22, 174.2; N2−Pd1−C29, 174.6; N3−Pd1−Cl1, 166.3; N3−Pd1−C29, 97.3; C29−Pd1−C22, 89.8; C22−Pd1−Cl1, 90.7.

example, they were stable in $CDCl_3$ solution for at least 2 weeks at room temperature. Complexes **10**−**13** did decompose after heating at 80 °C for several hours in DMSO solution. However, this transformation yielded an intractable mixture of organic and inorganic products that precluded definitive characterization.

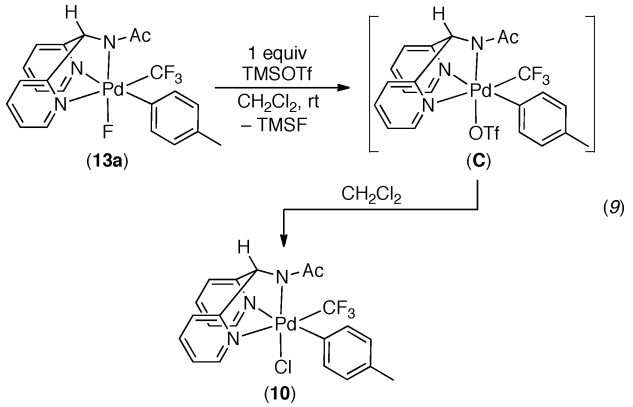
We next examined the reactivity of **10**−**13** toward ligand substitution. Remarkably, despite the relatively large trans influence of amide X-type ligands,[23] complexes **10**−**12** and **13a** showed no reaction upon treatment with 10 equiv of AgOTf or $AgBF_4$ in $CDCl_3$ or DMSO-d_6 for 2 h at room temperature (eq 8). In the reactions with Ag salts in $CDCl_3$, ^{1}H NMR spectroscopic analysis of the crude mixtures showed some



(8)

shifting of the amide ligand resonances; however, quenching with NBu_4I returned only starting material.

In contrast, these complexes did show some reactivity with the highly electrophilic reagent TMSOTf. For example, the treatment of **13a** with 1 equiv of TMSOTf in CD_2Cl_2 solution at room temperature produced chloride complex **10** in quantitative yield (eq 9). This transformation presumably



(9)

occurs via in situ generation of OTf complex **C**, which abstracts chloride from a molecule of solvent. Intermediate **C** was not detected by ^{1}H or ^{19}F NMR spectroscopy in CD_2Cl_2; however, when the reaction was conducted in $CDCl_3$, this putative intermediate was observed but underwent fast decomposition (over 2 h at room temperature) to a complex mixture of unidentified products.

Bipyridylaryl Ligands. We next pursued complexes containing facial tridentate NNC donor ligands, where N = pyridine and C = σ-aryl. The σ-aryl is expected to have a large trans influence,[21] thereby facilitating dissociation of a trans X-type ligand. Notably, while *mer*-NNC and *mer*-NCN pincer ligands have been widely used in high-valent Pd chemistry,[7,17] analogous *fac*-NNC ligands have not been well studied at Pd^{IV}.[24] Ligand **14** (dpph) was synthesized starting from 2-benzylpyridine by sequential deprotonation/arylation with 2-bromopyridine followed by deprotonation/alkylation with CH_3I (eq 10). Metalation of **14** with **1** afforded **15** in 70% yield as a single stereoisomer.

Resonances in the ^{1}H NMR spectrum of **15** are broad at room temperature and protons at the ortho and meta positions of the tolyl and phenyl rings appear to be nonequivalent, which indicates hindered rotation about the C−phenyl and Pd−tolyl bonds. At 50 °C the broad resonances resolve into sharp signals and the phenyl and tolyl fragments appear to be symmetrical. The endo configuration of **15** in solution was elucidated via a ^{1}H/^{1}H ROESY experiment: protons at the 3-position of the pyridine rings show NOE correlations with the exo methyl group but not with ortho protons of the endo phenyl ring (see the Supporting Information).

The solid-state structure and stereochemistry of **15** was confirmed by single-crystal X-ray diffraction analysis. Crystals of

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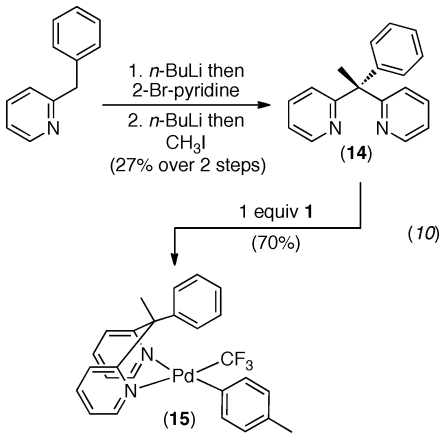


15 were obtained by slow evaporation of a saturated ethyl acetate solution at room temperature. A thermal ellipsoid plot of **15** as well as key bond distances and bond angles are shown in Figure 5. The phenyl ring above the square plane of

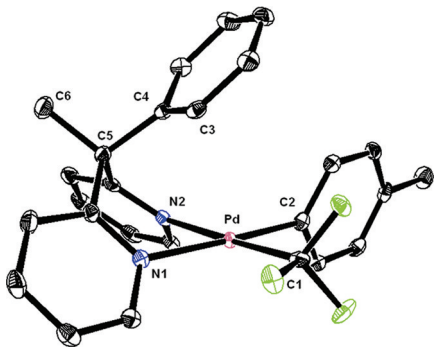
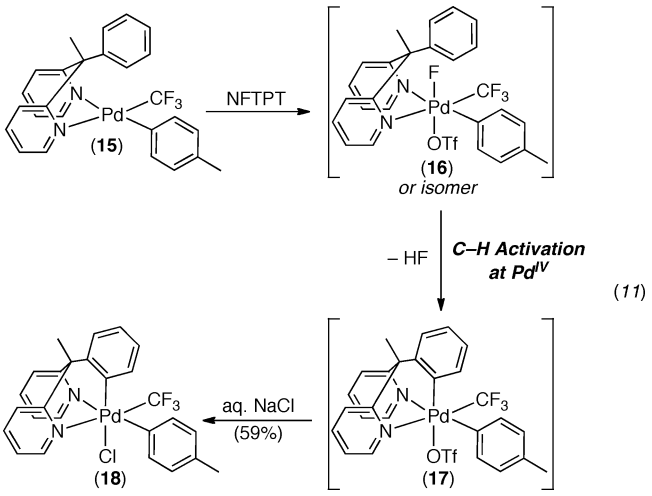


Figure 5. Thermal ellipsoid plot of complex **15**. Thermal ellipsoids are shown at the 50% probability level. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd–C1, 2.013; Pd–C2, 1.99; Pd–N1, 2.155; Pd–N2, 2.121; Pd–C4, 2.992; Pd–C3, 3.153; C6–C5–C4–C3, 103.80.

palladium is inclined toward the trifluoromethyl group, with a C6–C5–C4–C3 torsion angle 103.80°. The Pd–C4 (2.992 Å) and Pd–C3 (3.153 Å) distances are considerably longer than is typical (2.1–2.2 Å) in stable late-transition-metal η^2-arene complexes;[25] however, they are shorter than the sum of the van der Waals radii of the corresponding atoms. This apparent weak noncovalent interaction between palladium and the phenyl ring is likely the reason that **15** is formed as a single endo isomer.

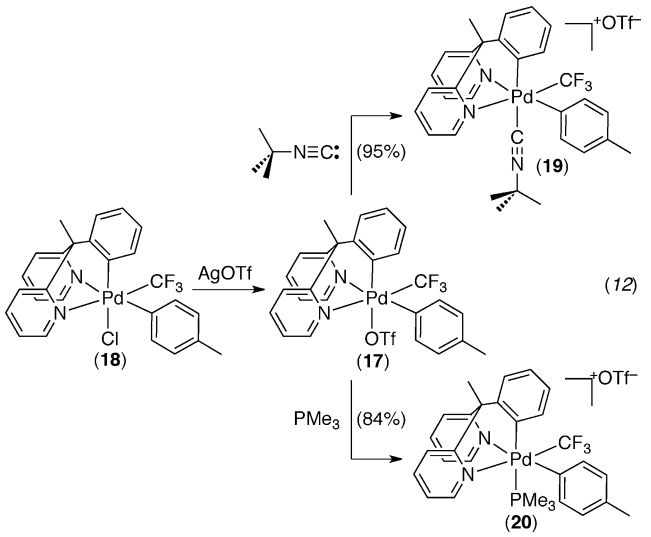
On the basis of the results discussed above (and prior work from our group),[8] we reasoned that NFTPT could oxidize **15** to form the Pd^{IV} complex **16** (eq 11). We have also recently shown that analogues of **16** can undergo intramolecular C–H activation to generate cyclometalated Pd^{IV} species.[10] Thus, we hypothesized that **16** might be capable of C–H activation to generate the NNC-ligated product **17**. Gratifyingly, the treatment of **15** with NFTPT for 5 min in CH_2Cl_2 at room temperature afforded **17**. Notably, neither **16** nor any other intermediates were detected in this transformation.[26] The triflate ligand of **17** was highly labile, and washing a CH_2Cl_2 solution of **17** with aqueous NaCl afforded the readily isolable chloride product **18** in 59% yield.

Complex **18** was characterized by ^1H, ^{13}C, and ^{19}F NMR spectroscopy. Interestingly, rotation about the Pd–tolyl bond



in **18** is slow on the NMR time scale. At room temperature, four broad but distinct ^1H NMR signals are observed for the aromatic protons of this ligand. When the temperature is lowered to 0 °C, these resonances resolve into four sharp doublets.

The strongly σ-donating aryl arm of the tridentate ligand rendered this complex highly reactive toward X-type ligand substitution. For example, sonication of **18** with 1.2 equiv of AgOTf for 10 min at room temperature in dichloromethane afforded complex **17** in situ. As shown in eq 12, this compound

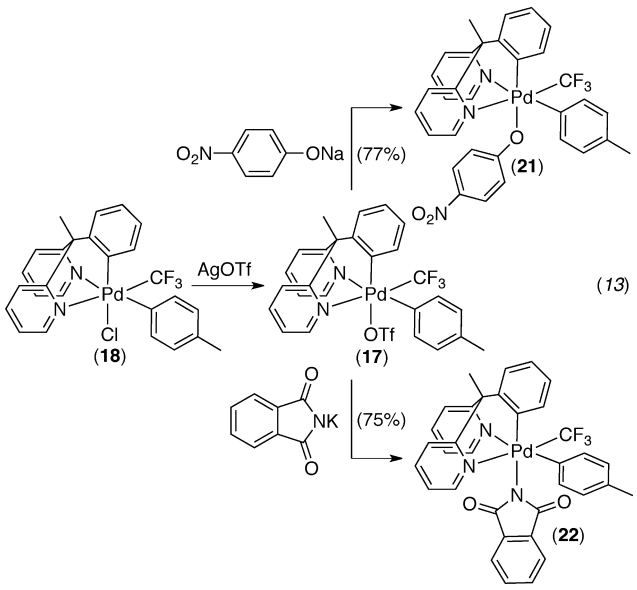


reacted with *tert*-butyl isocyanide (to afford **19** in 95% yield) and with PMe_3 (to generate **20** in 84% yield). Notably, examples of stable phosphine Pd^{IV} complexes such as **20** remain rare,[27] while **19** is, to our knowledge, the first example of a Pd^{IV} complex containing an isocyanide ligand. Complex **19** is stable in the solid state and in $CDCl_3$ solution for several days at room temperature. The coordinated *tert*-butyl isocyanide did not undergo insertion into the Pd–CF_3 or Pd–tolyl bonds, as was confirmed by $^1H/^{13}C$ HMBC and $^{19}F/^{13}C$ HMBC NMR spectroscopic experiments as well as IR spectroscopy. Remarkably, the CN stretching frequency in complex **19** (2225 cm^{-1}) is higher than that for the free isocyanide (2138 cm^{-1}).[28] This indicates that there is very little back-bonding occurring at the Pd^{IV} center.

Triflate complex **17** also underwent facile substitution with X-type ligands. As shown in eq 11, the addition of NaCl to **17**

dx.doi.org/10.1021/om200779j | Organometallics 2011, 30, 6617–6627

afforded chloride product **18**. Relatively basic X-type ligands such as *p*-nitrophenolate and phthalimide could also be introduced in high yield by reaction of **17** with the corresponding sodium or potassium salts (eq 13). Examples



of isolable Pd^{IV} phenolate and imide Pd^{IV} complexes remain rare in the literature,[29] likely because these basic ligands tend to destabilize Pd^{IV} and participate in fast reductive elimination processes. X-ray-quality crystals of phthalimide complex **22** were obtained by vapor diffusion of hexanes into a $CHCl_3$ solution at −20 °C. A thermal ellipsoid plot of this structure is shown in Figure 6 and shows the expected octahedral geometry with the phthalimide ligand trans to the σ-aryl group.

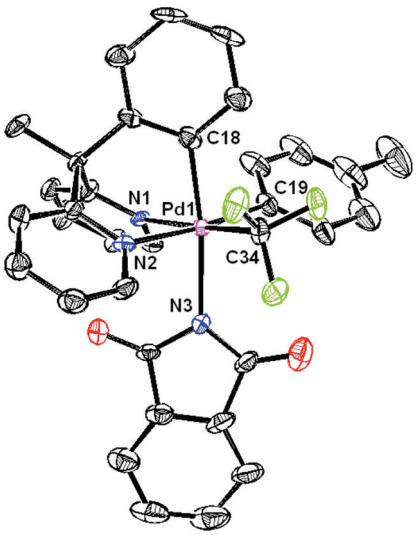
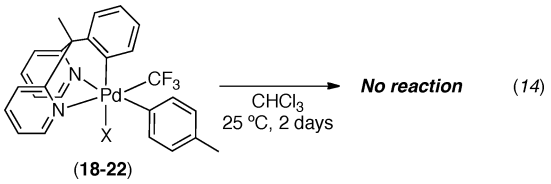


Figure 6. Thermal ellipsoid plot of complex **22**. Thermal ellipsoids are shown at 50% probability. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd1−C18, 2.033; Pd1−C34, 2.036; Pd1−C19, 2.081; Pd1−N1, 2.096; Pd1−N2, 2.146; Pd1−N3, 2.216; N2−Pd1−N1, 87.3; N2−Pd1−C18, 87.9; N1−Pd1−C18, 86.7; N1−Pd1−C34, 175.0, N2−Pd1−C19, 173.9; N3−Pd1−C18, 172.5; N2−Pd1−N3, 87.1; N3−Pd1−C19, 97.6.

Despite the fast rates of ligand substitution at **18**, this complex is still highly inert toward reductive elimination. For example, **18** was stable for several weeks in $CHCl_3$ at room temperature (eq 14). Furthermore, only ∼20% decomposition



was observed after heating to 110 °C for 2 h in DMSO-d_6. One possible explanation is that the restricted rotation about the Pd−tolyl bond precludes the complex from assuming the conformation required for aryl−CF_3 bond-forming reductive elimination. Complexes **19**−**22** were also stable for several days in $CDCl_3$ solution at room temperature. When the temperature was raised above 50 °C, dissociation/decomposition of the labile ligand occurred and complex mixtures of products were obtained.

A final set of studies focused on the reactivity of these NNC-ligated complexes toward oxidatively induced C−H activation processes. As shown in eq 15, treatment of in situ generated (dpph)Pd(2-PhC_6H_4)(TFA) (**25**) with NFTPT followed by aqueous NaCl at room temperature resulted in double C−H activation to generate the cyclometalated chloride complex **24**. We propose that this transformation proceeds via intermediates such as **26**−**28**.[10] This suggests the possibility that a single Pd^{IV} center can mediate more than one C−H activation event, a type of transformation that could potentially be exploited in catalytic C−C bond-forming reactions.

SUMMARY AND CONCLUSIONS

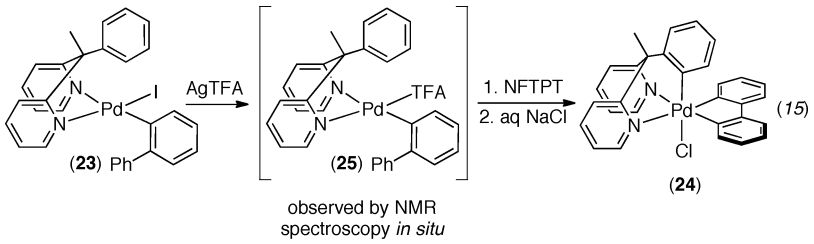
In summary, this report describes the oxidation of a series of Pd^{II} precursors to form Pd^{IV} σ-aryl products containing *fac*-NNN and *fac*-NNC donor ligands. In all cases, the Pd^{IV} complexes were stable to reductive elimination processes for prolonged periods (at minimum several days) in solution at room temperature. The NNC-ligated Pd^{IV} center participated in facile ligand substitution reactions in which a halide and/or triflate ligand was displaced by phosphine, isocyanide, phenoxide, or phthalimide donors. Furthermore, several examples of oxidatively induced C−H activation have been demonstrated. These systems add to a growing body of evidence that high-oxidation-state Pd centers are capable of participating in a diverse set of organometallic reactions beyond simply reductive elimination processes.

EXPERIMENTAL SECTION

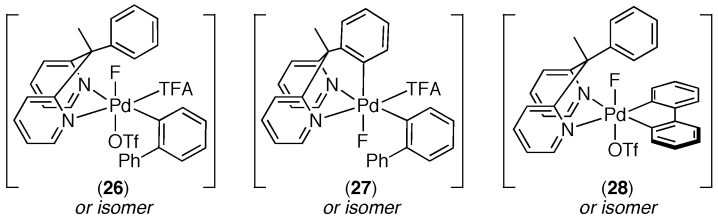
General Procedures. All syntheses were conducted under a nitrogen atmosphere unless otherwise stated. All reagents were purchased from commercial sources and used as received. Tetrahydrofuran, dichloromethane, and diethyl ether were purified using an Innovative Technologies (IT) solvent purification system consisting of a copper catalyst, activated alumina, and molecular sieves. Bis(dibenzylideneacetone)palladium was obtained as described in ref 31. Column chromatography was performed on silica gel (32−63 μm).

NMR spectra were obtained on a Varian vnmrs 700, Varian vnmrs 500, Varian Inova, or Varian MR400 spectrometer. ^1H, ^{19}F, and ^{13}C chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as an internal reference. ^{19}F NMR spectra are referenced on a unified scale, where the single primary reference is the frequency of the residual solvent peak in the ^1H NMR spectrum.[30] ^1H and ^{19}F multiplicities are reported as follows: singlet (s), doublet (d), quartet (q), and multiplet (m). Mass spectral

dx.doi.org/10.1021/om200779j | Organometallics 2011, 30, 6617−6627



Possible intermediates:



data were obtained on a Micromass magnetic sector mass spectrometer with an electrospray ionization mode. IR spectrum was recorded on a Perkin-Elmer Spectrum BX FT-IR spectrometer using a KBr pellet.

(4-MePy)$_2$Pd(4-MeC$_6$H$_4$)(I) (2). Pd(dba)$_2$ (1.25 g; 2.17 mmol) was added to a solution of 4-iodotoluene (1.20 g; 5.50 mmol) and 4-methylpyridine (2.05 g; 22.0 mmol) in THF (20 mL) at room temperature. The resulting homogeneous solution was stirred at room temperature. After 15 min, product started to precipitate from solution. The thick suspension was stirred at room temperature for another 30 min, and then hexane (30 mL) was added. The precipitate was filtered and washed with diethyl ether (4 × 50 mL) and hexanes (4 × 50 mL). Yield: 1.42 g (64%) of yellow crystals. The crude product contains some minor impurities, but it was used directly in the next step, as decomposition was observed during purification attempts. ^{1}H NMR (CDCl$_3$): δ 8.69 (d, J = 5.9 Hz, 4H), 7.00 (d, J = 5.9 Hz, 4H), 6.87 (d, J = 7.6 Hz, 2H), 6.66 (d, J = 7.6 Hz, 2H), 2.27 (s, 6H), 2.13 (s, 3H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 154.49, 153.02, 149.27, 132.82, 132.66, 127.86, 125.57, 21.06, 20.61.

(4-MePy)$_2$Pd(4-MeC$_6$H$_4$)(CF$_3$) (1). Cesium fluoride (1.06 g; 7.0 mmol) was placed in a Schlenk flask and dried under vacuum at 100 °C for 2 h. The flask was then cooled to room temperature under an atmosphere of nitrogen, (4-MePy)$_2$Pd(4-MeC$_6$H$_4$)(I) (**2**; 0.75 g, 1.7 mmol) was added, and the flask was then flushed with nitrogen and sealed with a rubber septum. Dry THF (20 mL) and TMSCF$_3$ (1.1 mL; 7.0 mmol) were added via cannula. The resulting suspension was stirred at room temperature for 15 min. During this period, the solution changed from yellow to dark green and some Pd black precipitate was observed. The volatiles were removed under reduced pressure at room temperature. The residue was suspended in dichloromethane (40 mL) and filtered through a pad of Celite. The solution was evaporated under reduced pressure. The resulting residue was suspended in diethyl ether (10 mL) and collected by filtration. The solid was washed with ethyl acetate (4 × 3 mL) and dried under reduced pressure. Yield: 0.36 g (54%) of white crystals. ^{1}H NMR (CDCl$_3$): δ 8.53 (d, J = 5.9 Hz, 2H), 8.14 (d, J = 5.9 Hz, 2H), 7.41 (d, J = 7.5 Hz, 2H), 7.12 (d, J = 5.5 Hz, 2H), 6.94 (d, J = 5.5 Hz, 2H), 6.81 (d, J = 7.5 Hz, 2H), 2.34 (s, 3H), 2.23 (s, 3H), 2.20 (s, 3H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 150.39, 150.04, 149.48 (q, J = 9.3 Hz), 149.40, 149.37, 135.96, 134.89 (q, J = 364 Hz), 131.36, 127.21, 125.72, 125.66, 21.07, 20.96, 20.94. ^{19}F NMR (CDCl$_3$): δ −21.00 (s).

(Tp)Pd^{IV}(4-MeC$_6$H$_4$)(CF$_3$)(Cl) (4). (4-MePy)$_2$Pd(4-MeC$_6$H$_4$)(CF$_3$) (**1**; 100 mg, 0.22 mmol) was added to the solution of KTp (58 mg, 0.23 mmol) in acetone (10 mL) at room temperature. The reaction mixture was stirred for 5 min at room temperature, and then triethylamine (25 mg; 0.25 mmol) and iodobenzene dichloride (61 mg; 0.22 mmol) were added. The solution was stirred at room temperature for 10 min, and then the volatiles were removed under reduced pressure. The resulting residue was purified on a silica gel column (mobile phase hexanes/EtOAc with gradient from 10/1 to 6/1). Yield: 56 mg (49%) of yellow crystals. The obtained product contains less than 5% of complex **4a**, which could not be separated via column chromatography. ^{1}H NMR (CDCl$_3$): δ 8.00 (d, J = 1.4 Hz, 1H), 7.83 (d, J = 2.2 Hz, 1H), 7.71 (d, J = 2.2 Hz, 1H), 7.67 (d, J = 2.2 Hz, 1H), 7.51 (d, J = 2.1 Hz, 1H), 7.33 (d, J = 1.9 Hz, 1H), 6.84 (d, J = 8.6 Hz, 2H), 6.80 (d, J = 8.6 Hz, 2H), 6.31 (multiple peaks, 2H), 6.16 (t, J = 2.2 Hz, 1H), 4.1−5.0 (br, 1H), 2.30 (s, 3H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 149.35 (q, J = 2.2 Hz), 142.15 (q, J = 2.1 Hz), 141.40, 141.36, 136.62, 136.08, 134.96, 134.89, 134.75, 129.01, 114.25 (q, J = 376 Hz), 106.81, 106.32, 106.10, 20.40. ^{19}F NMR (CDCl$_3$): δ −17.30 (s). ^{11}B NMR (CDCl$_3$): δ −3.44 (d, J = 74 Hz). HRMS electrospray (m/z): [M − Cl + MeCN]$^+$ calcd for C$_{19}$H$_{20}$BF$_3$N$_7$Pd, 520.0855; found, 520.0849.

(dpaa)Pd^{II}(4-MeC$_6$H$_4$)(CF$_3$) (8). (4-MePy)$_2$Pd(4-MeC$_6$H$_4$)(CF$_3$) (**1**; 120 mg, 0.26 mmol) was added to a solution of *N*-di(2-pyridyl)-methylacetamide (**6**; 68 mg, 0.30 mmol) in CH$_2$Cl$_2$ (3 mL) at room temperature. After the solution was stirred at room temperature for 5 min, it was filtered through a pad of Celite. The volume of the CH$_2$Cl$_2$ solution was reduced to 1 mL under reduced pressure, and the product was then precipitated with hexanes (15 mL). The precipitate was collected by filtration, washed with diethyl ether (3 × 2 mL), and dried under reduced pressure. Yield: 115 mg (88%) of a white powder. ^{1}H NMR (CDCl$_3$): δ 9.07 (d, J = 8.7 Hz, 1H), 8.99 (d, J = 5.1 Hz, 1H), 8.10 (d, J = 5.1 Hz, 1H), 7.86 (td, J = 7.8 Hz, 1.1 Hz, 1H), 7.73 (td, J = 6.6, 1.1 Hz, 1H), 7.61 (multiple peaks, 2H), 7.40 (t, J = 6.6 Hz, 1H), 7.31 (d, J = 7.3 Hz, 2H), 7.10 (t, J = 6.4 Hz, 1H), 6.88 (d, J = 7.3 Hz, 2H), 6.34 (d, J = 8.7 Hz, 1H), 2.25 (s, 3H), 2.21 (s, 3H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 169.86, 155.34, 154.47, 153.38, 152.76, 150.01 (q, J = 9.3 Hz), 139.35, 139.11, 135.74, 134.82 (q, J = 363 Hz), 132.39, 127.93, 125.40, 125.12, 124.66, 124.52, 59.62, 23.32, 20.95. ^{19}F NMR (CDCl$_3$): δ −20.39 (s). HRMS electrospray (m/z): [M − F]$^+$ calcd for C$_{21}$H$_{20}$F$_2$N$_3$OPd, 474.0604; found, 474.0605.

(dpsa)Pd^{II}(4-MeC$_6$H$_4$)(CF$_3$) (9). (4-MePy)$_2$Pd(4-MeC$_6$H$_4$)(CF$_3$) (**1**; 81 mg, 0.18 mmol) was added to a solution of 4-*tert*-butyl-*N*-[bis(pyridin-2-yl)methyl]benzenesulfonamide (**7**; 80 mg, 0.21 mmol) in EtOAc (2 mL) at room temperature. The reaction mixture was stirred at room temperature for 10 min and then filtered through a pad of Celite. The volume of the solution was reduced to 1 mL, and then hexane (10 mL) was added. The precipitate was collected by filtration, washed with a 1/1 mixture of hexane and diethyl ether (3 × 3 mL), and dried under reduced pressure. Yield: 106 mg (78%) of a white powder. ^{1}H NMR (CDCl$_3$): δ 8.80 (multiple peaks, 2H), 8.04 (d, J = 4.1 Hz, 1H), 7.68 (d, J = 6.9 Hz, 2H), 7.65 (td, J = 7.7, 1.5 Hz, 1H), 7.48 (td, J = 7.5, 1.5 Hz, 1H), 7.45 (d, J = 7.7 Hz, 1H), 7.38 (d, J = 6.9 Hz, 2H), 7.21 (d, J = 8.3 Hz, 2H), 7.13 (multiple peaks, 2H), 7.04 (t, J = 5.6 Hz, 1H), 6.87 (d, J = 7.5 Hz, 2H), 5.72 (d, J = 9.4 Hz, 1H), 2.23 (s, 3H), 1.21 (s, 9H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 156.49, 154.18, 153.48, 153.23, 152.69, 150.01 (q, J = 9.5 Hz), 139.41, 138.59, 136.71,

dx.doi.org/10.1021/om200779j | *Organometallics* 2011, 30, 6617−6627

135.70, 134.58 (q, J = 364 Hz), 132.41, 127.99, 127.04, 126.99, 125.94, 124.96, 124.70, 124.14, 63.11, 34.97, 30.98, 20.97. ^{19}F NMR ($CDCl_3$): δ −20.29 (s). HRMS electrospray (m/z): $[M - F]^+$ calcd for $C_{29}H_{30}F_2N_3O_2PdS$, 628.1056; found, 628.1058.

(dpaa)Pd^{IV}(4-MeC$_6$H$_4$)(CF$_3$)(Cl) (10). Iodobenzene dichloride (77 mg; 0.28 mmol) was added to a solution of (dpaa)Pd^{II}(4-MeC$_6$H$_4$)(CF$_3$) (**8**; 110 mg, 0.22 mmol) in acetonitrile (5 mL) at room temperature. The reaction mixture was stirred at room temperature for 20 min, and then solvent was removed under reduced pressure. The residue was purified on a silica gel column that was eluted first with ethyl acetate, then with THF, and finally with 10% methanol in THF. Fractions that contained pure product (TLC control) were evaporated under reduced pressure, and the resulting residue was dissolved in diethyl ether (20 mL). This solution was filtered through a cotton plug, and the volume of the solution was reduced to 10 mL. The product was then precipitated with hexanes (30 mL), collected by filtration, washed with hexanes, and dried under reduced pressure. Yield: 55 mg (47%) of an orange powder. ^{1}H NMR ($CDCl_3$): δ 9.03 (d, J = 5.0 Hz, 1H), 8.49 (d, J = 5.3 Hz, 1H), 7.87 (multiple peaks, 2H), 7.73 (multiple peaks, 2H), 7.43 (t, J = 6.0 Hz, 1H), 7.25 (multiple peaks, 2H), 6.95 (broad d, J = 8.1 Hz, 2H), 6.79 (d, J = 8.1 Hz, 2H), 2.25 (s, 3H), 1.69 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 175.06, 158.16, 158.10, 149.75, 149.49, 148.94 (q, J = 2.9 Hz), 140.43, 140.17, 135.76, 135.55, 129.15, 124.40, 124.19, 121.66, 121.32, 116.42 (q, J = 376 Hz), 71.72, 24.89 (q, J = 2.7 Hz), 20.40. ^{19}F NMR ($CDCl_3$): δ −13.08 (s). HRMS electrospray (m/z): $[M + H]^+$ calcd for $C_{21}H_{20}ClF_3N_3OPd$, 528.0276; found, 528.0269. The stereochemistry of this complex was assigned on the basis of the similarity of its ^{1}H NMR spectrum to that of complex **12**.

(dpsa)Pd^{IV}(4-MeC$_6$H$_4$)(CF$_3$)(Cl) (11). Iodobenzene dichloride (60 mg; 0.22 mmol) was added to a solution of (dpsa)Pd^{II}(4-MeC$_6$H$_4$)(CF$_3$) (**9**; 130 mg, 0.20 mmol) in MeCN (4 mL) at room temperature. The reaction mixture was stirred at room temperature for 15 min, and then the volatiles were removed under reduced pressure. The crude product was purified on a silica gel column (mobile phase: hexane/EtOAc 1/1). Fractions containing pure product (TLC control) were evaporated under reduced pressure. The resulting residue was dissolved in dichloromethane (~0.5 mL), and the product was precipitated with the addition of hexane (20 mL). The precipitate was collected by filtration, washed with diethyl ether, and dried under reduced pressure. Yield: 57 mg (42%) of a yellow powder. ^{1}H NMR ($CDCl_3$): δ 9.01 (d, J = 5.2 Hz, 1H), 8.57 (d, J = 5.2 Hz, 1H), 7.83 (td, J = 7.8, 1.0 Hz, 1H), 7.79 (td, J = 7.6, 1.0 Hz, 1H), 7.64 (d, J = 7.7 Hz, 1H), 7.55 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 7.7 Hz, 1H), 7.38 (t, J = 6.5 Hz, 1H), 7.28 (t, J = 6.4 Hz, 1H), 7.24 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.6 Hz, 2H), 6.82 (d, J = 8.6 Hz, 2H), 6.14 (s, 1H), 2.26 (s, 3H), 1.24 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 158.69, 157.62, 154.63, 149.79, 149.76, 146.96, 140.67, 140.30. 139.66, 135.70, 135.52, 129.11, 126.60, 125.22, 124.48, 124.14, 120.66, 120.59, 115.03 (q, J = 378 Hz), 74.80, 34.83, 31.08, 20.42. ^{19}F NMR ($CDCl_3$): δ −11.90 (s). HRMS electrospray (m/z): $[M + Na]^+$ calcd for $C_{29}H_{29}ClF_3N_3NaO_2PdS$, 704.0548; found, 704.0548.

(dpsa)Pd^{IV}(4-MeC$_6$H$_4$)(CF$_3$)(F) (12). NFTPT (64 mg, 0.22 mmol) was added to a solution of complex **9** (130 mg, 0.20 mmol) in MeCN (3 mL) at room temperature. The reaction mixture was stirred at room temperature for 15 min. The volatiles were removed under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 (15 mL), and this solution was washed with water (4 × 15 mL), dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The crude product was purified on a silica gel column that was eluted first with ethyl acetate and then with THF. Fractions containing pure product (TLC control) were evaporated under reduced pressure. The resulting residue was dissolved in dichloromethane (0.5 mL), and the product was precipitated with the addition of hexane (20 mL). This precipitate was collected by filtration, washed with diethyl ether, and dried under reduced pressure. Yield: 91 mg (68%) of a yellow powder. ^{1}H NMR ($CDCl_3$): δ 8.82 (d, J = 5.1 Hz, 1H), 8.30 (d, J = 5.2 Hz, 1H), 7.70 (d, J = 8.8 Hz, 2H), 7.67 (td, J = 6.7, 1.5 Hz, 1H), 7.60 (multiple peaks, 3H), 7.50 (td, J = 7.7, 1.3 Hz, 1H), 7.28 (t, J = 6.8 Hz, 1H), 7.24 (d, J = 8.8 Hz, 2H), 7.12 (t, J = 6.4 Hz, 1H), 6.90 (d, J = 8.6 Hz, 2H), 6.26 (d, J = 5.4 Hz, 1H), 2.28 (s, 3H), 1.22 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 157.94, 157.10, 155.10, 150.88 (m), 149.27, 148.23, 140.07, 139.52, 136.07, 131.58, 131.53, 129.08, 127.09, 125.28, 124.18, 124.02, 121.64, 121.08, 114.69 (q, J = 378 Hz), 74.26, 34.86, 31.07, 20.51. ^{19}F NMR ($CDCl_3$): δ −20.44 (d, J = 4.8 Hz), −285.11 (br m). HRMS electrospray (m/z): $[M + H]^+$ calcd for $C_{29}H_{30}F_4N_3O_2PdS$, 666.1024; found, 666.1021.

(dpaa)Pd^{IV}(4-MeC$_6$H$_4$)(CF$_3$)(F) (13a,b). (dpaa)Pd^{II}(4-MeC$_6$H$_4$)(CF$_3$) (**8**; 58 mg, 0.12 mmol) was dissolved in CH_2Cl_2 (4 mL), and NFTPT (38 mg, 0.13 mmol) was added at room temperature. The reaction mixture was stirred at room temperature for 20 min. The CH_2Cl_2 solution was then washed with water (4 × 5 mL), dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. ^{1}H NMR and ^{19}F NMR analysis of the crude residue showed the presence of two Pd(IV) complexes in an approximately 2:1 ratio. These compounds were separated by preparative TLC (mobile phase 10% methanol in THF) to yield the major isomer **13a** (24 mg, 40%) and minor isomer **13b** (20 mg, 33%) as yellow powders. When oxidation was conducted in acetonitrile, only isomer **13a** was formed (53% isolated yield). Analytical data for **13a** are as follows. ^{1}H NMR ($CDCl_3$): δ 9.01 (d, J = 5.4 Hz, 1H), 8.25 (d, J = 5.4 Hz, 1H), 7.91 (multiple peaks, 2H), 7.74 (multiple peaks, 2H), 7.48 (t, J = 5.4 Hz, 1H), 7.27 (t, J = 6.1 Hz, 1H), 7.14 (d, J = 5.4 Hz, 1H; coupled with F), 7.09 (multiple peaks, 2H), 6.90 (d, J = 7.8 Hz, 2H), 2.32 (s, 3H), 1.82 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 175.19 (d, J = 3.1 Hz), 157.69, 157.56, 152.01 (m), 149.22, 149.00, 140.46, 140.21, 136.01, 132.34 (d, J = 6.6 Hz), 129.05, 124.33, 124.25, 121.80, 121.33, 116.84 (q, J = 376 Hz), 71.03, 24.75 (m), 20.51. ^{19}F NMR ($CDCl_3$): δ −290.85 (m), −23.84 (d, J = 3.8 Hz). HRMS electrospray (m/z): $[M + H]^+$ calcd for $C_{21}H_{20}F_4N_3OPd$, 512.0572; found, 512.0574. Analytical data for **13b** are as follows. ^{1}H NMR ($CDCl_3$): δ 8.98 (d, J = 5.1 Hz, 1H), 8.55 (d, J = 5.5 Hz, 1H), 8.03 (t, J = 7.7 Hz, 1H), 7.89 (t, J = 7.7 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 7.7 Hz, 1H), 7.26 (multiple peaks, 2H), 7.07 (s, 1H), 6.90 (d, J = 8.0 Hz, 2H), 6.81 (multiple peaks, 2H), 2.32 (s, 3H) and 1.43 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 175.94, 161.56, 158.30, 151.35 (m), 151.21 (m), 150.16, 141.64, 140.00, 136.46, 130.67 (d, J = 16.4 Hz), 129.50, 125.24, 124.37, 122.80, 122.21, 121.90 (q, J = 384 Hz) 69.97, 22.98 (d, J = 4 Hz), 20.49. ^{19}F NMR ($CDCl_3$): δ −312.97 (m), −33.80 (d, J = 3.2 Hz). HRMS electrospray (m/z): $[M + H]^+$ calcd for $C_{21}H_{19}F_4N_3OPd$, 512.0572; found, 512.0570.

(dpph)Pd^{II}(4-MeC$_6$H$_4$)(CF$_3$) (15). (4-MePy)$_2$Pd(4-MeC$_6$H$_4$)(CF$_3$) (**1**; 300 mg, 0.66 mmol) was added to a solution of 1,1-bis(2-pyridyl)phenylethane (dpph, **14**; 182 mg, 0.70 mmol) in EtOAc (15 mL) at room temperature. After the solution was stirred at room temperature for 5 min, it was filtered through a pad of Celite. The volume of the solution was reduced to 3 mL, and the product then started to crystallize. This suspension was cooled at −20 °C for 2 h, and then the precipitate was collected by filtration, washed with ethyl acetate (3 × 1 mL), and dried under reduced pressure. Yield: 208 mg (60%) of a white powder. The mother liquor was evaporated under reduced pressure. The residue was suspended in diethyl ether, collected by filtration, and dried under reduced pressure to yield another 35 mg (10%) of the product. For complex **14** at room temperature there is a hindered rotation about palladium−tolyl and C−phenyl bonds on a NMR time scale. In order to resolve broad resonances, ^{1}H and ^{13}C NMR spectra were measured at 50 and 46 °C. ^{1}H NMR ($CDCl_3$ at 50 °C): δ 9.09 (d, J = 4.9 Hz, 1H), 8.25 (d, J = 5.3 Hz, 1H), 7.87 (td, J = 7.8, 1.5 Hz, 1H), 7.77 (multiple peaks, 3H), 7.41 (t, J = 7.6 Hz, 2H), 7.36 (t, J = 7.4 Hz, 1H), 7.33 (t, J = 6.5 Hz, 1H), 7.03 (td, J = 7.2 Hz, 1.7 Hz, 1H), 6.97 (d, J = 7.0 Hz, 2H), 6.78 (d, J = 7.8 Hz, 2H), 6.73 (d, J = 7.6 Hz, 2H), 2.24 (s, 3H), 2.18 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$ at 46 °C): δ 162.24, 160.53, 153.38, 152.78, 151.70 (q, J = 9.8 Hz), 148.27, 138.35, 138.10, 135.96, 134.61 (q, J = 366 Hz), 131.19, 128.87, 127.87, 127.12, 127.06, 123.04, 122.99, 122.78, 122.54, 57.52, 29.76, 20.91. ^{19}F NMR ($CDCl_3$ at 25 °C): δ −21.82 (s). HRMS electrospray (m/z): $[M - F]^+$ calcd for $C_{26}H_{23}F_2N_3Pd$, 507.0859; found, 507.0855.

(dpph)Pd^{IV}(4-MeC$_6$H$_4$)(CF$_3$)(Cl) (18). NFTPT (230 mg; 0.80 mmol) was added to a solution of (dpph)Pd^{II}(4-MeC$_6$H$_4$)(CF$_3$) (**15**;

dx.doi.org/10.1021/om200779j|Organometallics 2011, 30, 6617−6627

340 mg, 0.64 mmol) in CH_2Cl_2 (30 mL) at room temperature. The reaction mixture was stirred at room temperature for 10 min, and then it was washed with water (4 × 15 mL) and brine (2 × 15 mL). The CH_2Cl_2 layer was collected, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The resulting residue was suspended in ethyl acetate (5 mL), and the suspended solids were collected by filtration and washed with ethyl acetate (2 × 3 mL). The resulting white powder was dissolved in chloroform (4 mL), from which a crystalline product started to precipitate. This product was collected by filtration and dried under reduced pressure. Yield: 213 mg (59%) of a white powder. In order to resolve broad resonances, the ^{1}H and ^{13}C NMR spectra were obtained at 0 °C. Rotation around the palladium−tolyl bond at room temperature and below is slow on the NMR time scale; therefore, there is a distinct signal for each tolyl CH in both the ^{1}H and ^{13}C NMR spectra. ^{1}H NMR (CD_2Cl_2 at 0 °C): δ 9.42 (d, J = 5.4 Hz, 1H), 8.44 (d, J = 5.1 Hz, 1H), 8.12 (d, J = 7.8 Hz, 1H), 7.92 (t, J = 7.7 Hz, 1H), 7.84 (multiple peaks, 2H), 7.78 (d, J = 8.1 Hz, 1H), 7.55 (d, J = 7.8 Hz, 1H), 7.44 (multiple peaks, 2H), 7.22 (t, J = 7.3 Hz, 1H), 7.13 (t, J = 6.6 Hz, 1H), 7.06 (multiple peaks, 2H), 6.55 (d, J = 7.8 Hz, 1H), 5.83 (d, J = 7.7 Hz, 1H), 2.71 (br s, 3H), 2.27 (s, 3H). ^{13}C{^{1}H} NMR (CD_2Cl_2 at 0 °C): δ 159.84 (q, J = 2.4 Hz), 157.27, 156.78, 155.57 (q, J = 3.9 Hz), 154.20, 152.64, 139.96, 139.88, 137.35, 136.73, 136.47, 134.97, 134.35, 128.22, 128.13, 127.66, 126.20, 126.07 (q, J = 369 Hz), 124.84, 123.58, 123.27, 121.58, 121.26, 56.50, 23.24, 20.44. ^{19}F NMR (CD_2Cl_2 at 0 °C): δ −23.89 (s). HRMS electrospray (m/z): $[M - Cl]^+$ calcd for $C_{26}H_{22}F_3N_2Pd$, 525.0764; found, 525.0763.

[(dpph)Pd^{IV}(4-MeC$_6$H$_4$)(CF$_3$)(t-BuNC)]OTf (19). A suspension of (dpph)Pd^{IV}(4-MeC$_6$H$_4$)(CF$_3$)(Cl) (**18**; 110 mg, 0.20 mmol) and silver triflate (62 mg; 0.24 mmol) in CH_2Cl_2 (15 mL) was sonicated for 15 min at room temperature. The AgCl precipitate was removed by filtration, *tert*-butyl isocyanide (25.0 mg; 0.30 mmol) was added, and the resulting solution was stirred for 3 min. The volatiles were removed under reduced pressure, and the product was suspended in diethyl ether (10 mL), filtered, washed with diethyl ether (3 × 3 mL), and dried under reduced pressure. Yield: 114 mg (95%) of a white powder. In order to resolve broad resonances, the ^{1}H and ^{13}C NMR spectra were measured at 0 °C. Rotation around the palladium−tolyl bond at room temperature and below is slow on the NMR time scale; therefore, there is a distinct signal for each tolyl CH fragment in both ^{1}H and ^{13}C NMR spectra. Several overlapping signals in the ^{13}C NMR spectrum were resolved by ^{1}H/^{13}C HSQC, ^{1}H/^{13}C HMBC, ^{19}F/^{13}C HSQC, and ^{19}F/^{13}C HMBC NMR experiments. Because of a very low intensity, the carbon resonance of the CF_3 group could not be observed directly in the ^{13}C NMR spectrum. This value was extracted from the ^{19}F−^{13}C HSQC NMR spectrum. ^{1}H NMR ($CDCl_3$ at 0 °C): δ 8.87 (d, J = 4.9 Hz, 1H), 8.12 (multiple peaks, 4H), 7.93 (d, J = 5.1 Hz, 1H), 7.69 (d, J = 8.1 Hz, 1H), 7.51 (multiple peaks, 2H), 7.42 (d, J = 8.1 Hz, 1H), 7.29 (t, J = 6.4 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H), 7.06 (multiple peaks, 2H), 6.63 (d, J = 8.1 Hz, 1H), 5.81 (d, J = 8.1 Hz, 1H), 2.77 (br, 3H), 2.27 (s, 3H), 1.55 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$ at 0 °C): δ 159.77, 157.55, 157.17, 152.77, 151.80, 150.83, 142.32, 141.88, 137.18, 136.07 (two overlapping resonances), 135.60 (two overlapping resonances), 133.80, 130.38, 128.89, 128.84, 127.23, 125.84 (shift for the CF_3 group extracted from the ^{19}F/^{13}C HSQC spectrum), 125.49, 124.71, 124.69, 124.50 (two overlapping resonances), 120.75 (q, J = 321 Hz, $CF_3SO_2O^-$), 59.71, 57.41, 29.52, 23.36, 20.72. ^{19}F NMR ($CDCl_3$ at 0 °C): −20.12 (s), −78.28 (s). HRMS electrospray (m/z): $[M - CF_3SO_3]^+$ calcd for $C_{31}H_{31}F_3N_3Pd$, 608.1499; found, 608.1500. IR (KBr): ν 3490 (s, br), 2987 (s, br), 2225 (s), 1602 (s), 1561 (w), 1470 (s), 1275 cm^{-1} (s, br).

[(dpph)Pd^{IV}(4-MeC$_6$H$_4$)(CF$_3$)(PMe$_3$)]OTf (20). A suspension of (dpph)Pd^{IV}(4-MeC$_6$H$_4$)(CF$_3$)(Cl) (**18**; 110 mg, 0.20 mmol) and silver triflate (62 mg; 0.24 mmol) in CH_2Cl_2 (15 mL) was sonicated for 15 min at room temperature. The AgCl precipitate was removed by filtration, PMe_3 (50.0 mg; 0.66 mmol) was added, and the resulting solution was stirred for 3 min. The volatiles were removed under reduced pressure, and the product was suspended in diethyl ether (10 mL). The suspended solids were collected by filtration, washed with diethyl ether (3 × 3 mL), and dried under reduced pressure. Yield: 124 mg (84%) of a white powder. ^{1}H NMR (CD_2Cl_2): δ 8.86 (d, J = 5.4 Hz, 1H), 8.18 (multiple peaks, 4H), 8.08 (d, J = 5.6 Hz, 1H), 7.32 (t, J = 6.1 Hz, 1H), 7.58 (multiple peaks, 2H), 7.48 (dd, J = 9.6, 8.4 Hz, 1H), 7.40 (t, J = 6.2 Hz, 1H), 7.25 (t, J = 7.5 Hz, 1H), 7.17 (dd, J = 8.2, 1.9 Hz, 1H), 7.09 (m, 1H), 6.78 (d, J = 7.9 Hz, 1H), 6.09 (d, J = 7.9 Hz, 1H), 2.82 (br. s, 3H), 2.34 (s, 3H), 1.11 (d, J = 8.8 Hz, 9H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 163.27 (d, J = 133.5 Hz), 158.78, 158.10, 153.77, 151.42 (d, J = 3.4 Hz), 150.87 (d, J = 4.1 Hz), 142.12, 141.88, 137.19, 136.48 (d, J = 13.6 Hz), 136.24, 135.86, 134.32, 130.22, 128.87, 128.58 (d, J = 10.9 Hz), 127.47 (shift for the CF_3 group extracted from the ^{19}F/^{13}C ASAPHMQC spectrum), 126.87, 125.48 (d, J = 9.5 Hz), 124.70, 124.51, 124.34, 124.17, 120.97 (q, J = 321.5 Hz), 57.31, 23.78, 20.31, 13.45 (d, J = 19.1 Hz). ^{19}F NMR ($CDCl_3$): δ −18.11 (d, J = 20.7 Hz), −76.88 (s). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −16.38 (q, J = 20.8 Hz). HRMS electrospray (m/z): $[M]^+$ calcd for $C_{29}H_{31}F_3N_2PPd$, 601.1206; found, 601.1196.

[(dpph)Pd^{IV}(4-MeC$_6$H$_4$)(CF$_3$)(4-NO$_2$-C$_6$H$_4$O)] (21). A suspension of (dpph)Pd^{IV}(4-MeC$_6$H$_4$)(CF$_3$)(Cl) (**18**; 55 mg, 0.10 mmol) and silver triflate (33 mg; 0.13 mmol) in CH_2Cl_2 (15 mL) was sonicated for 15 min at room temperature. The AgCl precipitate was removed by filtration, and the resulting CH_2Cl_2 solution was washed with a solution of sodium 4-nitrophenolate (21 mg; 0.13 mmol) in water (2 mL). The CH_2Cl_2 solution was then washed with water (5 × 5 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the product was suspended in diethyl ether (10 mL). The suspended solids were collected by filtration, washed with diethyl ether (3 × 3 mL), and dried under reduced pressure. Yield: 50 mg (77%) of a yellow powder. In order to resolve broad resonances, the ^{1}H and ^{13}C NMR spectra were measured at −27 and −21 °C, respectively. Rotation around the palladium−tolyl bond at room temperature and below is slow on the NMR time scale; therefore, there is a distinct signal for each tolyl CH fragment in both ^{1}H and ^{13}C NMR spectra. ^{1}H NMR (CD_2Cl_2 at −27 °C): δ 8.94 (d, J = 5.3 Hz, 1H), 8.32 (d, J = 8.1 Hz, 1H), 7.97 (multiple peaks, 2H), 7.89 (d, J = 8.1 Hz, 1H), 7.83 (t, J = 7.5 Hz, 1H), 7.64 (d, J = 5.2 Hz, 1H), 7.55 (d, J = 7.9 Hz, 1H), 7.52 (d, J = 7.9 Hz, 1H), 7.46 (d, J = 9.1 Hz, 2H), 7.29 (t, J = 6.6 Hz, 1H), 7.24 (t, J = 7.2 Hz, 1H), 7.20 (d, J = 7.9 Hz, 1H), 7.10 (t, J = 7.4 Hz, 1H), 6.87 (t, J = 6.4 Hz, 1H), 6.62 (d, J = 7.6 Hz, 1H), 5.99 (d, J = 7.9 Hz, 1H), 5.33 (d, J = 8.9 Hz, 2H), 2.73 (br s, 3H), 2.29 (s, 3H). ^{13}C{^{1}H} NMR (CD_2Cl_2 at −21 °C): δ 178.23, 159.18, 158.99, 158.75, 156.74, 154.37, 153.29, 142.45, 142.38, 138.68, 137.99, 137.71, 136.99, 136.14, 135.54, 130.68, 130.57, 130.16, 128.24, 127.99, 126.86, 126.77 (shift for the CF_3 group extracted from the ^{19}F/^{13}C ASAPHMQC spectrum), 125.96, 125.67, 124.22, 123.93, 121.50, 58.62, 24.97, 22.50. ^{19}F NMR (CD_2Cl_2 at −21 °C): δ −29.67 (s). HRMS electrospray (m/z): $[M - NO_2C_6H_4O]^+$ calcd for $C_{26}H_{22}F_3N_2Pd$, 525.0764; found, 525.0771.

[(dpph)Pd^{IV}(4-MeC$_6$H$_4$)(CF$_3$)(NPhth)] (22). A suspension of (dpph)Pd^{IV}(4-MeC$_6$H$_4$)(CF$_3$)(Cl) (**18**; 50.0 mg, 0.089 mmol) and silver triflate (29 mg; 0.11 mmol) in CH_2Cl_2 (15 mL) was sonicated for 15 min at room temperature. The AgCl precipitate was removed by filtration, and the resulting CH_2Cl_2 solution was washed with a solution of potassium phthalimide (74 mg; 0.40 mmol) in water (2 mL). The CH_2Cl_2 solution was then washed with water (3 × 5 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the product was suspended in diethyl ether (10 mL). The suspended solids were collected by filtration, washed with diethyl ether (3 × 3 mL), and dried under reduced pressure. Yield: 45 mg (75%) of a white powder. In order to resolve broad resonances, the ^{1}H and ^{13}C NMR spectra were measured at −51 °C. Rotation around palladium−tolyl and palladium−NPhth bonds at −51 °C is slow on the NMR time scale; therefore, there is a distinct signal for each tolyl and NPhth atom in both ^{1}H and ^{13}C NMR spectra. ^{1}H NMR ($CDCl_3$ at −51 °C): δ 9.37 (d, J = 8.3 Hz, 1H), 8.89 (d, J = 5.1 Hz, 1H), 8.08 (d, J = 5.1 Hz, 1H), 7.92 (multiple peaks, 2H), 7.84 (multiple peaks, 2H), 7.78 (d, J = 7.3 Hz, 1H), 7.56 (d, J = 8.1 Hz, 1H), 7.52 (t, J = 7.2 Hz, 1H), 7.43 (d, J = 8.1 Hz, 1H), 7.28 (t, J = 7.2 Hz, 1H), 7.10−7.22 (multiple peaks, 4H), 7.02 (t, J = 7.5 Hz, 1H), 6.96 (t, J = 6.4 Hz, 1H), 6.40 (d, J = 8.3 Hz, 1H), 5.55 (d, J = 8.3 Hz, 1H), 2.96 (t, J = 12.5 Hz, 1H), 2.78 (t, J = 12.8 Hz, 1H), 2.71

dx.doi.org/10.1021/om200779j|*Organometallics* 2011, 30, 6617−6627

(t, J = 12.6 Hz, 1H), 2.22 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$ at −51 °C): δ 180.67, 180.52, 159.04, 156.40, 156.21, 155.66, 153.40, 150.28, 140.02 (two overlapping signals as evident in the $^1H/^{13}C$ ASAPHMQC spectrum), 139.72, 139.50, 138.27, 137.06, 135.63, 134.32, 134.21, 132.06, 131.68, 128.04, 128.01, 127.82, 125.98, 125.59 (shift for the CF_3 group extracted from the $^{19}F/^{13}C$ ASAPHMQC spectrum), 124.68, 123.81 (two overlapping signals as evident in the $^1H/^{13}C$ ASAPHMQC spectrum), 123.36, 121.89, 121.52, 120.76, 56.78, 24.00, 20.98. ^{19}F NMR ($CDCl_3$ at −51 °C): δ −23.03 (s). HRMS electrospray (m/z): $[M - NPhth]^+$ calcd for $C_{26}H_{22}F_3N_2Pd$, 525.0764; found, 525.0769.

(dpph)Pd^{II}(2-PhC$_6$H$_4$)(I) (23). $Pd(dba)_2$ (316 mg, 0.66 mmol) was added to a solution of 2-iodobiphenyl (390 mg, 1.40 mmol) and 4-*tert*-butylpyridine (300 mg, 2.2 mmol) in THF (12 mL) at room temperature. The resulting homogeneous solution was stirred at room temperature for 1 h, and then 1,1-bis(2-pyridyl)phenylethane (dpph) (**14**; 364 mg, 1.40 mmol) was added. The reaction mixture was stirred for 5 min and then filtered through a pad of Celite. The volatiles were removed under reduced pressure. The resulting residue was suspended in hexanes (30 mL), and the suspended solids were collected by filtration and washed with diethyl ether (5 × 15 mL). The crude product was obtained as a yellowish powder (387 mg; 46%), and it was typically used without further purification. A sample for characterization was obtained by crystallization from ethyl acetate. Rotation around the C−phenyl bond is slow on the NMR time scale at room temperature. In order to resolve broad resonances, the ^1H and ^{13}C NMR spectra were measured at 46 °C. ^1H NMR ($CDCl_3$ at 46 °C): δ 9.52 (d, J = 4.5 Hz, 1H), 8.47 (d, J = 6.2 Hz, 2H), 8.04 (d, J = 5.2 Hz, 1H), 7.83 (t, J = 7.6 Hz, 1H), 7.73 (multiple peaks, 2H), 7.68 (d, J = 7.2 Hz, 1H), 7.40 (multiple peaks, 5H), 7.28 (t, J = 6.6 Hz, 1H), 7.21 (multiple peaks, 2H), 6.96 (dd, J = 5.3, 9.1 Hz, 1H), 6.84 (t, J = 7.2 Hz, 1H), 6.74 (bs, 2H), 6.62 (t, J = 6.9 Hz, 1H), 6.52 (br s, 1H), 2.19 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$ at 46 °C): δ 161.80, 159.86, 155.36, 153.03, 148.03, 145.31, 144.77, 142.47, 138.66, 137.97, 137.76, 130.59, 129.46, 129.28, 128.95, 127.43, 127.32, 126.07, 123.59, 123.40, 123.25, 123.17, 123.11, 122.45, 57.89, 30.30. HRMS electrospray (m/z): $[M - I]^+$ calcd for $C_{30}H_{25}N_2Pd$, 519.1047; found, 519.1052.

(dpph)Pd^{IV}(biphe)(Cl) (24). Silver trifluoroacetate (77 mg, 0.35 mmol) was added to a solution of (dpph)Pd^{II}(2-PhC$_6$H$_4$)(I) (**23**; 200 mg, 0.31 mmol) in CH_2Cl_2 (10 mL) at room temperature. The reaction mixture was stirred at room temperature for 15 min, and then this mixture was filtered through a pad of Celite. The volume of the solution was reduced to 15 mL. NFTPT (116 mg; 0.4 mmol) was added, and the reaction mixture was stirred at room temperature for 15 min. The reaction mixture was then washed with water (3 × 10 mL) and brine (2 × 10 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The resulting residue was dissolved in a minimal amount of CH_2Cl_2 and filtered through a plug of silica gel that had been pre-equilibrated with a 1/1 mixture of MeOH and CH_2Cl_2. The filtrate was collected and evaporated under reduced pressure, the resulting residue was suspended in ethyl acetate (5 mL), and the suspended solids were collected by filtration, washed with ethyl acetate (3 × 3 mL), and dried under vacuum. Yield: 89 mg (52%) of a white powder. ^1H NMR (CD_2Cl_2): δ 9.26 (dd, J = 5.5, 1.7 Hz, 2H), 7.95 (td, J = 7.7, 1.7 Hz, 2H), 7.88 (d, J = 8.3 Hz, 2H), 7.74 (dd, J = 7.6 Hz, 1.6 Hz, 2H), 7.54 (dd, J = 7.9, 1.2 Hz, 1H), 7.48 (t, J = 4.5 Hz, 2H), 7.20 (t, J = 7.4 Hz, 2H), 7.00 (t, J = 5.3 Hz, 1H), 6.83 (td, J = 7.4, 1.4 Hz, 2H), 6.73 (d, J = 7.9 Hz, 2H), 6.64 (t, J = 5.4 Hz, 1H), 6.46 (dd, J = 7.9, 1.2 Hz, 1H), 2.77 (s, 3H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 169.60, 157.85, 152.98, 151.22, 149.69, 139.49, 137.28, 136.60, 130.57, 126.84, 125.97, 125.25, 125.12, 124.75, 123.67, 123.11, 121.15, 56.24, 23.40. HRMS electrospray (m/z): $[M + Na]^+$ calcd for $C_{30}H_{23}ClN_2NaPd$, 575.0477; found 575.0479.

■ ASSOCIATED CONTENT

Supporting Information

Text, tables, figures, and CIF files giving complete experimental details for ligand syntheses, X-ray crystallography data, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: mssanfor@umich.edu.

■ ACKNOWLEDGMENTS

This work was supported by the National Science Foundation (No. CHE-1111563). We also acknowledge funding from NSF Grant No. CHE-0840456 for X-ray instrumentation. We thank Dr. Jeff Kampf for X-ray crystallographic analyses of complexes **11**, **12**, **15**, and **22**.

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