ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

Stoichiometric Reactivity Relevant to the Mor-DalPhos/Pd-Catalyzed Cross-Coupling of Ammonia and 1-Bromo-2-(phenylethynyl)benzene

Pamela G. Alsabeh,[†] Robert McDonald,[‡] and Mark Stradiotto*,[†]

[†]Department of Chemistry, Dalhousie University, 6274 Coburg Road, P.O. Box 15000, Halifax, Nova Scotia, Canada B3H 4R2

[‡]X-ray Crystallography Laboratory, Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Supporting Information

ABSTRACT: While Mor-DalPhos/Pd precatalyst mixtures have in general proven to be highly effective for the monoarylation of ammonia employing a range of (hetero)aryl (pseudo)halide cross-coupling partners, we have observed previously that 1-bromo-2-(phenylethynyl)benzene (Ar*Br) is a challenging substrate for this catalyst system. We report herein on our efforts to examine some possible modes of catalyst inhibition by this substrate. Treatment of [CpPd(allyl)] with Mor-DalPhos in the presence of Ar*Br afforded [(κ^2-*P,N*-Mor-DalPhos)Pd(Br)(Ar*)] (**1**; 85%), which was transformed into [(κ^3-*P,N,O*-Mor-DalPhos)Pd(Ar*)]$^+$OTf$^-$ (**3**; 83%) upon treatment with AgOTf. The characterization of **3** establishes the ability of the Mor-DalPhos ligand to adopt a κ^3-P,N,O structure, which may influence the course of some Pd-catalyzed amination processes. While treatment of **1** with AgOTf in the presence of ammonia, or alternatively treatment of **3** with ammonia, resulted in the clean formation of [(κ^2-*P,N*-Mor-DalPhos)Pd(NH_3)(Ar*)]$^+$OTf$^-$ (**2**), our efforts to isolate this compound were thwarted by the facile loss of ammonia from **2** to give **3**. Neither NMR spectroscopic nor X-ray crystallographic data obtained for **1** and **3** support the existence of significant Pd···alkyne interactions in these complexes. Treatment of the Pd(0) species [L_2Pd(diphenylacetylene)] (L_2 = Mor-DalPhos, **4**; L_2 = CyPF*t*Bu-JosiPhos, **5**) with Ar*Br resulted in divergent behavior: while multiple phosphorus-containing products were observed in the case of **4**, under analogous conditions **5** was transformed cleanly into [(κ^2-*P,P*-JosiPhos)Pd(Br)(Ar*)] (**6**). The identification of **6** was facilitated via independent synthesis from Ar*Br, JosiPhos, and [CpPd(allyl)] (90%). These observations suggest that the inferior performance of Mor-DalPhos relative to JosiPhos in the arylation of ammonia using Ar*Br may be attributable in part to the inefficiency with which putative [(Mor-DalPhos)Pd(alkyne)] species re-enter the catalytic cycle via C−Br oxidative addition.

The development of synthetic protocols that utilize ammonia as a synthon is attractive, given the low cost and abundant nature of this reagent, and in terms of the opportunities afforded by such synthetic methods with regard to streamlining the synthesis of nitrogen-containing organic molecules.[1] However, despite the remarkable advances that have been achieved in metal-catalyzed C−N bond-forming reactions, including the emergence of the Pd-catalyzed cross-coupling of amines and (hetero)aryl (pseudo)halides (i.e., Buchwald−Hartwig amination),[2] the successful incorporation of ammonia into synthetic protocols that are well-established for other classes of amines has proven challenging.[1] Indeed, whereas Buchwald−Hartwig amination was established in 1995,[3] the Pd-catalyzed arylation of ammonia has emerged only recently.[4−6]

The successful development of Buchwald−Hartwig amination protocols that accommodate ammonia as a substrate can be attributed largely to the identification of suitable ancillary coligands that enable the synthesis of arylamines in high yield and with useful selectivity (e.g., monoarylation vs polyarylation) and substrate scope. In this vein, we have recently reported on the development of Mor-DalPhos (Chart 1),[5] which is a broadly effective ligand for use in the selective Pd-catalyzed monoarylation of challenging substrates, including ammonia,[5] hydrazine,[7] and acetone.[8,9] In building on this chemistry, we developed a previously unknown tandem ammonia cross-coupling/cyclization protocol that enables the construction of NH-indoles via arylation of ammonia by using 1-bromo-2-(phenylethynyl)benzene (Ar*Br) and related derivatives.[6] However, as part of this investigation, we noted that Mor-DalPhos/Pd mixtures performed poorly under a range of experimental conditions (e.g., 5 mol % of Pd, 3 equiv of KO*t*Bu, 3 equiv of NH_3, 90 °C, 18 h) involving the test substrate Ar*Br, affording the desired 2-phenylindole product in less than 50%

Chart 1

Mor-DalPhos JosiPhos (CyPF*t*Bu)

Received: November 14, 2011
Published: January 19, 2012

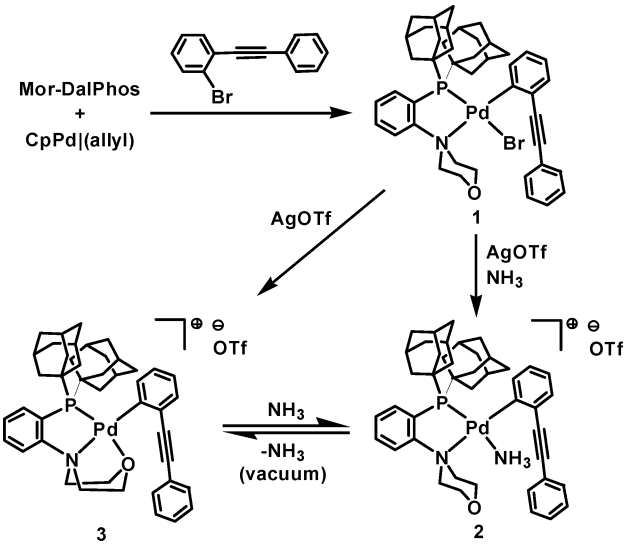
dx.doi.org/10.1021/om201122q | *Organometallics* 2012, 31, 1049−1054

yield. By comparison, we found that the use of the CyPF*t*Bu variant of JosiPhos (Chart 1), a ligand that has been shown by Hartwig and co-workers to be highly effective for the arylation of both amines[2a,b,10] and ammonia,[4a,c] afforded a range of ammonia-derived 2-arylindole products, as well as analogous cross-coupling/cyclization products derived from methylamine and hydrazine, in good to excellent yield.[6] In an effort to shed some light on the divergent behavior of Mor-DalPhos and JosiPhos in this catalytic chemistry, we conducted a brief stoichiometric reactivity survey relevant to the Mor-DalPhos/Pd-catalyzed cross-coupling of ammonia and Ar*Br, including selected comparisons to the analogous JosiPhos-based catalyst system. We report herein on the results of these studies, including the first observation of a κ^3-P,N,O binding mode for the Mor-DalPhos ligand.

RESULTS AND DISCUSSION

The oxidative addition of aryl halides to in situ generated (Mor-DalPhos)Pd^0 species has been shown to occur under mild conditions, and the arylation of ammonia using this catalyst system proceeds smoothly with ortho-substituted aryl halides other than Ar*Br.[5] Given these observations, we initially turned our attention to examining the spectroscopic and structural features of the product obtained from C−Br oxidative addition of Ar*Br to (Mor-DalPhos)Pd^0, in an effort to assess whether alkyne coordination to Pd(II) in this putative catalytic intermediate might underpin the relatively poor performance of the Mor-DalPhos/Pd system with this substrate. Treatment of [CpPd(allyl)] with Mor-DalPhos in the presence of Ar*Br in THF solution afforded the desired oxidative addition product [(κ^2-*P,N*-Mor-DalPhos)Pd(Br)(Ar*)] (**1**) as an analytically pure beige solid in 85% isolated yield (Scheme 1). Solution

Scheme 1



NMR spectroscopic characterization data support the identity of **1** as being the expected square-planar complex, devoid of any significant Pd···alkyne interactions. Indeed, the alkyne carbon ^{13}C NMR chemical shifts observed for **1** (90.0 and 97.0 ppm) are only very modestly downfield of those of the Ar*Br precursor (88.0 and 93.9 ppm). The crystallographic characterization of **1** corroborates these solution NMR data;[11] an ORTEP[12] diagram of **1** is presented in Figure 1, which confirms

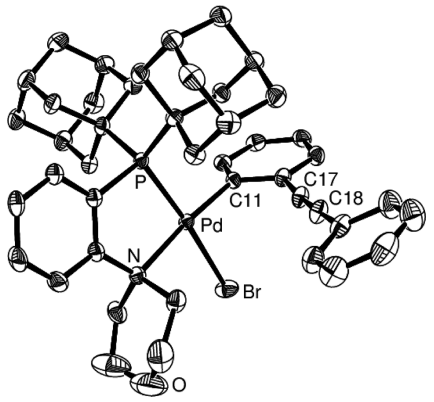


Figure 1. ORTEP diagram of **1**·CH_2Cl_2 shown with 50% ellipsoids. All hydrogen atoms and the dichloromethane solvate have been omitted for clarity. Selected interatomic distances (Å): Pd−P, 2.2681(7); Pd−N, 2.232(2); Pd−Br, 2.5154(4); Pd−C11, 2.011(3); Pd···C17, 3.200(3); Pd···C18, 3.891(3).

the κ^2-P,N nature of the Mor-DalPhos ligand, the trans disposition of Br and P as well as that of C and N (in keeping with the greater trans-directing abilities of P relative to N), and the notably long Pd···alkyne contacts (3.200(3) and 3.891(3) Å).

We have demonstrated previously that treatment of [(κ^2-*P,N*-Mor-DalPhos)Pd(Cl)(Ar)] (Ar = Ph, 4-MeOC$_6$H$_4$) with AgOTf in the presence of 3 equiv of ammonia in a mixture of dichloromethane and 1,4-dioxane affords isolable cationic ammine complexes that resist loss of ammonia upon exposure to vacuum.[5] Under similar conditions **1** is transformed cleanly into the analogous cationic ammine complex **2** (Scheme 1). In monitoring the progress of the reaction by using ^{31}P NMR spectroscopic methods, the disappearance of **1** (56.3 ppm) is accompanied by the clean formation of **2** (62.6 ppm); the ammine ligand in **2** gives rise to a broad ^{1}H NMR resonance at 2.82 ppm. However, efforts to isolate **2** via removal of the reaction solvent in vacuo resulted in a decrease in the intensity of the ^{31}P NMR resonance associated with **2** and the appearance of a single new phosphorus-containing species (**3**; $\delta(^{31}P)$ 80.0). We were successful in our efforts to generate **3** rationally via addition of AgOTf to **1** in the absence of ammonia, and in turn **3** was isolated as an analytically pure dark yellow solid in 83% isolated yield. Treatment of solutions of **3** with 3 equiv of ammonia resulted in the clean regeneration of the ammine adduct **2** (^{31}P NMR). The observed propensity of **2** to release ammonia differs from our previously reported [(κ^2-*P,N*-Mor-DalPhos)Pd(NH$_3$)(Ar)]$^+$OTf$^-$ (Ar = Ph, 4-MeOC$_6$H$_4$) complexes[5]—a phenomenon that we initially envisioned might be attributable to the competitive binding of the alkyne fragment to Pd, leading to **3**. However, as in **1**, the frequencies of the ^{13}C NMR resonances associated with the alkyne carbons in **3** (93.7 and 90.1 ppm) are inconsistent with the existence of significant Pd···alkyne interactions. The crystallographic characterization of **3** is in keeping with this assertion;[11] an ORTEP[12] diagram of this complex is presented in Figure 2. The Pd···alkyne distances in **3** (3.148(4) and 3.790(4) Å), while statistically shorter than the related contacts in **1**, can still be viewed as being sufficiently long so as to preclude significant Pd···alkyne bonding interactions. Rather, the coordinative and electronic unsaturation that results from the loss of ammonia in **2** is instead apparently compensated by the Mor-DalPhos ligand adopting a tridentate κ^3-P,N,O binding

dx.doi.org/10.1021/om201122q | *Organometallics* 2012, 31, 1049−1054

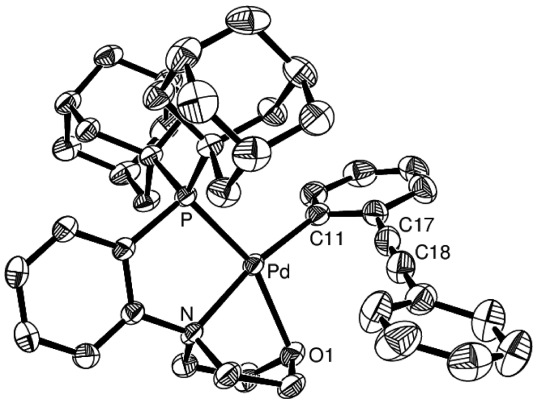
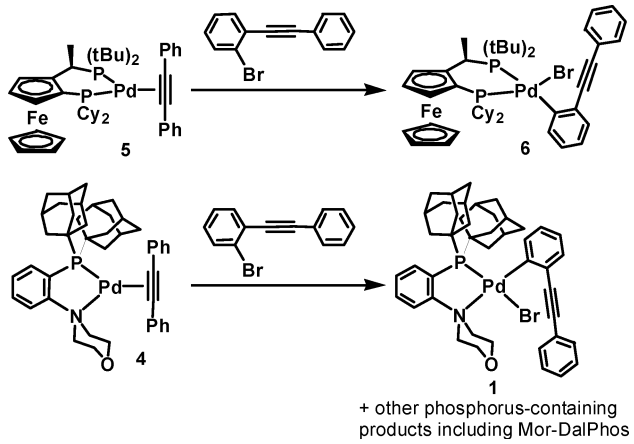


Figure 2. ORTEP diagram of $3{\cdot}OEt_2$ shown with 50% ellipsoids. All hydrogen atoms, the diethyl ether solvate, and the triflate counteranion have been omitted for clarity. Selected interatomic distances (Å): Pd–P, 2.2264(7); Pd–N, 2.106(3); Pd–O, 2.246(2); Pd–C11, 1.997(3); Pd···C17, 3.148(4); Pd···C18, 3.790(4).

motif. On the basis of these observations, it appears that the congestion imposed by the *o*-(phenylethynyl)phenyl ligand, rather than the propensity of this fragment to engage in π-bonding to Pd, may represent the primary factor leading to the loss of ammonia and the formation of **3**. It is unclear whether cationic ammonia adducts analogous to **2**, arising from the displacement of (pseudo)halide (X) on Pd by ammonia in Ar–X oxidative addition products such as **1**, represent important reactive intermediates in the Mor-DalPhos/Pd-catalyzed cross-coupling of ammonia and Ar*Br or other aryl (pseudo)halides. However, should such intermediates be accessible, the ability of the Mor-DalPhos ligand to adopt a κ^3-P,N,O binding motif in response to the loss of ammonia promoted by the presence of a sterically demanding Pd–Ar ligand (such as *o*-(phenylethynyl)-phenyl) may contribute in part to the inferior catalytic performance of the Mor-DalPhos/Pd catalyst system, relative to catalysts featuring ligands that are not obviously capable of tridentate coordination (e.g., JosiPhos).

Alkyne coordination to (Mor-DalPhos)Pd^0 species generated following C–N reductive elimination[13] involving the Ar*Br substrate, the derived aniline prior to cyclization, and/or the diphenylacetylene that is formed as a byproduct in catalysis employing Mor-DalPhos/Pd[6] might also inhibit the Mor-DalPhos/Pd catalyst system. As such, we turned our attention to examining the efficiency of C–Br oxidative addition of Ar*Br to the [L_2Pd(diphenylacetylene)] complexes **4** (L_2 = Mor-DalPhos) and **5** (L_2 = JosiPhos) to give the Pd(II) products **1** and **6**, respectively (Scheme 2). In monitoring the reaction of the JosiPhos complex **5** with 1 equiv of Ar*Br in THF at room temperature (over 48 h) or 65 °C (over 2.5 h), clean conversion to the anticipated oxidative addition product **6** was observed by use of ^{31}P NMR methods.[14] The identity of **6** was confirmed via independent synthesis; the addition of Ar*Br to a mixture of JosiPhos and [CpPd(allyl)] afforded **6** as an analytically pure orange solid in 90% isolated yield. In contrast, treatment of the Mor-DalPhos precursor **4** with Ar*Br under analogous experimental conditions resulted in the consumption of **4**, along with the formation of multiple phosphorus-containing species, including the target oxidative addition product **1** and free Mor-DalPhos ligand. These observations qualitatively suggest that the comparatively poor catalytic performance of Mor-DalPhos/Pd mixtures, relative to the JosiPhos-based catalyst, in the monoarylation of Ar*Br and

Scheme 2



related derivatives may be attributable in part to the inefficiency with which putative [(Mor-DalPhos)Pd(alkyne)] species re-enter the catalytic cycle via Ar–X oxidative addition.

In summary, we report herein on our efforts to identify possible modes of Mor-DalPhos/Pd catalyst inhibition when using 1-bromo-2-(phenylethynyl)benzene (Ar*Br) as a substrate for the monoarylation of ammonia. In the course of these studies we noted that neither the putative oxidative addition product [(κ^2-*P,N*-Mor-DalPhos)Pd(Br)(Ar*)] (**1**) nor the corresponding product derived from bromide abstraction using AgOTf [(κ^3-*P,N,O*-Mor-DalPhos)Pd(Ar*)]$^+$OTf$^-$ (**3**) featured significant Pd···alkyne interactions in solution or the solid state. These observations would appear to rule out substrate inhibition arising from intramolecular alkyne coordination to Pd following initial C–Br oxidative addition. The characterization of **3** establishes for the first time the ability of the Mor-DalPhos ligand to adopt a κ^3-P,N,O structure, which may play a role in Pd-catalyzed amination processes, especially where the (pseudo)halide ligand is labile. We also observed that whereas [(κ^2-*P,N*-Mor-DalPhos)Pd(NH_3)(Ph)]$^+$OTf$^-$ is an isolable complex that resists loss of ammonia upon prolonged exposure to vacuum, the more facile loss of ammonia from [(κ^2-*P,N*-Mor-DalPhos)Pd(NH_3)(Ar*)]$^+$OTf$^-$ (**2**) to give **3** precluded the isolation of **2**. It is feasible that the capacity of the Mor-DalPhos ligand to adopt a κ^3-P,N,O binding motif in response to the loss of ammonia promoted by the sterically demanding Pd–Ar* ligand could contribute to the challenges encountered with this substrate when using the Mor-DalPhos/Pd catalyst system. Finally, in contrast to the clean C–Br oxidative addition of Ar*Br to [(JosiPhos)Pd(diphenylacetylene)] that was observed (giving **6**), the analogous chemistry involving [(Mor-DalPhos)Pd(diphenylacetylene)] afforded the target oxidative addition product **1**, accompanied by the generation of free Mor-DalPhos and other unidentified phosphorus-containing species. These observations suggest that the inefficiency with which putative [(Mor-DalPhos)Pd(alkyne)] species re-enter the catalytic cycle via C–Br oxidative addition may also contribute to the observed inferior performance of Mor-DalPhos/Pd versus JosiPhos/Pd catalyst systems in the Buchwald–Hartwig amination of Ar*Br using ammonia.

■ EXPERIMENTAL SECTION

General Considerations. All manipulations were conducted under dinitrogen within an inert-atmosphere glovebox, utilizing

dx.doi.org/10.1021/om201122q | *Organometallics* 2012, 31, 1049–1054

glassware that was oven-dried (130 °C) and evacuated while hot prior to use. Pentane and dichloromethane were deoxygenated by sparging with dinitrogen followed by passage through a double-column solvent purification system purchased from MBraun Inc. equipped with either one alumina-packed column and one column packed with copper-Q5 reactant (pentane) or two alumina-packed columns (dichloromethane). THF and diethyl ether were each dried over Na/benzophenone followed by distillation under an atmosphere of dinitrogen. Deuterated solvents (Cambridge Isotopes) were degassed by using three repeated freeze−pump−thaw cycles and stored over 4 Å molecular sieves for 24 h prior to use. All solvents were stored under dinitrogen over activated 4 Å molecular sieves. Mor-DalPhos,[5] [CpPd(allyl)],[15] and 1-bromo-2-(phenylethynyl)benzene[6] were prepared according to literature procedures. Silver trifluoromethanesulfonate (Strem), CyPF*t*Bu-JosiPhos (Solvias), diphenylacetylene (Aldrich), and 0.5 M solutions of ammonia in 1,4-dioxane (Aldrich) were used as received. ^{1}H, ^{13}C, and ^{31}P NMR characterization data were collected at 300 K on a Bruker AV-500 spectrometer operating at 500.1, 125.8, and 202.5 MHz (respectively), with chemical shifts reported in parts per million downfield of $SiMe_4$ (for ^{1}H and ^{13}C) and 85% H_3PO_4 in D_2O (for ^{31}P). Structural elucidation was enabled through analysis of ^{1}H−^{1}H COSY, ^{1}H−^{13}C HSQC, ^{1}H−^{13}C HMBC, and DEPTQ-135 data. In some cases, fewer than expected unique ^{13}C NMR resonances were observed, despite prolonged acquisition times, and the OTf signals are not assigned. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, BC (Canada) and Midwest Microlab, LLC, Indianapolis, IN (USA).

Synthesis of 1. A vial was charged with a magnetic stir bar, Mor-DalPhos (112.1 mg, 0.242 mmol), [CpPd(allyl)] (55.3 mg, 0.260 mmol), 1-bromo-2-(phenylethynyl)benzene (186.5 mg, 0.725 mmol), and THF (2 mL). The vial containing the resulting red-brown reaction mixture was sealed with a PTFE-lined cap, removed from the glovebox, and heated at 65 °C for 16 h under the influence of magnetic stirring, at which time the consumption of Mor-DalPhos and the clean formation of **1** was confirmed by use of ^{31}P NMR methods. The resulting slurry was concentrated to dryness in vacuo, washed with diethyl ether (5 × 2 mL) until the washings remained colorless, and dried in vacuo to afford **1** as an analytically pure beige powder in 85% isolated yield (169.1 mg, 0.204 mmol). Anal. Calcd for $C_{44}H_{51}BrNOPPd$: C, 63.89; H, 6.21; N, 1.69. Found: C, 63.62; H, 6.19; N, 1.41. Crystals suitable for single-crystal X-ray diffraction analysis were obtained from vapor diffusion of diethyl ether into a concentrated dichloromethane solution of **1**. ^{1}H NMR ($CDCl_3$): δ 8.18 (dd, J = 8.0, 2.5 Hz, 1H, ArH), 7.87 (m, 1H, ArH), 7.61 (m, 1H, ArH), 7.56 (d, J = 8.0 Hz, 1H, Pd-ArH), 7.46−7.44 (m, 2H, alkyne Ph), 7.36 (m, 1H, ArH), 7.28 (m, 1H, Pd-ArH), 7.24−7.18 (m, 3H, alkyne Ph), 6.97 (m, 1H, Pd-ArH), 6.84 (m, 1H, Pd-ArH), 5.50 (m, 1H, morph CH_2), 5.40 (m, 1H, morph CH_2), 4.22 (m, 1H, morph CH_2), 3.99−3.92 (m, 2H, morph CH_2), 3.85 (m, 1H, morph CH_2), 3.10 (m, 1H, morph CH_2), 2.91 (m, 1H, morph CH_2), 2.48−2.45 (m, 3H, 1-Ad CH_2), 2.27−2.26 (m, 3H, 1-Ad CH_2), 2.13−2.05 (m, 6H, 1-Ad CH/CH_2), 1.89−1.75 (15H, 1-Ad CH/CH_2), 1.59−1.56 (m, 3H, 1-Ad CH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 160.3 (d, J_{PC} = 12.6 Hz, aryl C_{quat}), 145.4 (d, J_{PC} = 5.0 Hz, Pd-aryl C_{quat}), 138.7 (Pd-aryl CH), 136.0 (aryl CH), 132.5 (aryl CH), 131.6 (Pd-aryl CH), 131.3 (alkyne Ph C_{quat}), 131.1 (alkyne Ph CH), 128.8 (d, J_{PC} = 7.5 Hz, aryl CH), 128.2 (alkyne Ph CH), 127.5 (alkyne Ph CH), 127.4 (d, J_{PC} = 27.7 Hz, aryl C_{quat}), 126.1 (Pd-aryl CH), 126.0 (d, J_{PC} = 5.0 Hz, aryl CH), 125.0 (Pd-aryl C_{quat}), 122.7 (Pd-aryl CH), 97.0 (alkyne), 90.0 (alkyne), 62.2 (morph CH_2), 61.7 (morph CH_2), 56.4 (morph CH_2), 55.2 (morph CH_2), 43.4 (1-Ad C_{quat}), 43.3 (d, J_{PC} = 25.2 Hz, 1-Ad C_{quat}), 41.3 (1-Ad CH_2), 39.3 (1-Ad CH_2), 36.3 (1-Ad CH_2), 36.0 (1-Ad CH_2), 28.8−28.6 (m, 1-Ad CH_2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 56.3.

Generation of 2. A vial was charged with a magnetic stir bar, **1** (44.2 mg, 0.0534 mmol), and CH_2Cl_2 (2 mL). The vial was sealed with a PTFE-lined cap equipped with a septum and transferred out of the glovebox, and NH_3 (0.5 M in 1,4-dioxane, 0.321 mL, 0.160 mmol) was added via syringe. The solution was stirred briefly and then was transferred back into the glovebox, at which point the cap was removed, silver trifluoromethanesulfonate (15.1 mg, 0.0588 mmol) was added, and the vial was resealed with the cap. The resulting mixture was stirred magnetically for 1 h at room temperature, during which time a gray precipitate formed. ^{31}P NMR analysis of the reaction mixture indicated the consumption of **1** and complete conversion to a single new phosphorus-containing species (**2**). The precipitate was removed by filtration over Celite, the filtrate was triturated with pentane (2 × 2 mL), and the mixture was concentrated to apparent dryness, affording the desired product **2** as a yellow powder (50.5 mg isolated) that was found to contain varying amounts of 1,4-dioxane (ca. 0.75 equiv), as well as trace amounts of other solvents used in the synthesis. Our efforts to obtain solvent-free samples of **2** for elemental analysis were thwarted by the loss of the ammine ligand from **2** (to give **3**) upon prolonged exposure to vacuum. ^{1}H NMR ($CDCl_3$): δ 8.07 (dd, J = 8.4, 3.1 Hz, 1H, ArH), 7.87 (m, 1H, ArH), 7.70 (m, 1H, ArH), 7.65 (d, J = 7.7 Hz, 1H, Pd-ArH), 7.46 (m, 1H, ArH), 7.38−7.36 (m, 3H, Pd-ArH, Ph), 7.29−7.28 (m, 3H, Ph), 7.07 (td, J = 7.5, 1.3 Hz, 1H, Pd-ArH), 7.00 (m, 1H, Pd-ArH), 4.37 (m, 1H, morph CH_2), 4.13−4.07 (m, 3H, morph CH_2), 3.96−3.89 (m, 2H, morph CH_2), 3.33 (m, 1H, morph CH_2), 3.20 (m, 1H, morph CH_2), 2.82 (br s, 3H, NH_3), 2.42−2.39 (m, 3H, 1-Ad CH_2), 2.25−2.23 (m, 3H, 1-Ad CH_2), 2.10 (br s, 6H, 1-Ad CH/CH_2), 1.88−1.69 (m, 15H, 1-Ad CH/CH_2), 1.60−1.58 (m, 3H, 1-Ad CH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 160.9 (d, J_{PC} = 12.8 Hz, aryl C_{quat}), 148.3 (Pd-aryl C_{quat}), 138.2 (Pd-aryl CH), 135.9 (aryl CH), 133.8 (aryl CH), 133.0 (Pd-aryl CH), 131.0 (alkyne Ph CH), 129.4 (alkyne Ph C_{quat}), 128.8 (alkyne Ph CH), 128.6 (aryl CH), 127.5 (alkyne Ph CH), 127.1 (m, aryl CH), 126.1 (d, J_{PC} = 29.2 Hz, aryl C_{quat}), 124.6 (alkyne Ph CH), 123.3 (Pd−Ar C_{quat}), 122.1 (aryl CH), 119.6 (aryl CH), 94.5 (alkyne), 90.3 (alkyne), 61.7 (morph CH_2), 61.6 (morph CH_2), 56.4 (morph CH_2), 56.0 (morph CH_2), 43.4 (d, J_{PC} = 16.2 Hz, 1-Ad C_{quat}), 42.8 (d, J_{PC} = 14.7 Hz, 1-Ad C_{quat}), 41.3 (1-Ad CH_2), 39.6 (1-Ad CH_2), 36.3 (1-Ad CH_2), 35.9 (1-Ad CH_2), 28.7−28.5 (m, 1-Ad CH). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 62.6.

Synthesis of 3. In a vial containing a magnetic stir bar, **1** (100.0 mg, 0.121 mmol), and CH_2Cl_2 (3 mL) was added silver trifluoromethanesulfonate (34.2 mg, 0.133 mmol), and the resulting mixture was stirred magnetically for 1 h at room temperature, at which time complete consumption of **1** and conversion to a new product (**3**) was confirmed by use of ^{31}P NMR. The reaction mixture was filtered, and the resulting filtrate was concentrated and dried in vacuo to afford a green-yellow solid. The solid was washed with diethyl ether (4 × 2 mL) to afford **3** as a dark yellow powder in 83% yield (89.5 mg, 0.100 mmol). Anal. Calcd for $C_{45}H_{51}F_3NO_4PPdS$: C, 60.30; H, 5.74; N, 1.56. Found: C, 60.55; H, 5.66; N, 1.49. Crystals suitable for X-ray diffraction analysis were obtained from vapor diffusion of diethyl ether into a dichloromethane solution of **3**. ^{1}H NMR ($CDCl_3$): δ 8.12 (dd, J = 8.5, 3.5 Hz, 1H, ArH), 7.81 (t, J = 7.5 Hz, 1H, ArH), 7.75 (m, 1H, ArH), 7.61 (m, 1H, Pd-ArH), 7.56 (m, 1H, ArH), 7.44 (m, 1H, Pd-ArH), 7.37−7.34 (m, 2H, alkyne Ph), 7.31−7.29 (m, 3H, alkyne Ph), 7.14−7.09 (m, 2H, Pd-ArH), 4.82 (br s, 1H, morph CH_2), 4.69 (br s, 1H, morph CH_2), 4.23−4.19 (m, 2H, morph CH_2), 3.98 (br s, 1H, morph CH_2), 3.86 (br s, 1H, morph CH_2), 3.60 (br s, 2H, morph CH_2), 2.42−2.27 (m, 6H, 1-Ad CH_2), 2.13 (br s, 6H, 1-Ad CH_2/CH), 1.97−1.71 (m, 15H, 1-Ad CH_2/CH), 1.61−1.58 (m, 3H, 1-Ad CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 153.8 (m, aryl C_{quat}), 148.8 (Pd-aryl C_{quat}), 136.6 (Pd-aryl CH), 135.6 (aryl CH), 134.2 (aryl CH), 133.2 (Pd-aryl CH), 130.6 (alkyne Ph CH), 129.7 (Pd-aryl C_{quat}), 128.8−128.4 (aryl CH and C_{quat}), 126.8 (d, J_{PC} = 7.5 Hz, aryl CH), 126.5 (Pd-aryl CH), 124.7 (Pd-aryl CH), 122.9 (alkyne Ph C_{quat}), 121.7 (aryl CH), 119.2 (aryl CH), 93.7 (alkyne C_{quat}), 90.1 (alkyne C_{quat}), 70.3 (m, morph CH_2), 55.3 (morph CH_2), 54.8 (morph CH_2), 43.9 (d, J_{PC} = 16.4 Hz, 1-Ad C_{quat}), 43.5 (d, J_{PC} = 15.1 Hz, 1-Ad C_{quat}), 41.2 (1-Ad CH_2), 40.0 (1-Ad CH_2), 36.0 (1-Ad CH_2), 35.6 (1-Ad CH_2), 28.6−28.4 (m, 1-Ad CH). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 80.0.

Generation of 4. A vial charged with a magnetic stir bar, Mor-DalPhos (75.0 mg, 0.162 mmol), [CpPd(allyl)] (36.1 mg, 0.170 mmol), diphenylacetylene (31.7 mg, 0178 mmol), and THF (1.8 mL) was removed from the glovebox and heated at 65 °C for 2−4 h, under the influence of magnetic stirring and with monitoring by use of ^{31}P NMR techniques. When the consumption of Mor-DalPhos and the

dx.doi.org/10.1021/om201122q | *Organometallics* 2012, 31, 1049−1054

formation of **4** was observed, the reaction mixture was then concentrated to dryness in vacuo and the resulting residue was washed with cold pentane (5 × 2 mL, precooled to −30 °C) and dried in vacuo to afford the desired product **4** as a light brown powder (41.2 mg isolated). Our efforts to obtain **4** in analytically pure form were thwarted by the propensity of this material to retain fractional amounts of solvent, despite prolonged exposure to vacuum. ^{1}H NMR (THF-d_8): δ 7.93−7.90 (m, 2H, ArH), 7.54 (t, J = 7.0 Hz, 1H, ArH), 7.34−7.33 (m, 5H, ArH), 7.18−7.15 (m, 4H, ArH), 7.03−7.00 (m, 2H, ArH), 5.28−5.24 (m, 2H, morph CH_2), 3.78−3.76 (m, 2H, morph CH_2), 3.15−3.10 (m, 2H, morph CH_2), 2.70−2.68 (m, 2H, morph CH_2), 2.12−2.10 (m, 6H, 1-Ad CH_2), 1.92−1.89 (m, 6H, 1-Ad CH_2), 1.81 (br s, 6H, 1-Ad CH), 1.63 (br s, 12H, 1-Ad CH_2). ^{13}C{^{1}H} NMR (THF-d_8): δ 161.8 (d, J_{PC} = 18.9 Hz, aryl C_{quat}), 136.6 (aryl CH), 133.0 (d, J_{PC} = 15.1 Hz, aryl C_{quat}), 131.7 (aryl CH), 128.3 (alkyne Ph CH), 128.1 (alkyne Ph CH), 126.7 (aryl CH), 126.2 (d, J_{PC} = 5.1 Hz, aryl CH), 124.6 (alkyne Ph CH), 68.3 (morph CH_2), 58.9 (morph CH_2), 42.1 (d, J_{PC} = 6.3 Hz, 1-Ad CH_2), 39.3 (d, J_{PC} = 5.0 Hz, 1-Ad C_{quat}), 37.4 (1-Ad CH_2), 29.7 (d, J_{PC} = 9.2 Hz, 1-Ad CH). ^{31}P{^{1}H} NMR (THF-d_8): δ 60.3.

Generation of 5. A vial was charged with a magnetic stir bar, JosiPhos (56.0 mg, 0.101 mmol), [CpPd(allyl)] (22.5 mg, 0.106 mmol), diphenylacetylene (19.7 mg, 0.111 mmol), and THF (1.2 mL). The vial containing the resulting red-brown reaction mixture was sealed with a PTFE-lined cap and was removed from the glovebox and heated at 65 °C for 2 h, at which time complete conversion to the desired product (**5**) was confirmed by use of ^{31}P NMR methods. The resulting red solution was concentrated to dryness in vacuo, washed with cold pentane (3 × 2 mL, precooled to −30 °C), and dried in vacuo to afford an orange powder (64.5 mg isolated). Although we have thus far not been able to isolate **5** in analytically pure form, due to the presence of minor unidentified impurities, the NMR characterization data obtained from this material are consistent with the target complex (**5**, >90% pure on the basis of ^{31}P NMR data); as such, the crude material obtained was used without further purification. ^{1}H NMR (THF-d_8): δ 7.22−7.20 (m, 2H, Ph), 7.16−7.13 (m, 2H, Ph), 7.09−7.04 (m, 4H, Ph), 6.99 (m, 1H, Ph), 6.89 (m, 1H, Ph), 4.66 (br s, 1H, Cp CH), 4.52 (br s, 1H, Cp CH), 4.32 (br s, 1H, Cp CH), 4.22 (s, 5H, C_5H_5), 3.16 (m, 1H, C*H*Me), 2.50 (m, 1H, Cy), 2.22 (m, 1H, Cy), 1.98−0.85 (m, 41H, Cy, *CH_3, CMe_3). ^{13}C NMR (THF-d_8): δ 141.5 (m, Ph C_{quat}), 140.4 (m, Ph C_{quat}), 128.4 (Ph CH), 128.1 (Ph CH), 127.9 (Ph CH), 127.8 (Ph CH), 124.7 (d, J_{PC} = 70.4 Hz, alkyne), 124.6 (Ph CH), 124.0 (Ph CH), 122.3 (d, J_{PC} = 64.1 Hz, alkyne), 98.0 (dd, J_{PC} = 18.9, 7.5 Hz, Cp C_{quat}), 75.9 (m, Cp C_{quat}), 73.3 (Cp CH), 70.0 (m, Cp CH), 69.8 (C_5H_5), 68.0 (d, J_{PC} = 3.8 Hz, Cp CH), 39.1 (d, J_{PC} = 13.8 Hz, Cy), 37.8 (CMe_3), 36.2 (CMe_3), 35.5 (dd, J_{PC} = 16.4, 4.3 Hz, Cy), 35.2 (m, *C*HMe), 32.1 (d, J_{PC} = 7.8 Hz, Cy), 31.8 (d, J_{PC} = 8.3 Hz, CMe_3), 31.6 (d, J_{PC} = 8.2 Hz, CMe_3), 30.6 (Cy), 30.0 (d, J_{PC} = 8.2 Hz, Cy), 28.6−27.2 (m, Cy), 17.7 (d, J_{PC} = 5.3 Hz, CH*Me*). ^{31}P{^{1}H} NMR (THF-d_8): δ 85.7 (d, J_{PP} = 8.1 Hz), 22.4 (d, J_{PP} = 6.1 Hz).

Synthesis of 6. A vial was charged with a magnetic stirbar, JosiPhos (55.5 mg, 0.100 mmol), [CpPd(allyl)] (22.3 mg, 0.105 mmol), 1-bromo-2-(phenylethynyl)benzene (51.4 mg, 0.200 mmol), and THF (1 mL). The vial containing the resulting red-brown mixture was sealed with a PTFE-lined cap, removed from the glovebox, and heated at 65 °C for 16 h, at which time complete conversion to the desired product (**6**) was confirmed by use of ^{31}P NMR methods. The resulting orange slurry was concentrated to dryness in vacuo, washed with Et_2O (10 × 2 mL) until the washings remained colorless, and dried in vacuo to afford **6** as an orange powder in 90% yield (82.7 mg, 0.090 mmol). Anal. Calcd for $C_{46}H_{61}P_2FeBrPd$: C, 60.16; H, 6.70. Found: C, 59.87; H, 6.66. ^{1}H NMR ($CDCl_3$): δ 7.53−7.51 (m, 2H, Ph), 7.39−7.31 (m, 4H, Ph, Pd-ArH), 7.17 (d, J = 7.6 Hz, 1H, Pd-ArH), 7.09 (m, 1H, Pd-ArH), 6.85 (t, J = 7.3 Hz, 1H, Pd-ArH), 4.95 (s, 1H, Cp CH), 4.50 (br s, 1H, Cp CH), 4.45 (m, 1H, Cp CH), 4.25 (s, 5H, C_5H_5), 3.15 (m, 1H, C*H*Me), 2.67 (m, 1H, Cy), 2.54 (m, 1H, Cy), 2.46−2.31 (m, 3H, Cy), 2.08 (m, 1H, Cy), 1.91−1.77 (m, 10H, Cy, CH*Me*), 1.72−1.09 (m, 27H, Cy, CMe_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 160.3 (d, J_{PC} = 118.0 Hz, Pd-aryl C_{quat}), 138.0 (Pd-aryl CH), 131.9 (d, J_{PC} = 5.7 Hz, Pd-aryl CH), 131.8 (alkyne Ph CH), 129.7 (Pd-aryl C_{quat}), 128.2 (alkyne Ph CH), 128.1 (Pd-aryl CH), 127.6 (alkyne Ph CH), 125.5 (alkyne Ph C_{quat}), 122.8 (Pd-aryl CH), 97.4 (dd, J_{PC} = 14.2, 6.9 Hz, Cp C_{quat}), 95.2 (alkyne), 89.6 (alkyne), 73.2 (dd, J_{PC} = 27.5, 10.8 Hz, Cp C_{quat}), 72.8 (Cp CH), 69.6 (C_5H_5), 69.3 (d, J_{PC} = 7.4 Hz, Cp CH), 68.3 (d, J_{PC} = 5.3 Hz, Cp CH), 42.6 (d, J_{PC} = 22.4 Hz, Cy), 38.8 (CMe_3), 37.3 (CMe_3), 33.5 (d, J_{PC} = 31.5 Hz, Cy), 32.4 (d, J_{PC} = 4.3 Hz, *C*HMe), 32.0 (CMe_3), 31.1 (d, J_{PC} = 3.9 Hz, CMe_3), 29.7 (Cy), 28.3 (Cy), 27.7 (d, J_{PC} = 8.3 Hz, Cy), 27.2 (d, J_{PC} = 11.1 Hz, Cy), 27.0 (d, J_{PC} = 14.3 Hz, Cy), 26.6 (Cy), 17.9 (d, J_{PC} = 6.2 Hz, CH*Me*). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 73.2 (d, J_{PP} = 34.4 Hz), 17.3 (d, J_{PP} = 34.5 Hz).

Crystallographic Solution and Refinement Details. Crystallographic data were obtained at 173(±2) K on a Bruker D8/APEX II CCD diffractometer using graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation, employing samples that were mounted in inert oil and transferred to a cold gas stream on the diffractometer. Programs for diffractometer operation, data collection, and data reduction (including SAINT) were supplied by Bruker. Gaussian integration (face-indexed) was employed as the absorption correction method for **1**·CH_2Cl_2. The crystal of **3**·OEt_2 used for data collection was found to display nonmerohedral twinning; as such, multiscan (TWINABS) was employed as the absorption correction method. Both components of the twin were indexed with the program CELL_NOW (Bruker AXS Inc., Madison, WI, 2004). The second twin component can be related to the first component by a 3.2° rotation about the [1,−0.35,−0.14] axis in real space and about the [−0.71,$^1/_2$,1] axis in reciprocal space. Integrated intensities for the reflections from the two components were written into a SHELXL-97 HKLF 5 reflection file with the data integration program SAINT (version 7.68A), using all reflection data (exactly overlapped, partially overlapped and nonoverlapped). The refined value of the twin fraction (SHELXL-97 BASF parameter) was 0.3651(11). The structures were solved by use of a Patterson search/structure expansion and refined by use of full-matrix least-squares procedures (on F^2) with R1 based on $F_o^2 \geq 2\sigma(F_o^2)$ and wR2 based on $F_o^2 \geq -3\sigma(F_o^2)$. Anisotropic displacement parameters were employed for all the non-hydrogen atoms. Disorder involving the triflate counteranion in **3**·OEt_2 was identified during the solution process. As a result, the distances within the disordered triflate ion were restrained as follows: (a) the S1A−C91A and S1B−C91B distances were constrained to be equal (within 0.03 Å); (b) the F91B−C91B, F92B−C91B, and F93B−C91B distances were constrained to be equal (within 0.03 Å). All hydrogen atoms were added at calculated positions and refined by use of a riding model employing isotropic displacement parameters based on the isotropic displacement parameter of the attached atom. In the case of **1**·CH_2Cl_2, which crystallizes in the chiral space group $P2_12_12_1$, the near-zero final refined value of the Flack[16] absolute structure parameter (0.021(6)) confirmed that the correct absolute configuration had been implemented. Additional crystallographic information is provided in the Supporting Information.

■ ASSOCIATED CONTENT

Supporting Information

CIF files giving single-crystal X-ray diffraction data for **1**·CH_2Cl_2 and **3**·OEt_2. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Fax: 1-902-494-1310. Tel: 1-902-494-7190. E-mail: mark.stradiotto@dal.ca.

■ ACKNOWLEDGMENTS

We thank the NSERC of Canada (including a Discovery Grant for M.S. and a Postgraduate Scholarship for P.G.A.), the Killam Trusts, and Dalhousie University for their generous support of this work. Dr. Michael Lumsden (NMR-3, Dalhousie) is

thanked for technical assistance in the acquisition of NMR data. Solvias is thanked for a gift of JosiPhos.

REFERENCES

(1) For recent reviews, see: (a) Klinkenberg, J. L.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **2011**, *50*, 86. (b) Aubin, Y.; Fischmeister, C.; Thomas, C. M.; Renaud, J.-L. *Chem. Soc. Rev.* **2010**, *39*, 4130. (c) van der Vlugt, J. I. *Chem. Soc. Rev.* **2010**, *39*, 2302.

(2) For selected reviews, see: (a) Hartwig, J. *Organotransition Metal Chemistry*; University Science Books: Sausalito, CA, 2010; p 907. (b) Hartwig, J. F. *Acc. Chem. Res.* **2008**, *41*, 1534. (c) Surry, D. S.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 6338. (d) Buchwald, S. L.; Mauger, C.; Mignani, G.; Scholz, U. *Adv. Synth. Catal.* **2006**, *348*, 23. (e) Busacca, C. A.; Fandrick, D. R.; Song, J. J.; Senanayake, C. H. *Adv. Synth. Catal.* **2011**, *353*, 1825. (f) Surry, D. S.; Buchwald, S. L. *Chem. Sci.* **2011**, *2*, 27.

(3) (a) Guram, A. S.; Rennels, R. A.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **1995**, *34*, 1348. (b) Louie, J.; Hartwig, J. F. *Tetrahedron Lett.* **1995**, *36*, 3609.

(4) (a) Shen, Q.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 10028. (b) Surry, D. S.; Buchwald, S. L. *J. Am. Chem. Soc.* **2007**, *129*, 10354. (c) Vo, G. D.; Hartwig, J. F. *J. Am. Chem. Soc.* **2009**, *131*, 11049. (d) Schulz, T.; Torborg, C.; Enthaler, S.; Schäffner, B.; Dumrath, A.; Spannenberg, A.; Neumann, H.; Börner, A.; Beller, M. *Chem. Eur. J.* **2009**, *15*, 4528. (e) Lundgren, R. J.; Sappong-Kumankumah, A.; Stradiotto, M. *Chem. Eur. J.* **2010**, *16*, 1983. (f) Dumrath, A.; Lübbe, C.; Neumann, H.; Jackstell, R.; Beller, M. *Chem. Eur. J.* **2011**, *17*, 9599. (g) Tsvelikhovsky, D.; Buchwald, S. L. *J. Am. Chem. Soc.* **2011**, *133*, 14228.

(5) Lundgren, R. J.; Peters, B. D.; Alsabeh, P. G.; Stradiotto, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 4071.

(6) Alsabeh, P. G.; Lundgren, R. J.; Longobardi, L. E.; Stradiotto, M. *Chem. Commun.* **2011**, *47*, 6936.

(7) Lundgren, R. J.; Stradiotto, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 8686.

(8) Hesp, K. D.; Lundgren, R. J.; Stradiotto, M. *J. Am. Chem. Soc.* **2011**, *133*, 5194.

(9) For a recent review detailing the development and application of Mor-DalPhos, see: Lundgren, R. J.; Hesp, K. D.; Stradiotto, M. *Synlett* **2011**, 2443.

(10) (a) Avaro, E.; Hartwig, J. F. *J. Am. Chem. Soc.* **2009**, *131*, 7858. (b) Shen, Q.; Hartwig, J. F. *Org. Lett.* **2008**, *10*, 4109. (c) Fernández-Rodríguez, M. A.; Shen, Q.; Hartwig, J. F. *Chem. Eur. J.* **2006**, *12*, 7782. (d) Shen, Q.; Shekhar, S.; Stambuli, J. P.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **2005**, *44*, 1371.

(11) (a) Selected crystallographic data for **1**·CH_2Cl_2: empirical formula, $C_{45}H_{53}BrCl_2NOPPd$; formula weight, 912.06; crystal dimensions (mm^3), 0.48 × 0.17 × 0.09; crystal system, orthorhombic; space group, $P2_12_12_1$; a (Å), 10.9036(3); b (Å), 14.6554(4); c (Å), 25.5143(6); V (Å^3), 4077.10(18); Z, 4; ρ_{calcd} (g cm^{-3}), 1.486; μ (mm^{-1}), 1.641; 2θ limit (deg), 55.02 with $-14 \le h \le 14$, $-19 \le k \le 19$, $-33 \le l \le 33$; total data collected, 37 022; independent reflections, 9345; R_{int} = 0.0198; observed reflections, 9018; range of transmission, 0.8610−0.5088; data/restraints/parameters, 9345/0/478; R1 ($F_o^2 \ge 2\sigma(F_o^2)$), 0.0282; wR2 ($F_o^2 \ge 3\sigma(F_o^2)$), 0.0849; goodness of fit, 1.076; largest peak, hole (e Å^{-3}), 1.108, −0.753. (b) Selected crystallographic data for **3**·OEt_2: empirical formula, $C_{49}H_{61}F_3NO_5PSPd$; formula weight, 970.42; crystal dimensions (mm^3), 0.47 × 0.38 × 0.14; crystal system, monoclinic; space group, $P2_1/n$; a (Å), 10.7231(8); b (Å), 16.1892(12); c (Å), 26.826(2); β (deg), 105.5094(9); V (Å^3), 4487.4(6); Z, 4; ρ_{calcd} (g cm^{-3}), 1.436; μ (mm^{-1}), 0.556; 2θ limit (deg), 55.40 with $-13 \le h \le 13$, $-0 \le k \le 21$, $0 \le l \le 34$; total data collected, 11 664; independent reflections, 11 664; observed reflections, 10 624; range of transmission, 0.9252−0.7812; Ddata/restraints/parameters, 11 664/4/583; R1 ($F_o^2 \ge 2\sigma(F_o^2)$), 0.0481; wR2 ($F_o^2 \ge 3\sigma(F_o^2)$), 0.1239; goodness of fit, 1.145; largest peak, hole (e Å^{-3}), 1.992, −0.790.

(12) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

(13) We do not anticipate that the diminished performance of the Mor-DalPhos/Pd catalyst system in the monoarylation of ammonia when using Ar*Br in comparison to (for example) PhBr is attributable to the C−N reductive elimination step, given that the more sterically demanding Ar* group should promote reductive elimination in a putative intermediate of the type [(κ^2-*P,N*-Mor-DalPhos)Pd(NH_2)(aryl)]. Nonetheless, we are currently conducting an in-depth kinetic study regarding the Mor-DalPhos/Pd catalyzed monoarylation of ammonia with (hetero)aryl (pseudo)halides, including analyses of the rates of C−X oxidative addition and C−N reductive elimination; we will report on these studies elsewhere.

(14) Compound **6** was formed as a single isomer on the basis of NMR spectroscopic data. The stereochemistry assigned for **6** is given by analogy with the crystallographically characterized analogue [(κ^2-*P,P*-JosiPhos)Pd(Br)(Ph)], which features Br trans to the PCy_2 group: Roy, A. H.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 8704.

(15) Mitchell, E. A.; Baird, M. C. *Organometallics* **2007**, *26*, 5230.

(16) (a) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876. (b) Flack, H. D.; Bernardinelli, G. *Acta Crystallogr.* **1999**, *A55*, 908. (c) Flack, H. D.; Bernardinelli, G. *J. Appl. Crystallogr.* **2000**, *33*, 1143.