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An Examination of the Palladium/Mor-DalPhos Catalyst System in the Context of Selective Ammonia Monoarylation at Room Temperature**

Pamela G. Alsabeh,[a] Rylan J. Lundgren,[a] Robert McDonald,[b] Carin C. C. Johansson Seechurn,[c] Thomas J. Colacot,[d] and Mark Stradiotto*[a]

Abstract: An examination of the [{Pd(cinnamyl)Cl}$_2$]/Mor-DalPhos (Mor-DalPhos = di(1-adamantyl)-2-morpholinophenylphosphine) catalyst system in Buchwald–Hartwig aminations employing ammonia was conducted to better understand the catalyst formation process and to guide the development of precatalysts for otherwise challenging room-temperature ammonia monoarylations. The combination of [{Pd(cinnamyl)Cl}$_2$] and Mor-DalPhos afforded [(κ^2-*P,N*-Mor-DalPhos)Pd(η^1-cinnamyl)Cl] (**2**), which, in the presence of a base and chlorobenzene, generated [(κ^2-*P,N*-Mor-DalPhos)Pd(Ph)Cl] (**1a**). Halide abstraction from **1a** afforded [(κ^3-*P,N,O*-Mor-DalPhos)Pd(Ph)]OTf (**5**), bringing to light a potential stabilizing interaction that is offered by Mor-DalPhos. An examination of [(κ^2-*P,N*-Mor-DalPhos)Pd(aryl)Cl] (**1b–f**) and related precatalysts for the coupling of ammonia and chlorobenzene at room temperature established the suitability of **1a** in such challenging applications. The scope of reactivity for the use of **1a** (5 mol%) encompassed a range of (hetero)aryl (pseudo)halides (X = Cl, Br, I, OTs) with diverse substituents (alkyl, aryl, ether, thioether, ketone, amine, fluoro, trifluoromethyl, and nitrile), including chemoselective arylations.

Keywords: amination · anilines · N,P ligands · palladium · precatalysts

Introduction

The construction of carbon–carbon and carbon–heteroatom bonds has been facilitated in recent years by the development of efficient palladium-catalyzed cross-coupling protocols.[1] Notably, C–C bond-forming methods of this type were recognized by the awarding of the 2010 Nobel Prize for Chemistry for research in this area.[2] Closely related C–N bond-forming techniques (i.e., Buchwald–Hartwig amination (BHA)) have also gained prominence in both academic and industrial settings as a means of synthesizing (hetero)aryl amine derivatives that would otherwise be difficult to prepare.[1c,d,3] Advances in palladium-catalyzed cross-coupling chemistry, including BHA, have been achieved largely through the design and implementation of ancillary ligands,[4] most notably sterically hindered and strongly σ-donating monophosphines[5] or bisphosphines,[6] as well as N-heterocyclic carbenes.[7] Collectively, these efforts have enabled a broad range of (hetero)aryl (pseudo)halide and amine substrate pairings to be coupled successfully. Despite the significant progress that has been made with regard to the development of highly effective ligands/catalysts for the BHA of primary and secondary amines,[8] only a select few catalyst systems have proven useful in the monoarylation of ammonia (see below).[9] Challenges associated with the use of ammonia as a substrate include: catalyst deactivation through ammonia-induced ligand displacement; slow C–N bond reductive elimination from sterically unencumbered parent amido intermediates of the type [L$_n$Pd(aryl)(NH$_2$)] or catalyst inhibition by the formation of dinuclear amino-bridged variants of such intermediates; and uncontrolled polyarylation of the product aniline derivatives.[9] Significant progress has been made with regard to the development of copper catalysts for ammonia monoarylation,[9b–d] with the more successful systems containing carbonyl-based ancillary ligands such as L-proline,[10] 2,4-pentadione,[11] or a 2-pyridinyl-β-ketone.[12] Nonetheless, copper-based catalyst systems often exhibit a number of limitations, such as the need for high catalyst loadings and temperatures, and poor performance with (hetero)aryl chloride and pseudohalide substrates.[13] In this regard, palladium-based catalysts currently offer optimal performance for the monoarylation of ammonia.

The research groups of Hartwig,[6c,14] Buchwald,[15] and Beller[16] have made important contributions toward the de-

[a] P. G. Alsabeh, Dr. R. J. Lundgren, Prof. Dr. M. Stradiotto
Department of Chemistry, Dalhousie University
6274 Coburg Road, PO Box 15000
Halifax, Nova Scotia B3H 4R2 (Canada)
Fax: (+1) 902-494-7190
E-mail: mark.stradiotto@dal.ca

[b] Dr. R. McDonald
X-Ray Crystallography Laboratory, Department of Chemistry
University of Alberta, Edmonton, Alberta T6G 2G2 (Canada)

[c] Dr. C. C. C. Johansson Seechurn
Johnson Matthey Catalysis and Chiral Technologies
Orchard Road, Royston SG8 5HE (UK)

[d] Dr. T. J. Colacot
Johnson Matthey Catalysis and Chiral Technologies
2001 Nolte Drive, West Deptford, New Jersey 08066 (USA)

[**] Mor-DalPhos = di(1-adamantyl)-2-morpholinophenylphosphine.

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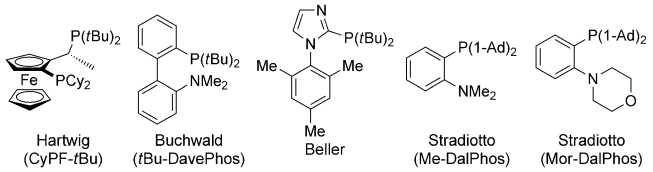
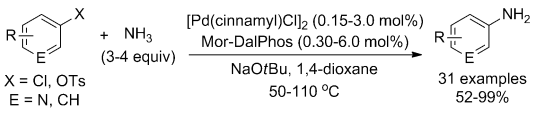


Figure 1. Important ligands for selective monoarylation in the BHA of (hetero)aryl (pseudo)halides and ammonia.



Scheme 1. Pd-catalyzed monoarylation of ammonia by using [{Pd(cinnamyl)Cl}$_2$]/Mor-DalPhos precatalyst mixtures.

velopment of useful BHA protocols for the selective monoarylation of ammonia (Figure 1). Hartwig et al.[6c,14a] utilized the bulky bisphosphine ligand JosiPhos (CyPF-*t*Bu)[17] in conjunction with the palladium precursor [Pd{P(*o*-tol)$_3$}$_2$][18] for the monoarylation of ammonia with a variety of aryl halides and sulfonates ($\geq$50 °C). Limitations of CyPF-*t*Bu-based catalysts include substrate-scope challenges with respect to the monoarylation of electronically deactivated and sterically unhindered aryl chloride substrates, the frequent requirement of relatively high reaction temperatures, and, in some cases, the need for high pressures of ammonia. CyPF-*t*Bu-based catalysts have subsequently been applied to the tandem ammonia coupling/alkyne amination reactions with 2-bromoarylacetylenes to generate NH-indoles.[19]

The biaryl monophosphine ligand *t*Bu-DavePhos (Figure 1) has been employed in the BHA of ammonia (80–120 °C).[15] Although only four examples of isolable monoarylation products were featured in the initial report from Surry and Buchwald,[15a] it was subsequently demonstrated that *t*Bu-DavePhos-based catalysts can be employed in Pd-catalyzed ammonia cross-couplings leading to dibenzodiazepines and related biologically active heterocycles.[15b] Beller and co-workers have also reported that 2-phosphino-*N*-arylimidazole based monophosphines are capable of supporting active palladium catalysts for the monoarylation of ammonia; however, high temperatures (120–140 °C) and elevated pressures (10 bar of N_2) were required to achieve optimal reactivity.[16a]

In 2010, we disclosed a new class of P,N-phenylene "DalPhos" ligands.[20] The design of these heterobidentate ligands was intended to provide a middle ground between traditionally employed monophosphine ligands and chelating bisphosphine ligands.[20b] The Me-DalPhos ligand (Figure 1), as well as the P(*t*Bu)$_2$ variant, were found to be broadly useful in BHA chemistry that employs primary and secondary amines, and to a limited extent, ammonia.[20a] Whereas both high yields and good monoarylation selectivity were achieved with *ortho*-substituted aryl chlorides, poor selectivity was achieved with alternative classes of aryl chloride substrates. In the pursuit of a ligand that would address these substrate scope limitations, Mor-DalPhos (Figure 1) proved to be highly effective in challenging ammonia monoarylation reactions employing both aryl chlorides and tosylates.[21] In using [{Pd(cinnamyl)Cl}$_2$]/Mor-DalPhos precatalyst mixtures, electron-rich, electron-poor, and heterocyclic products of ammonia monoarylation were prepared (50–110 °C) in high isolated yields (Scheme 1). Mor-DalPhos has also been found to be useful in facilitating the Pd-catalyzed monoarylation of hydrazine,[22] acetone,[23] and other carbonyl compounds[24] in chemoselective[25] and aqueous BHA chemistry,[26] as well as in the Au-catalyzed hydroamination of internal alkynes with dialkylamines.[27] Whereas the room-temperature BHA of aryl chlorides with ammonia was not successful when using [{Pd(cinnamyl)Cl}$_2$]/Mor-DalPhos precatalyst mixtures, unprecedented room-temperature transformations of a small number of aryl chlorides were achieved with good monoarylation selectivity by use of the chlorobenzene oxidative addition product [(κ^2-*P*,*N*-Mor-DalPhos)Pd(Ph)Cl] (**1a**) as a precatalyst. Encouraged by this latter observation, we have undertaken a more thorough investigation of the Pd/Mor-DalPhos catalyst system in the context of ammonia monoarylation under mild conditions in an effort to better understand what underpins this unique catalytic reactivity.

Herein, we report the results of these investigations, which included stoichiometric reactivity studies directed toward understanding the catalyst formation process and the binding modes of the Mor-DalPhos ligand. We also report on our analysis of the influence of the palladium source on the efficiency with which putative catalytic intermediates are generated, and the influence of varying the Pd-aryl group in precatalysts of the type [(κ^2-*P*,*N*-Mor-DalPhos)Pd(aryl)Cl] on catalytic performance. Synthetic studies establishing the expanded room-temperature substrate scope of ammonia monoarylations encompassing a range of (hetero)aryl (pseudo)halides (X = Cl, Br, I, OTs) with a diversity of substituents (alkyl, aryl, ether, thioether, ketone, amine, fluoro, trifluoromethyl, and nitrile) are also disclosed.

Results and Discussion

In our initial development of ammonia monoarylation chemistry at elevated temperatures (50–110 °C), we found [{Pd(cinnamyl)Cl}$_2$] to be a suitable palladium source.[21] In an effort to better understand the factors that might enable the BHA of ammonia at room temperature with a broad substrate scope, we conducted a reactivity survey in which several Pd^0 and Pd^{II} reagents were treated with Mor-DalPhos (and NaO*t*Bu in the case of chloride or acetate precursors[28]) at room temperature for 0.25 h, followed by the addition of chlorobenzene and heating at 65 °C for 3 h (Figure 2). In doing so we sought to indirectly measure the amount of the putative Mor-DalPhos/Pd^0 species that formed after 0.25 h at room temperature by detecting the

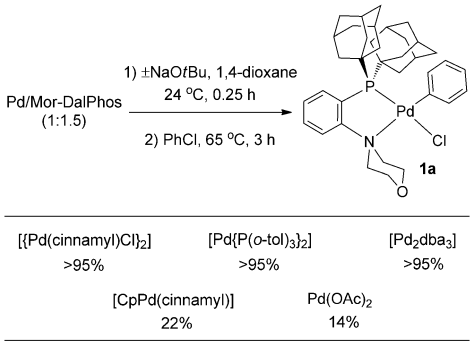
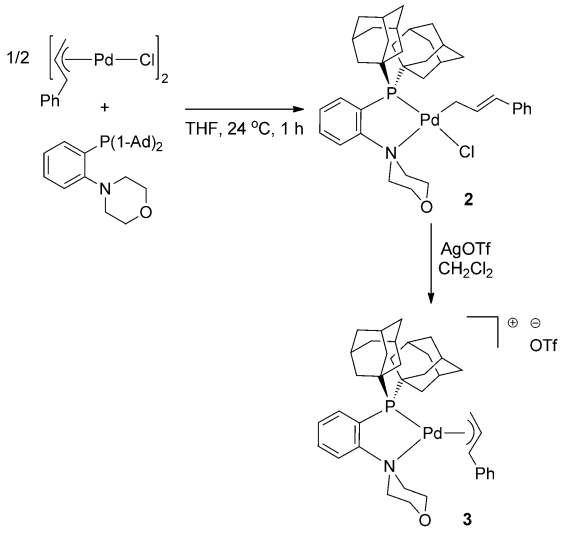


Figure 2. Survey of palladium sources for the in situ generation of a putative (Mor-DalPhos)/Pd^0 species. General conditions: Pd source (5 mol% Pd), Mor-DalPhos (7.5 mol%), NaO*t*Bu (2 equiv for chloride or acetate precursors), 1,4-dioxane (0.5 M), PhCl (1.0 equiv), followed by the addition of CH_2Cl_2. Yields determined on the basis of ^{31}P NMR analysis with $PMes_3$ as an internal standard. dba = dibenzylideneacetone.



Scheme 2. Synthesis of Pd/Mor-DalPhos complexes featuring η^1- or η^3-cinnamyl coordination.

appearance of the presumed oxidative addition catalytic intermediate [(κ^2-*P,N*-Mor-DalPhos)Pd(Ph)Cl] (**1a**). An authentic sample of **1a** was prepared in 93% yield (isolated product) by heating [CpPd(allyl)] and Mor-DalPhos in a mixture of chlorobenzene and THF at 65 °C for 18 h. Solution NMR data support the identity of **1a** as the expected square-planar complex in which Mor-DalPhos is bound to Pd in a κ^2-P,N bidentate fashion, as suggested by the observation of diastereotopic morpholino resonances. The structure of **1a** was also confirmed by the use of single-crystal X-ray diffraction techniques (see below).

Less than 25% conversion to **1a** was observed when using either [CpPd(cinnamyl)][29] or $Pd(OAc)_2$ under the room temperature activation conditions employed, whereas the use of [$Pd_2(dba)_3$], [Pd{P(*o*-tol)$_3$}$_2$], or [{Pd(cinnamyl)Cl}$_2$] afforded high yields of the target complex **1a**. Altering the duration of the first room-temperature activation step of the reaction (5–30 min) resulted in negligible variation of the amount of **1a** that formed for all palladium sources examined. Given the potential inhibiting effect of dba and P(*o*-tol)$_3$ under catalytic conditions, we concluded that [{Pd(cinnamyl)Cl}$_2$] was the palladium source of choice for this application.[30]

Encouraged by the diversity of reports highlighting the reactivity benefits that can be derived from the use of preformed palladium–ligand complexes in BHA chemistry,[6c,d,7d,31] we turned our attention to preparing precatalysts featuring Mor-DalPhos. In particular, we were interested in preparing adducts derived from [{Pd(cinnamyl)Cl}$_2$], as well as Pd/Mor-DalPhos-containing species that are of relevance to room temperature BHA chemistry involving ammonia. We began our study by determining the identity of the species formed in the precatalyst mixture. Combining Mor-DalPhos (2 equiv) with [{Pd(cinnamyl)Cl}$_2$] in THF afforded the [(κ^2-*P,N*-Mor-DalPhos)Pd(η^1-cinnamyl)Cl] complex (**2**) as an analytically pure yellow solid that was isolated in 92% yield (Scheme 2). The features of the cinnamyl ^1H NMR resonances of **2** are consistent with the proposed η^1 formulation, with the two alkenyl protons appearing at 6.80 and 6.39 ppm, and the resonance for the benzylic Pd–CH_2 group appearing at 3.61 ppm.[32] The solution η^1-cinnamyl structure proposed for **2** on the basis of NMR data was further substantiated through a single-crystal analysis of the yellow crystalline material that was grown from the bulk isolated solid (Figure 3); selected metrical parameters for **2** and each of the other crystallographically characterized compounds reported herein are collected in Table 1. Indeed, the presence of an η^1-cinnamyl ligand in the solid-state structure of **2** is immediately evident, with the C(1)–C(2) (1.466(5) Å), C(2)–C(3) (1.336(5) Å), and C(3)–C(4) (1.465(5) Å) distances in keeping with single, double, and single bonds, respec-

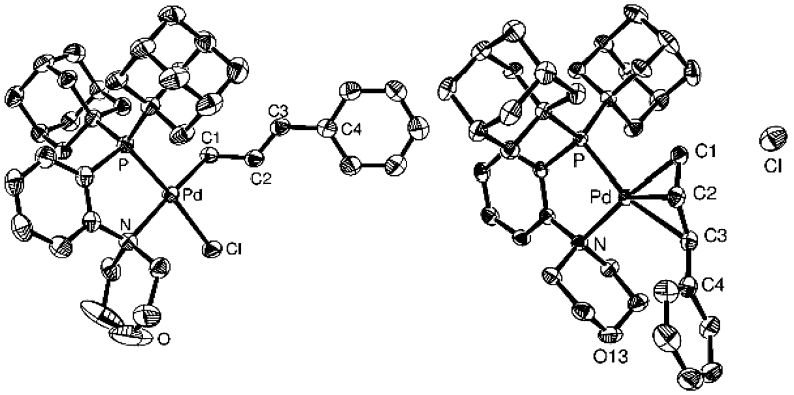


Figure 3. ORTEP diagrams of **2** (left) and **2′**·CH_2Cl_2·H_2O (right) shown with 50% displacement ellipsoids. All hydrogen atoms and solvate molecules have been omitted for clarity.

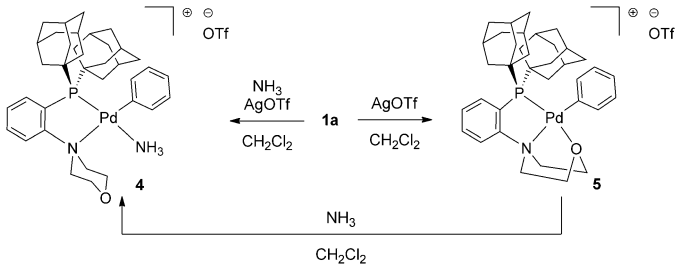
Table 1. Selected interatomic distances [Å] for the crystallographically characterized complexes.

	Pd–P	Pd–N	Pd–Cl	Pd–C_{aryl}	P–C_{aryl}	N–C_{aryl}
1a	2.2563(7)	2.253(2)	2.3873(7)	2.001(3)	1.831(3)	1.468(3)
1b	2.2572(5)	2.2260(16)	2.3818(5)	2.000(2)	1.840(2)	1.468(3)
1d	2.2625(7)	2.230(2)	2.3832(7)	2.005(3)	1.836(3)	1.478(3)
1e	2.2591(7)	2.214(2)	2.3735(7)	1.990(3)	1.838(3)	1.467(4)
2[a]	2.2357(9)	2.261(3)	2.3952(9)	–	1.840(4)	1.464(4)
2′[b]	2.2666(4)	2.2625(14)	–	–	1.8375(17)	1.479(2)
3[c]	2.2774(16)	2.212(5)	–	–	1.829(6)	1.476(7)
4[d]	2.2733(4)	2.2138(16)	–	2.0009(17)	1.8335(16)	1.474(2)
5[e]	2.2207(8)	2.116(2)	–	2.001(3)	1.859(3)	1.463(4)
5[f]	2.2188(8)	2.110(2)	–	2.008(3)	1.848(3)	1.460(4)

[a] Pd–C(1) 2.074(3); C(1)–C(2) 1.466(5); C(2)–C(3) 1.336(5); C(3)–C(4) 1.465(5). [b] Pd–C(1) 2.0951(17); Pd–C(2) 2.2432(17); Pd–C(3) 2.5100(18); C(1)–C(2) 1.418(3); C(2)–C(3) 1.374(3); C(3)–C(4) 1.470(3). [c] Pd–C(11) 2.053(6); Pd–C(12) 2.249(6); Pd–C(13) 2.580(7); C(11)–C(12) 1.420(9); C(12)–C(13) 1.377(10); C(13)–C(14) 1.458(9). [d] Pd–N(1) (minor disorder component) 2.215(6); N–C_{aryl} (minor disorder component) 1.470(7); Pd–N(2) 2.1308(15). [e] Pd–O 2.227(2). [f] Within the second crystallographically independent molecule of **5**; Pd–O 2.228(2).

tively. Interestingly, on being left to stand, a minute quantity of red crystalline material formed from the same mother liquor that afforded the yellow single crystals of **2**. Single-crystal X-ray analysis enabled the identification of this red material as [(κ^2-*P,N*-Mor-DalPhos)Pd(η^3-cinnamyl)]Cl (**2′**), the cationic η^3-cinnamyl isomer of **2** featuring an outer-sphere chloride counteranion (Figure 3). The analogous triflate complex [(κ^2-*P,N*-Mor-DalPhos)Pd(η^3-cinnamyl)]OTf (**3**, Scheme 2) was prepared by treatment of **2** with AgOTf and was isolated as an analytically pure solid in 98% yield. The observation of four distinct allylic-type resonances in the ^{1}H NMR spectrum of **3** is in keeping with an η^3-cinnamyl coordination mode in solution, which in turn was confirmed in the solid state on the basis of single-crystal X-ray-diffraction data (see the Supporting Information). Each of **2′** and **3** exhibit an unsymmetrically bound η^3-cinnamyl ligand in the solid state, with the Pd–CH_2 distance being significantly shorter than the other two Pd–C distances in each complex (Table 1). The facile and clean formation of **2**, and the observation that both **2** and **2′** can be produced from the same crystallization solution, suggest that these isomeric complexes represent the products that are formed initially when combining Mor-DalPhos and [{Pd(cinnamyl)Cl}$_2$] during catalyst pre-activation. Although complexes **2** and **3** proved incapable of catalyzing room-temperature BHA chemistry involving ammonia and chlorobenzene (see below), these precatalysts did effectively mediate the transformation at elevated temperature (3 mol% Pd, 110°C, 1 h), achieving full conversion with high monoarylation selectivity.

Ancillary ligand displacement by ammonia represents a challenge that must be overcome when using ammonia as a substrate. In this regard, we became interested in examining the behavior of Mor-DalPhos within a putative catalytic intermediate (**1a**) upon exposure to excess ammonia. Exposure of **1a** to 2–10 equivalents of ammonia in 1,4-dioxane afforded no discernible reaction when monitored by ^{31}P NMR techniques, suggesting that the Mor-DalPhos ligand is neither hemilabile nor completely displaced under these conditions. In probing the coordination chemistry of **1a** further, we were successful in preparing the cationic ammine adduct **4** upon treatment of **1a** with AgOTf in the presence of excess ammonia (Scheme 3); complex **4**·CH_2Cl_2 was isolated



Scheme 3. Reactivity of the oxidative addition product **1a** under halide abstraction conditions.

as an analytically pure solid in 90% yield. The ammine resonance in **4** is clearly visible among the adamantyl signals in the ^{1}H NMR spectrum of **4** and the ammine signal does not disappear upon prolonged exposure of the sample to vacuum. Single crystals of **1a**·CH_2Cl_2 and **4**·CH_2Cl_2 were grown successfully from the isolated material and were subjected to X-ray diffraction analysis (Figure 4). The solid-state structural data obtained for **1a** and **4** are consistent

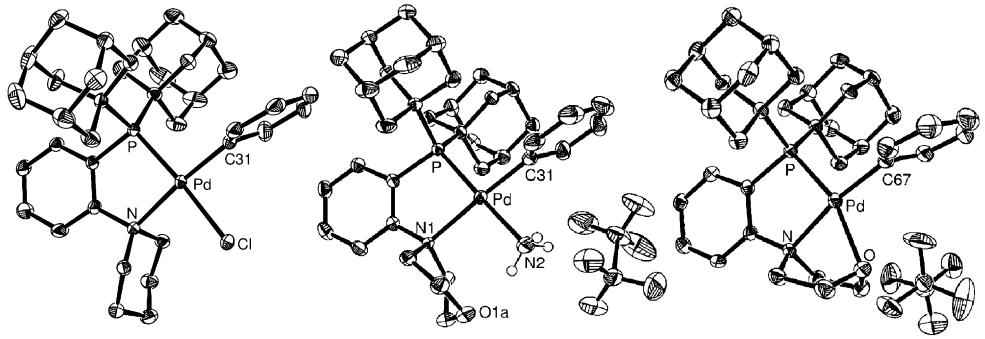


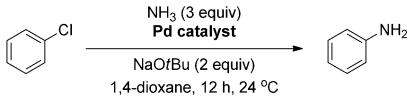
Figure 4. ORTEP diagrams of **1a**·CH_2Cl_2 (left), **4**·CH_2Cl_2 (middle) and **5** (right) shown with 50% displacement ellipsoids. All hydrogen atoms and solvate molecules have been omitted for clarity.

with the solution-NMR characterization data obtained for these compounds, and in the case of **1a**, reveal the expected *trans*-disposition of chloride and phosphine ligands within a κ^2-*P,N*-Mor-DalPhos complex, which is in keeping with the relative *trans*-directing ability of phosphorus relative to nitrogen. Preliminary efforts to generate a [(Mor-DalPhos)Pd(Ph)(NH_2)] intermediate were carried out, in which **4** was treated with $NaN(TMS)_2$ at room temperature. ^{31}P NMR data obtained from the resulting mixture indicated the formation of multiple phosphorus-containing species, including free Mor-DalPhos. Performing the same reaction in the presence of chlorobenzene resulted in the regeneration of **1a** (as indicated by ^{31}P NMR spectroscopy) in the absence of detectable intermediates.

Interestingly, in carrying out halide abstraction from **1a** using AgOTf in the absence of ammonia, the clean formation of a single product (**5**) was indicated in the ^{31}P NMR spectrum (Scheme 3). Solution ^1H NMR data served to establish the presence of both Mor-DalPhos and phenyl groups within this new complex, and X-ray diffraction analysis enabled the tridentate connectivity within [(κ^3-*P,N,O*-Mor-DalPhos)Pd(Ph)]OTf (**5**) to be determined (Figure 4). Complex **5** exhibits a distorted square-planar geometry in which the oxygen donor has taken the former coordination site of the abstracted chloride. The structure of **5** confirms the ability of the Mor-DalPhos ligand to respond to a reduction in coordination number at Pd through the provision of a third ligating group. It is perhaps feasible that in alternative catalytic settings, by employing reagents with more labile leaving groups (e.g., aryl sulfonates), the tridentate κ^3-P,N,O ligation of the Mor-DalPhos ligand might represent an important stabilizing interaction during catalysis. The lability of the oxygen donor in **5** was confirmed by the clean formation of **4** upon exposure of **5** to ammonia (3 equiv) after stirring at room temperature for 3 h.

In considering the likely intermediacy of oxidative addition complexes of the type [(κ^2-*P,N*-Mor-DalPhos)Pd(Ar)Cl] in the BHA of (hetero)aryl chlorides (Ar = aryl or heteroaryl) with ammonia in the presence of Pd/Mor-DalPhos catalysts, we sought to evaluate in more detail the utility of these and related complexes as precatalysts for otherwise challenging room temperature ammonia arylation reactions. Remarkably, the use of 5 mol% of **1a** at room temperature allowed a >90% conversion of chlorobenzene and 76% GC yield of aniline after 12 h (Table 2, entry 1); similar results were achieved when using the ammine adduct **4** (Table 2, entry 2). In employing either [{Pd(cinnamyl)Cl}$_2$]/Mor-DalPhos mixtures (Table 2, entry 3) or the related preformed complexes **2** or **3** (Table 2, entries 4 and 5), both a low conversion of the chlorobenzene and poor yields (<25%) of the target aniline were obtained. [Pd{P(*o*-tol)$_3$}$_2$]/CyPF-*t*Bu, which has been employed successfully in the BHA of ammonia at elevated temperatures,[14a] and the oxidative addition complex [(CyPF-*t*Bu)Pd(Ph)Cl] (by analogy with **1a**)[14b] both performed poorly under the room temperature conditions employed, affording less than 20% GC yield of aniline (Table 2, entries 6 and 7).

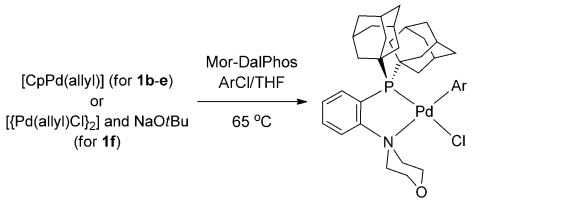
Table 2. Catalyst screening for the room temperature ammonia arylation with chlorobenzene.[a]



Entry	Pd cat. (5 mol%)	GC conv. [%][b]	GC yield [%][b]
1	[(M-DP)Pd(Ph)Cl] (**1a**)	91	76
2	[(M-DP)Pd(Ph)NH_3]OTf (**4**)	84	75
3	[{Pd(cinnamyl)Cl}$_2$]/M-DP	30	23
4	[(M-DP)Pd(cinnamyl)Cl] (**2**)	22	14
5	[(M-DP)Pd(cinnamyl)]OTf (**3**)	30	22
6	[Pd{P(*o*-tol)$_3$}$_2$]/CyPF-*t*Bu	23	15
7	[(CyPF-*t*Bu)Pd(Ph)Cl]	14	13
	[(M-DP)Pd(Ar)Cl]		
8	Ar = 4-PhOMe (**1b**)	64	53
9	Ar = 4-PhMe (**1c**)	84	68
10	Ar = 2-PhMe (**1d**)	90	76
11	Ar = 4-PhCF$_3$ (**1e**)	68	58
12	Ar = 3-pyridyl (**1f**)	82	73

[a] General conditions: Pd source (5 mol%; plus 7.5 mol% ligand for entries 3 and 6), NaO*t*Bu (2 equiv), PhCl (1.0 equiv), 1,4-dioxane (0.1 M); M-DP = Mor-DalPhos. [b] Conversions and yields were determined on the basis of calibrated GC data with dodecane as the internal standard.

Having identified **1a** as being a suitable precatalyst for the BHA of ammonia with chlorobenzene at room temperature, we then sought to evaluate the possible impact of altering the aryl group within precatalyst **1a** on the catalytic performance. A set of [(κ^2-*P,N*-Mor-DalPhos)Pd(Ar)Cl] derivatives with 4-OMe (**1b**), 4-Me (**1c**), 2-Me (**1d**), and 4-CF_3 (**1e**) substitution was successfully prepared and isolated, starting from [CpPd(allyl)] in a manner similar to that employed for the synthesis of the parent phenyl complex **1a** (Scheme 4). Although attempts to synthesize the 3-pyridyl



Ar = 4-anisolyl (**1b**, 79%)
Ar = 4-tolyl (**1c**, 66%)
Ar = 2-tolyl (**1d**, 75%)
Ar = 4-trifluoromethylphenyl (**1e**, 80%)
Ar = 3-pyridyl (**1f**, 90%)

Scheme 4. Synthesis of oxidative addition complexes of the type [(κ^2-*P,N*-Mor-DalPhos)Pd(Ar)Cl] with variation of the aryl group.

variant **1f** by this protocol failed, the combination of [{Pd(allyl)Cl}$_2$], Mor-DalPhos, and NaO*t*Bu in a solution of THF/3-chloropyridine (2:1 by volume) generated the desired complex over the course of 3 h at 65 °C, thereby enabling the isolation of **1f** in 90% yield. The solution NMR characterization of **1b–f** was corroborated in the case of **1b**, **1d**, and **1e** by single-crystal X-ray diffraction data. The solid-state structures of **1b**, **1d**, and **1e** (Figure 5) feature

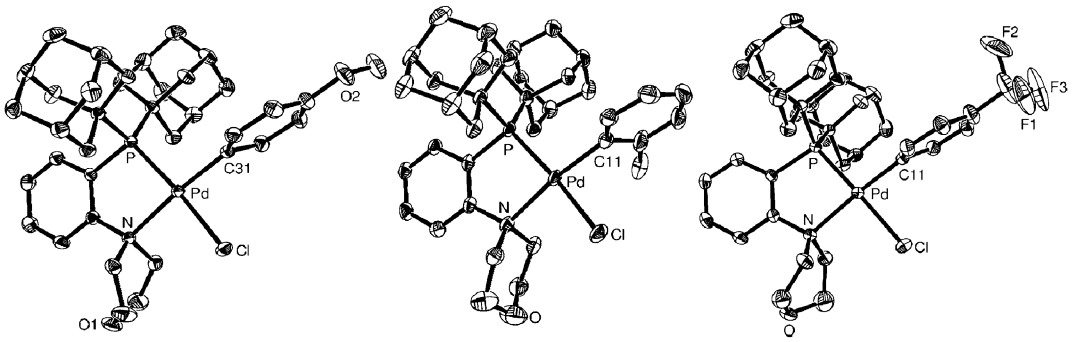


Figure 5. ORTEP diagrams of oxidative addition complexes **1b**·CH_2Cl_2 (left), **1d**·CH_2Cl_2 (middle), **1e**·CH_2Cl_2 (left) shown with 50% displacement ellipsoids. All hydrogen atoms and solvate molecules have been omitted for clarity.

the expected square-planar geometry and relative disposition of ligands around palladium, as was observed in **1a** (Figure 4).

Each of the complexes **1b–f** (5 mol% Pd) proved to be effective as precatalysts for the room temperature BHA of ammonia with chlorobenzene to give aniline (Table 2, entries 8–12). In comparing the performance of **1a** to that of **1b–f** in terms of the production of aniline, there is an inherent bias towards **1a** given that this precatalyst contains the parent phenyl ligand, which in turn can go on to form the target unsubstituted aniline product. In contrast, precatalysts **1b–f** feature (hetero)aryl ligands that generate the corresponding substituted anilines (for **1b–e**) or 3-aminopyridine (for **1f**) upon initial catalytic turnover, thereby leading to an artificially lower product yield (up to 5%) for these later precatalysts. This notwithstanding, it is apparent that the performance of precatalysts **1b** and **1e**, which feature electron-donating (4-anisolyl) and -withdrawing (4-trifluoromethylphenyl) Pd–aryl ligands respectively, is inferior to that of the parent complex **1a**, the tolyl variants **1c** and **1d**, and the 3-pyridyl precatalyst **1f**. Whereas the performance of precatalyst **1d** can possibly be viewed as being marginally better than that of **1a** in terms of the conversion to aniline in the room temperature test reaction that was employed (Table 2, entries 1 and 10), **1a** was deemed to be the favored precatalyst for this reaction on the basis of the higher-yielding synthesis of **1a** (93%) versus **1d** (75%).

The variation of some additional experimental parameters was examined in an effort to optimize reactivity. The use of 2 mol% **1a** as a precatalyst afforded only 27% conversion of chlorobenzene (cf. 91% conversion, 76% yield with 5 mol% **1a**; Table 2, entry 1), and when substituting NaO*t*Bu for alternative bases (K_3PO4, Cs_2CO_3, or lithium hexamethyl disilazane (LiHMDS)), the yield did not improve. Also, the use of 7.5 mol% **2** did not exceed the capabilities of **1a** at the 5 mol% loading level. Thus, the use of 5 mol% **1a** and NaO*t*Bu as the base was employed for examining the scope of reactivity.

A variety of aryl and heteroaryl halides and tosylates were accommodated under the room temperature ammonia-arylation conditions (Figure 6). Although good yields were obtained for the parent aniline (**6a**), the *ortho*-tolyl variant (**6d**), and the 4-CF_3 variant (**6e**), comparatively poor performances were observed under analogous conditions with the use of 4-chloroanisole, 4-chlorotoluene, and 3-chloropyridine (leading to **6b**, **6c**, and **6f**, respectively); either poor conversion or selectivity for the target aniline derivative was the source of difficulty. The ability of this catalyst system to accommodate aryl bromides and iodides was demonstrated in reactions leading to **6e**. In general, *ortho* substitution proved to be particularly favorable among the chloride substrates that were examined (**6d**, **6g**, **6h**, **6s**, **6u**, **6v**, and **6aa**), affording good to high isolated yields. Attempts to prepare **6v** from 1-bromonaphthalene achieved only 50% conversion, and thus resulted in a poor isolated yield. Chemoselective, room temperature ammonia-arylation reactions were successful for the formation of **6o** and **6p**, resulting in the desired ammonia-coupled products with high yields despite the presence of potentially competitive primary and secondary aniline functionalities. Further functional-group tolerance was established in the formation of anilines featuring fluoro (**6q–u**), benzyl ether (**6i**), thioether (**6n**), nitrile (**6j**), and ketone (**6k**) substituents. Nitrogen-containing heterocycles that were also tolerated in this chemistry include chloroquinolines (**6l**, **6aa**) and a pyrrolylphenyl substrate (**6z**). The demonstrated substrate scope was broadened further by use of a selection of aryl tosylates, which provided the corresponding anilines in yields ranging from 45-86% (**6a**, **6w–ab**). Although we routinely carried out reactions under inert-atmosphere conditions for convenience, we were pleased to observe that the prototypical reaction of chlorobenzene and ammonia could be executed without the use of a glovebox. The solid components NaO*t*Bu and **1a** were weighed out in air and placed under nitrogen, followed by addition of the reactants and 1,4-dioxane. Upon stirring the mixture at room temperature for 16 h, **6a** was generated in 81% yield on the basis of calibrated GC analysis.

Despite the broad efficacy of **1a** for catalyzing room temperature, ammonia-arylation reactions, some limitations in the substrate scope were identified. Notably, our efforts to extend the substrate scope to include alternative aryl chloride or tosylate substrates, including those featuring base-sensitive addenda (hydroxyl or ester substituents) or other heteroaryl chlorides (thiophene or benzodioxole), were un-

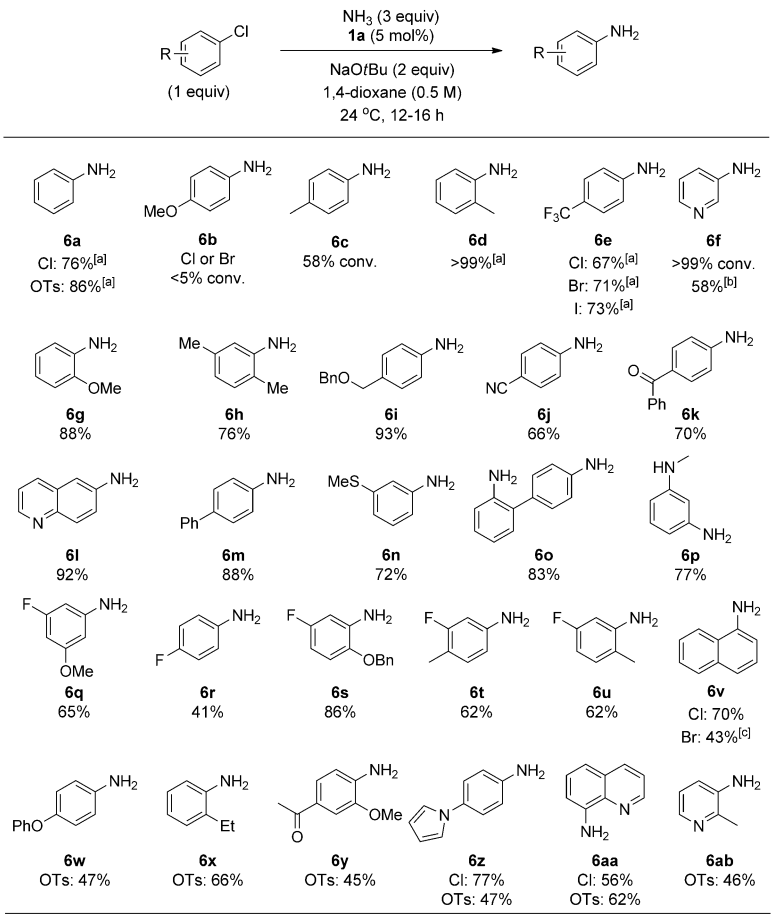


Figure 6. Room temperature cross-coupling of aryl halides and tosylates with ammonia. Conversions were determined by GC analysis and yields are of isolated material unless otherwise indicated. [a] Yields were determined on the basis of calibrated GC data with dodecane as the internal standard. [b] Yield was determined on the basis of ^{1}H NMR data. [c] Yield of the isolated product with approximately 50% conversion of ArBr was determined on the basis of GC analysis.

successful. In all cases, low yields of the product aniline derivative were observed due to either a lack of consumption of substrate or degradation of the starting material.

Conclusion

We have described our efforts to develop a more thorough understanding of the Pd/Mor-DalPhos catalyst system in the context of ammonia monoarylation under mild conditions. Stoichiometric reactivity studies established that the combination of [{Pd(cinnamyl)Cl}$_2$] and Mor-DalPhos (1:2) generates the adduct [(κ^2-*P,N*-Mor-DalPhos)Pd(η^1-cinnamyl)Cl] (**2**), which, upon treatment with base followed by the addition of chlorobenzene, affords the presumptive catalytic intermediate [(κ^2-*P,N*-Mor-DalPhos)Pd(Ph)Cl], **1a**. The lack of reactivity observed upon exposure of **1a** to an excess of ammonia suggests that the Mor-DalPhos ligand is neither hemilabile nor completely displaced under these conditions. Although treatment of **1a** with AgOTf in the presence of excess ammonia afforded the ammine adduct [(κ^2-*P,N*-Mor-DalPhos)Pd(Ph)NH$_3$]OTf (**4**), in the absence of ammonia the tridentate complex [(κ^3-*P,N,O*-Mor-DalPhos)Pd(Ph)]OTf (**5**) was obtained, thereby bringing to light the potential for Mor-DalPhos to stabilize low-coordinate catalytic intermediates. In surveying the catalytic abilities of these various Mor-DalPhos/Pd^{II} complexes for challenging ammonia monoarylation reactions conducted at room temperature, including a set of [(κ^2-*P,N*-Mor-DalPhos)Pd(Ar)Cl] derivatives (**1b–f**) featuring various substitution patterns on the Pd–aryl fragment, **1a** was identified as the optimal precatalyst. The scope of the room temperature ammonia monoarylation that was enabled through the use of **1a** (5 mol%) was found to encompass a range of (hetero)aryl (pseudo)halides (X = Cl, Br, I, OTs) with a diversity of substituents (alkyl, aryl, ether, thioether, ketone, amine, fluoro, trifluoromethyl, and nitrile). Although not exhaustively explored, the ability to conduct reactions of this type under benchtop conditions was also confirmed. Having established the Mor-DalPhos complex **1a** as an effective precatalyst for the challenging monoarylation of ammonia at room temperature, our current research efforts are focused on expanding our appreciation of the mechanistic subtleties of these transformations through a combination of experimental and computational techniques. We will report on the outcome of these studies, along with the results of our ongoing efforts to further optimize the DalPhos ligand architecture to enable challenging chemical transformations, in due course.

Experimental Section

General considerations: Unless otherwise noted, all manipulations were conducted under dinitrogen within an inert-atmosphere glovebox, utilizing 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. that was equipped with either one alumina-packed column and one column packed with copper-Q5 reactant (pentane), or two alumina-packed columns (dichlorometh-

ane). 1,4-Dioxane, THF, and diethyl ether were 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,[21] [CpPd(allyl)],[33] and [{Pd(cinnamyl)Cl}$_2$][34] were prepared according to literature procedures. Silver trifluoromethanesulfonate (Strem), JosiPhos (CyPF-*t*Bu; Solvias), and 0.5 M solutions of ammonia in 1,4-dioxane (Aldrich) were used as received. Ammonia cross-coupling reactions were best conducted with fresh bottles (<2 weeks after opening) of 0.5 M ammonia in 1,4-dioxane. ^{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). Column chromatography was carried out using Silicycle SiliaFlash 60 with particle size 40–63 μm (230–400 mesh). Conversions and yields based on gas chromatography data were corrected by calibration with internal standards of dodecane and product identity was confirmed on the basis of ^{1}H NMR spectroscopy and/or by comparison with authentic samples. 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. NMR data were acquired with the technical assistance of Dr. Michael Lumsden (NMR-3, Dalhousie University), and mass spectrometric data were acquired by Mr. Xiao Feng (Mass Spectrometry Laboratory, Dalhousie University). Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, BC (Canada) and Midwest Microlab, LLC, Indianapolis, IN (USA).

Crystallographic characterization details: Crystallographic data were obtained at 180(±2) K on a Nonius Kappa CCD diffractometer (for **2** and **2′**·CH_2Cl_2·H_2O) or at 193(±2) K (all others) on either a Bruker PLATFORM/SMART 1000 CCD diffractometer or a Bruker D8/APEX II CCD diffractometer, by using graphite-monochromated $Mo_{K\alpha}$ (λ = 0.71073 Å) radiation and 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 were supplied by the respective vendors. Absorption correction for **2** and **2′**·CH_2Cl_2·H_2O was carried out by using a semi-empirical method from equivalents, whereas Gaussian integration (face-indexing) was employed for all other samples. In the case of **5**, the values of the cell parameters (*a* approximately equal to *c*; β close to 90°) and the relatively high values of *R*1 and *wR*2 during early refinement cycles suggested that the data might be rotationally twinned. The twin law [0 0 1 0 −1 0 1 0 0] (90° rotation about the *b* axis) was derived by inspection and was applied during refinement using the *SHELXL-97* TWIN instruction. The refined value of the twin fraction (*SHELXL-97* BASF parameter) was 0.4541(5). The structures were solved by use of direct methods, with the exception of **1d**·CH_2Cl_2, **1e**·CH_2Cl_2, **3**·$CHCl_3$, and **5**, for which a Patterson search/structure expansion was employed. Refinements were carried out by the use of full-matrix least-squares procedures (on F^2) with R_1 based on F_o^2 $2\sigma(F_o^2)$ and wR_2 based on $F_o^2 \geq -3\sigma(F_o^2)$. For **5**, two crystallographically independent molecules were located in the asymmetric unit and were refined appropriately; an ORTEP diagram of only one of the two crystallographically independent molecules is presented in the text for clarity. In several cases, structural disorder was identified during the solution and refinement process and was modeled in a satisfactory manner (occupancy ratio given in parentheses). For **3**·$CHCl_3$, disorder in an adamantyl fragment (55:45) and in the triflate ion (70:30) was noted and the following distance restraints were applied to impose an idealized geometry upon the minor (30% occupancy) conformer of the disordered triflate ion: d(S1B–C50B) = 1.75(1) Å; d(S1B–O2B) = d(S1B–O3B) = d(S1B–O4B) = 1.45(1) Å; d(F1B–C50B) = d(F2B–C50B) = d(F3B–C50B) = 1.35(1) Å; d(S1B···F1B) = d(S1B···F2B) = d(S1B···F3B) = 2.60(1) Å; d(F1B···F2B) = d(F1B···F3B) = d(F2B···F3B) = 2.10(1) Å; d(O2B···O3B) = d(O2B···O4B) = d(O3B···O4B) = 2.45(1) Å. In the case of **1b**·CH_2Cl_2 and **1e**·CH_2Cl_2, the disordered morpholino fragments were treated successfully by using a two-position (55:45 and 50:50, respectively) disorder model; the latter structure also featured a disordered trifluoromethyl group (80:20). In the case of **1e**·CH_2Cl_2, the F–C distances within the rotationally disordered trifluoromethyl group were fixed during refinement: d(F1A–C17) = d(F2A–C17) = d(F3A–C17) = d(F1B–C17) = d(F2B–C17) = d(F3B–C17) = 1.35(2) Å. Additionally, F–F distances involving the minor (20%) conformer of this CF_3 group were fixed: d(F1B···F2B) = d(F1B···F3B) = d(F2B···F3B) = 2.20(2) Å. Furthermore, within **1d**·CH_2Cl_2, the following pairs of distances within the disordered morpholino group were constrained to be equal (within 0.03 Å) during definement: d(O1A–C8A) = d(O1B–C8B); d(O1A–C9A) = d(O1B–C9B); d(C8A···C9A) = d(C8B···C9B). For **1b**·CH_2Cl_2, the dichloromethane solvate was modeled in a satisfactory manner by using a two-position (75:25) disorder model. Similarly, the following pairs of distances within the disordered morpholino group (80:20) in **4**·CH_2Cl_2 were constrained to be equal (within 0.03 Å) during definement: d(Pd–N1A) = d(Pd–N1B); d(N1A–C2) = d(N1B–C2). Refinement of **4**·CH_2Cl_2 was further facilitated by using the SADI constraint on the Pd–N1(A,B) and N1-(A,B)–C2 fragments. Additional crystallographic information is provided in the accompanying tables, as well as in the deposited CIFs. Anisotropic displacement parameters were employed throughout for the non-hydrogen atoms, and hydrogen atoms were added at calculated positions and refined by the use of a riding model that employed isotropic displacement parameters based on the isotropic displacement parameter of the attached atom. CCDC-763339 (**1a**·CH_2Cl_2), CCDC-763337 (**1b**·CH_2Cl_2), CCDC-877541 (**1d**·CH_2Cl_2), CCDC-877540 (**1e**·CH_2Cl_2), CCDC-877537 (**2**), CCDC-877536 (**2′**·CH_2Cl_2·H_2O), CCDC-877538 (**3**·$CHCl_3$), CCDC-763338 (**4**·CH_2Cl_2), and CCDC-877539 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Representative procedure for the synthesis of oxidative addition complexes: *[(κ^2-P,N-Mor-DalPhos)Pd(Ph)Cl] (**1a**):* Mor-DalPhos (690 mg, 1.49 mmol), followed by THF (6 mL) and chlorobenzene (6 mL), was added to a vial containing [CpPd(allyl)] (330 mg, 1.55 mmol). The vial was sealed, removed from the glovebox, and heated at 65 °C for 12 h. The reaction was concentrated to approximately 6 mL and the resulting slurry was washed with pentane (3×5 mL) and dried to yield **1a** as a pale grey powder in 93% yield (943 mg, 1.38 mmol). Crystals of **1a**·CH_2Cl_2 suitable for X-ray diffraction analysis were obtained from vapor diffusion of diethyl ether into a solution of **1a** in dichloromethane. ^{1}H NMR (500.1 MHz $CDCl_3$): δ = 8.23 (dd, J = 3.4, 8.3 Hz, 1H; ArH), 7.84 (t, J = 7.0 Hz, 1H; ArH), 7.64 (t, J = 7.7 Hz, 1H; ArH), 7.54 (d, J = 7.7 Hz, 2H; Pd-Ph), 7.39 (t, J = 7.7 Hz, 1H; ArH), 7.00 (t, J = 7.6 Hz, 2H; Pd–Ph), 6.86 (t, J = 7.2 Hz, 1H; Pd–Ph), 5.29–5.24 (m, 2H; morph CH_2), 4.15–4.11 (m, 2H; morph CH_2), 4.02–3.97 (m, 2H; morph CH_2), 3.07–3.03 (m, 2H; morph CH_2), 2.30–2.28 (m, 6H; 1-Ad CH), 2.01–1.94 (m, 12H; 1-Ad CH), 1.68 ppm (br s, 12H; 1-Ad CH); ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ = 160.6 (d, J_{PC} = 12.6 Hz, aryl C_{quat}), 141.7 (Pd–Ph C_{quat}), 138.9 (Pd–Ph CH), 136.2 (aryl CH), 132.6 (aryl CH), 128.9 (d, J_{PC} = 29.9 Hz, aryl CH), 127.7 (d, J_{PC} = 28.5 Hz, aryl C_{quat}), 126.6 (Pd–Ph CH), 126.0 (d, J_{PC} = 4.3 Hz, aryl CH), 122.9 (Pd–Ph CH), 62.0 (morph CH_2), 55.2 (morph CH_2), 40.8 (1-Ad CH_2), 36.4 (1- Ad CH_2), 28.7 ppm (1-Ad CH); ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ = 59.3 ppm; elemental analysis calcd (%) for $C_{36}H_{47}PdClPNO$ (682.6112 g mol^{-1}): C 63.32, H 6.94, N 2.05; found: C 63.03, H 6.92, N 2.05.

*[(κ^2-P,N-Mor-DalPhos)Pd(4-PhOMe)Cl] (**1b**)*: Isolated as a grey powder in 79% yield (331 mg, 0.46 mmol). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 8.23 (dd, J = 2.9, 7.8 Hz, 1H; ArH), 7.86–7.81 (m, 1H; ArH), 7.66–7.61 (m, 1H; ArH), 7.40–7.36 (m, 3H; ArH), 6.71–6.66 (m, 2H; ArH), 5.30–5.21 (m, 2H; morph CH_2), 4.17–4.10 (m, 2H; morph CH_2), 4.03–3.95 (m, 2H; morph CH_2), 3.75 (s, 3H; OCH_3), 3.08–3.00 (m, 2H; morph CH_2), 2.31–2.27 (m, 6H; 1-Ad), 2.00–1.94 (br m, 12H; 1-Ad), 1.68 ppm (br s, 12H; 1-Ad); ^{13}C{1H} NMR (125.8 MHz, $CDCl_3$): δ = 160.6 (d, J_{PC} = 12.5 Hz; aryl C_{quat}), 156.2 (Pd–aryl C_{quat}), 138.5 (Pd–aryl CH), 136.2 (aryl CH), 132.6 (aryl CH), 128.9 (d, J_{PC} = 7.5 Hz; aryl CH), 127.6 (d, J_{PC} = 28.2 Hz; (Pd–aryl C_{quat}), 125.9 (d, J_{PC} = 4.4 Hz; aryl CH), 112.8 (Pd–aryl CH), 62.0 (morph CH_2), 55.2 (morph CH_2), 55.0 (OCH_3), 43.2 (d, J_{PC} = 14.1 Hz; 1-Ad C_{quat}), 40.8 (1-Ad CH_2), 36.4 (1-Ad CH_2), 28.6 ppm (d, J_{PC} = 9.3 Hz; 1-Ad CH); ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ = 59.6; ele-

mental analysis calcd (%) for $C_{37}H_{49}PdCl_1PNO_2$ (712.6372 g mol^{-1}): C 62.34, H 6.93, N 1.97; found: C 62.44, H 6.86, N 1.72.

*[(κ^2-P,N-Mor-DalPhos)Pd(4-PhMe)Cl] (**1c**)*: Isolated as an off-white solid in 66% yield (46.3 mg, 0.066 mmol). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 8.25–8.21 (m, 1H; ArH), 7.86–7.82 (m, 1H; ArH), 7.65–7.60 (m, 1H; ArH), 7.40–7.37 (m, 3H; 2Pd-ArH, ArH), 6.83 (d, J = 7.9 Hz, 2H; Pd–ArH), 5.29–5.23 (m, 2H; morph CH_2), 4.15–4.11 (m, 2H; morph CH_2), 4.02–3.97 (m, 2H; morph CH_2), 3.06–3.01 (m, 2H; morph CH_2), 2.31–2.28 (m, 6H; 1-Ad CH_2), 2.23 (s, 3H; $ArCH_3$), 2.01–1.99 (m, 6H; 1-Ad CH_2), 1.95–1.94 (m, 6H; 1-Ad CH), 1.71–1.65 ppm (m, 12H; 1-Ad CH_2); ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ = 160.5 (d, J_{PC} = 12.6 Hz; aryl C_{quat}), 138.3 (Pd–aryl CH), 136.5 (Pd–aryl C_{quat}), 136.1 (aryl CH), 132.5 (aryl CH), 131.6 (Pd–aryl C_{quat}), 128.8 (d, J_{PC} = 7.5 Hz; aryl CH), 127.7 (Pd–aryl CH), 127.5 (aryl C_{quat}), 126.9 (d, J_{PC} = 4.4 Hz; aryl CH), 62.0 (morph CH_2), 55.1 (morph CH_2), 43.2 (d, J_{PC} = 14.2 Hz; 1-Ad C_{quat}), 40.7 (1-Ad CH_2), 36.4 (1-Ad CH_2), 28.7 (d, J_{PC} = 9.4 Hz; 1-Ad CH), 21.0 ppm (Ar CH_3); ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ = 59.4; elemental analysis calcd (%) for $C_{37}H_{49}ClNOPPd$ (696.6378 g mol^{-1}): C 63.79, H 7.09, N 2.01; found: C 63.58, H 6.89, N 1.92.

*[(κ^2-P,N-Mor-DalPhos)Pd(2-PhMe)Cl] (**1d**)*: Isolated as a beige powder in 75% yield (52.4 mg, 0.075 mmol). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 8.23 (ddd, J = 8.4, 3.6, 1.0 Hz, 1H; ArH), 7.89–7.86 (m, 1H; ArH), 7.65–7.61 (m, 1H; ArH), 7.54–7.52 (m, 1H; Pd–ArH), 7.40–7.37 (m, 1H; ArH), 6.91–6.88 (m, 1H; Pd–ArH), 6.85–6.80 (m, 2H; Pd–ArH), 5.33–5.27 (m, 1H; morph CH_2), 5.24–5.18 (m, 1H; morph CH_2), 4.18–4.12 (m, 2H; morph CH_2), 4.03–3.96 (m, 2H; morph CH_2), 3.09–2.99 (m, 2H; morph CH_2), 2.87 (s, 3H; $ArCH_3$), 2.45–2.43 (m, 3H; 1-Ad CH_2), 2.13–2.03 (m, 9H; 1-Ad CH/CH_2), 1.86 (brs, 6H; 1-Ad CH/CH_2), 1.79–1.71 (m, 6H; 1-Ad CH_2), 1.66–1.59 ppm (m, 6H; 1-Ad CH_2); ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ = 160.3 (d, J_{PC} = 12.8 Hz; aryl C_{quat}), 142.4 (Pd–aryl C_{quat}), 142.0 (d, J_{PC} = 3.6 Hz; Pd–aryl C_{quat}), 137.4 (d, J_{PC} = 2.7 Hz; Pd–aryl CH), 135.8 (aryl CH), 132.5 (aryl CH), 128.9 (d, J_{PC} = 7.3 Hz; aryl CH), 128.6 (Pd–aryl CH), 127.9 (d, J_{PC} = 28.2 Hz; aryl C_{quat}), 126.0 (d, J_{PC} = 4.2 Hz; aryl CH), 123.4 (Pd–aryl CH), 123.1 (Pd–aryl CH), 62.0 (morph CH_2), 61.9 (morph CH_2), 55.2 (morph CH_2), 54.6 (morph CH_2), 42.7 (d, J_{PC} = 15.1 Hz; 1-Ad C_{quat}), 42.5 (d, J_{PC} = 12.9 Hz; 1-Ad C_{quat}), 41.0 (1-Ad CH_2), 39.7 (1-Ad CH_2), 36.4 (1-Ad CH_2), 36.3 (1-Ad CH_2), 28.8 (Ar CH_3), 28.8 (d, J_{PC} = 9.4 Hz; 1-Ad CH), 28.5 ppm (d, J_{PC} = 9.2 Hz; 1-Ad CH); ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ = 58.3; elemental analysis calcd (%) for $C_{37}H_{49}ClNOPPd$ (696.6378 g mol^{-1}): C 63.79, H 7.09, N 2.01; found: C 63.88, H 6.97, N 1.89.

*[(κ^2-P,N-Mor-DalPhos)Pd(4-PhCF$_3$)Cl] (**1e**)*: Isolated as an off-white powder in 80% yield (59.7 mg. 0.080 mmol). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 8.24 (dd, J = 8.4, 3.1 Hz; ArH), 7.85–7.82 (m, 1H; ArH), 7.70 (d, J = 7.8 H, 2H; Pd-ArH), 7.67–7.64 (m, 1H; ArH), 7.41 (t, J = 7.6 Hz; ArH), 7.21 (d, J = 8.1 Hz, 2H; Pd–ArH), 5.28–5.23 (m, 2H; morph CH_2), 4.16–4.11 (m, 2H; morph CH_2), 4.03–3.98 (m, 2H; morph CH_2), 3.09–3.04 (m, 2H; morph CH_2), 2.29–2.26 (m, 6H; 1-Ad CH_2), 1.96 (brs, 12H; 1-Ad CH/CH_2), 1.68 ppm (brs, 12H; 1-Ad CH_2); ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ = 160.4 (d, J_{PC} = 12.5 Hz; aryl C_{quat}), 149.3 (Pd–aryl C_{quat}), 138.7 (Pd–aryl CH), 136.1 (aryl CH), 132.8 (aryl CH), 128.8 (d, J = 7.6 Hz; aryl CH), 127.1 (d, J_{PC} = 29.1 Hz; aryl C_{quat}), 126.2 (d, J_{PC} = 4.6 Hz; aryl CH), 125.2 (J_{CF} = 270.7 Hz; CF_3), 125.0 (J_{CF} = 31.8 Hz; Pd–aryl C_{quat}), 122.4 (Pd–aryl CH), 61.9 (morph CH_2), 55.4 (morph CH_2), 43.4 (d, J_{PC} = 14.4 Hz; 1-Ad C_{quat}), 40.8 (1-Ad CH_2), 36.3 (1-Ad CH_2), 28.6 ppm (d, J_{PC} = 9.3 Hz; 1-Ad CH); ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ = 60.5; elemental analysis calcd (%) for $C_{37}H_{46}ClF_3NOPPd$ (750.6092 g mol^{-1}): C 59.20, H 6.18, N 1.87; found: C 59.15, H 6.22, N 1.90.

*[(κ^2-P,N-Mor-DalPhos)Pd(3-pyridyl)Cl] (**1f**)*: Mor-DalPhos (46.4 mg, 0.100 mmol, 1.0 equiv), NaO*t*Bu (34.6 mg, 0.360 mmol, 1.2 equiv), 3-chloropyridine (1 mL), and THF (2 mL) were added to a vial containing [{Pd(allyl)Cl}$_2$] (57.6 mg, 0.158 mmol, 0.525 equiv). The resulting brown mixture was sealed, removed from the glovebox, and heated at 65 °C for 3 h, at which time complete consumption of the ligand was confirmed by use of ^{31}P NMR spectroscopy. The resulting slurry was concentrated to dryness, dissolved in CH_2Cl_2 (2 mL) and filtered (removing insoluble impurities). The filtrate was triturated with CH_2Cl_2/Et_2O (1:1, 2×2 mL) and CH_2Cl_2/pentane (1:1, 3×2 mL) mixtures, forming a pale orange powder that was dried in vacuo for several days to afford the desired compound (containing 5.5% Et_2O as observed by ^{1}H NMR spectroscopy) in 90% yield (184.7 mg, 0.270 mmol). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 8.77 (d, J = 1.6 Hz, 1H; pyridyl H), 8.24 (ddd, J = 8.4, 3.5, 0.9 Hz, 1H; ArH), 8.04 (dd, J = 4.7, 1.5 Hz, 1H; pyridyl H), 7.85–7.80 (m, 2H; pyridyl + ArH), 7.67–7.64 (m, 1H; ArH), 7.43–7.40 (m, 1H; ArH), 6.93 (dd, J = 7.8, 4.7 Hz, 1H; pyridyl H), 5.29–5.24 (m, 2H; morph CH_2), 4.16–4.11 (m, 2H; morph CH_2), 4.03–3.98 (m, 2H; morph CH_2), 3.10–3.05 (m, 2H; morph CH_2), 2.26 (brs, 6H; 1-Ad CH_2), 1.95 (brs, 12H; 1-Ad CH/CH_2), 1.67 ppm (brs, 12H; 1-Ad CH_2); ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ = 160.4 (d, J_{PC} = 12.5 Hz; aryl C_{quat}), 157.0 (pyridyl CH), 146.4 (pyridyl CH), 143.9 (pyridyl CH), 138.5 (pyridyl C_{quat}), 136.0 (aryl CH), 132.9 (aryl CH), 128.7 (d, J_{PC} = 7.8 Hz; aryl CH), 127.0 (d, J_{PC} = 29.5 Hz; aryl C_{quat}), 126.2 (d, J_{PC} = 4.6 Hz; aryl CH), 122.7 (pyridyl CH), 61.9 (morph CH_2), 55.5 (morph CH_2), 55.4 (morph CH_2), 43.4–43.3 (m; 1-Ad C_{quat}), 40.8 (1-Ad CH_2), 36.3 (1-Ad CH_2), 28.6 ppm (d, J_{PC} = 9.3 Hz; 1-Ad CH); ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ = 61.9; elemental analysis calcd (%) for $C_{35}H_{46}ClN_2OPPd$ (683.5993 g mol^{-1}): C 61.49, H 6.78, N 4.10; found: C 61.11, H 6.73, N 3.87.

*[(κ^2-P,N-Mor-DalPhos)Pd(η^1-cinnamyl)Cl] (**2**)*: A vial was charged with Mor-DalPhos (139.1 mg, 0.300 mmol, 1.0 equiv), [{Pd(cinnamyl)Cl}$_2$] (77.7 mg, 0.300 mmol, 1.0 equiv), and THF (4 mL). The resulting clear orange solution was stirred at room temperature for 1 h during which time the reaction became cloudy and lighter in color, forming a milky yellow solution. The presence of a new product (**2**) was confirmed by use of ^{31}P NMR techniques. The resulting slurry was concentrated to dryness, washed with Et_2O (5×2 mL) until the washings remained colorless, and dried to afford the title compound as a yellow powder in 92% yield (200 mg, 0.277 mmol). Crystals suitable for single-crystal X-ray diffraction analysis were obtained from vapour diffusion of hexanes into a dichloromethane/ethyl acetate solution of the title compound. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 7.89–7.83 (m, 2H; ArH), 7.73–7.71 (m, 2H; cin Ph), 7.63–7.60 (m, 1H; ArH), 7.44–7.41 (m, 1H; ArH), 7.39–7.33 (m, 3H; cin Ph), 6.80 (dd, J = 14.5, 8.8 Hz, 1H; alkenyl H), 6.42–6.36 (m, 1H; alkenyl H), 3.86–3.81 (m, 2H; morph CH_2), 3.74–3.68 (m, 2H; morph CH_2), 3.62–3.60 (m, 4H; Pd–CH_2/morph CH_2), 3.14–3.10 (m, 2H; morph CH_2), 2.28–2.26 (m, 6H; 1-Ad CH_2), 2.02 (brs, 6H; 1-Ad CH), 1.96–1.94 (m, 6H; 1-Ad CH_2), 1.74–1.67 ppm (m, 12H; 1-Ad CH_2); ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ = 160.3 (d, J_{PC} = 14.1 Hz; aryl C_{quat}), 136.9 (d, J_{PC} = 6.3 Hz; Ph C_{quat}), 135.7 (aryl CH), 133.0 (aryl CH), 129.4 (Ph CH), 128.6 (aryl CH), 127.8 (Ph CH), 127.4 (d, J_{PC} = 28.9 Hz; aryl C_{quat}), 127.4 (aryl CH), 126.6 (d, J_{PC} = 7.6 Hz; aryl CH), 122.5 (d, J_{PC} = 17.4 Hz; alkenyl CH), 114.5 (alkenyl CH), 65.0 (morph CH_2), 58.5 (morph CH_2), 43.0 (d, J_{PC} = 12.1 Hz; 1-Ad C_{quat}), 41.1 (1-Ad CH_2), 36.2 (1-Ad CH_2), 35.7 (Pd–CH_2), 28.7 ppm (d, J_{PC} = 9.3 Hz; 1-Ad CH); ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ = 75.4 ppm; elemental analysis calcd (%) for $C_{39}H_{51}ClNOPPd$ (722.6751 g mol^{-1}): C 64.82, H 7.11, N 1.94; found: C 64.55, H 7.02, N 1.89.

*[(κ^2-P,N-Mor-DalPhos)Pd(η^3-cinnamyl)]OTf (**3**)*: Silver trifluoromethanesulfonate (28.3 mg, 0.110 mmol, 1.1 equiv) was added to a vial containing **2** (72.3 mg, 0.100 mmol, 1.0 equiv) in CH_2Cl_2 (2 mL). The resulting yellow solution was stirred for ≈1 h, during which time a gray precipitate formed. Reaction completion was determined by the presence of a single new phosphorus-containing species, as observed by ^{31}P NMR spectroscopy. The mixture was filtered over Celite and the filtrate was treated with pentane (3 mL) to afford a yellow solid in solution, which in turn was separated from the solvent and washed with pentane (2×3 mL). The solid was dried to afford the title compound as a yellow powder in 98% yield (81.6 mg, 0.098 mmol). Crystals suitable for single-crystal X-ray diffraction analysis were obtained via slow evaporation of a $CHCl_3$ solution of the title compound. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 7.90–7.84 (m, 2H; ArH), 7.79–7.77 (m, 2H; cin Ph), 7.67–7.64 (m, 1H; ArH), 7.48 (t, J = 7.6 Hz, 1H; ArH), 7.46–7.42 (m, 3H; cin Ph), 6.32 (dd, J = 14.1, 9.8 Hz, 1H; allyl CH), 6.21–6.15 (m, 1H; allyl CH), 4.05 (d, J = 5.5 Hz, 1H; allyl CH), 4.00–3.92 (m, 2H; morph CH_2), 3.63–3.61 (m, 1H; morph CH_2), 3.46–3.43 (m, 1H; morph CH_2), 3.32–3.22 (m, 2H; morph CH_2), 3.13–3.09 (m, 1H; allyl CH), 3.02–2.94 (m, 2H; morph CH_2), 2.30–2.27 (m, 3H; 1-Ad CH_2), 2.08–1.97 (m, 12H; 1-Ad CH/CH_2), 1.84 (brs, 3H;

1-Ad CH_2), 1.73–1.67 ppm (m, 12H; 1-Ad CH_2); $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): $\delta = 160.1$ (d, $J_{PC} = 14.6$ Hz; aryl C_{quat}), 135.7 (aryl CH), 135.5 (d, $J_{PC} = 6.9$ Hz; Ph C_{quat}), 133.5 (aryl CH), 129.8 (Ph CH), 129.6 (Ph CH), 128.6 (m, Ph CH), 128.0 (d, $J_{PC} = 4.1$ Hz; aryl CH), 126.6 (aryl CH), 126.5 (d, $J_{PC} = 28.9$ Hz; aryl C_{quat}), 119.3 (d, $J_{PC} = 20.7$ Hz; allyl CH), 109.9 (d, $J_{PC} = 7.0$ Hz; allyl CH), 65.3 (morph CH_2), 64.0 (morph CH_2), 58.9 (morph CH_2), 58.6 (morph CH_2), 43.1 (d, $J_{PC} = 11.7$ Hz; 1-Ad C_{quat}), 42.6 (d, $J_{PC} = 13.0$ Hz; 1-Ad C_{quat}), 41.8 (1-Ad CH_2), 41.3 (1-Ad CH_2), 41.1 (allyl CH_2), 36.2 (1-Ad CH_2), 28.6 ppm (d, $J_{PC} = 4.2$ Hz; 1-Ad CH); $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$): $\delta = 79.1$ ppm; elemental analysis calcd (%) for $C_{40}H_{51}F_3NO_4PPdS$ (836.2912 g mol^{-1}): C, 57.45; H, 6.15; N, 1.67; found: C, 57.22; H, 6.12; N, 1.74.

*[(κ^2-P,N-Mor-DalPhos)Pd(Ph)NH_3]OTf·CH_2Cl_2 (**4**·CH_2Cl_2)*: A vial was charged with **1a** (341 mg, 0.50 mmol) followed by CH_2Cl_2 (5 mL). The vial was sealed, removed from the glovebox, and NH_3 (0.5 M in 1,4-dioxane, 3.00 mL, 1.50 mmol) was added. The solution was stirred briefly and then transferred back into the glovebox, at which point silver trifluoromethanesulfonate (141 mg, 0.55 mmol) was added. The resulting mixture was stirred for 30 min at room temperature, during which time a gray precipitate formed. ^{31}P NMR analysis of the reaction mixture indicated complete conversion to a single new phosphorus-containing species. The precipitate was removed by filtration over Celite and the solution was concentrated under vacuum. The resulting solid was washed with pentane/CH_2Cl_2 (5×2 mL) and concentrated to afford **4**·CH_2Cl_2 as a light brown solid in 90% yield (406 mg, 0.45 mmol). Crystals of **4**·CH_2Cl_2 suitable for X-ray diffraction analysis were obtained from vapor diffusion of diethyl ether into a dichloromethane solution of **4**. ^1H NMR (500.1 MHz, $CDCl_3$): $\delta = 8.14$–8.12 (m, 1H; ArH), 7.83 (t, $J = 6.6$ Hz, 1H; ArH), 7.69 (t, $J = 7.6$ Hz, 1H; ArH), 7.52 (d, $J = 7.9$ Hz, 2H; Pd-Ph), 7.45 (t, $J = 7.5$ Hz, 1H; ArH), 7.06 (t, $J = 7.5$ Hz, 2H; Pd–Ph), 6.93 (t, $J = 7.1$ Hz, 1H; Pd–Ph), 4.34–4.31 (m, 2H; morph CH_2), 4.07 (brs, 4H; morph CH_2), 3.25–3.23 (m, 2H; morph CH_2), 2.64 (brs, 3H; NH_3), 2.25–2.23 (m, 6H; 1-Ad), 1.97 (brs, 12H; 1-Ad), 1.68 ppm (brs, 12H; 1-Ad); $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): $\delta = 160.6$ (m; aryl C_{quat}), 143.2 (Ph C_{quat}), 137.7 (Pd–Ph CH), 135.9 (aryl CH), 133.3 (aryl CH), 127.8 (Pd–Ph CH), 127.1 (d, $J_{PC} = 7.5$ Hz; aryl CH), 126.6 (aryl CH), 124.0 (Pd–Ph CH), 61.6 (morph CH_2), 55.6 (morph CH_2), 43.1 (d, $J_{PC} = 5.4$ Hz; 1-Ad C_{quat}), 40.6 (1-Ad CH2), 36.1 (1-Ad CH_2), 28.4 ppm (d, $J_{PC} = 0.5$ Hz; 1-Ad CH); $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$): $\delta = 61.7$ ppm; elemental analysis calcd (%) for $C_{38}H_{52}Pd_1Cl_2P_1N_2O_4S_1F_3$ (898.191 g mol^{-1}): C 50.80, H 5.84, N 3.12; found: C 50.84, H 5.90, N 3.30.

*[(κ^3-P,N,O-Mor-DalPhos)Pd(Ph)]OTf (**5**)*: Silver trifluoromethanesulfonate (42.4 mg, 0.165 mmol, 1.1 equiv) was added to a vial containing **1a** (102.4 mg, 0.150 mmol, 1.0 equiv) in CH_2Cl_2 (2 mL). The resulting yellow solution was stirred for ≈1 h, during which time a gray precipitate formed. Reaction completion was determined by the presence of a single new phosphorus-containing species as observed by ^{31}P NMR spectroscopy. The mixture was filtered over Celite, the collected eluent was concentrated to a minimum volume (<1 mL), and the remaining solution was treated with pentane (3 mL) to afford a yellow solid (fresh precipitate), which was separated from the solvent and washed with pentane (3× 3 mL). The solid was dried in vacuo at 75 °C for 60 hrs (approx. 3 days) to afford the title compound as an analytically pure light-yellow powder in 95% yield (113.1 mg, 0.142 mmol). Crystals suitable for single-crystal X-ray diffraction analysis were obtained from vapor diffusion of diethyl ether into a solution of the title compound in dichloromethane. ^1H NMR (500.1 MHz, $CDCl_3$): $\delta = 8.16$ (dd, $J = 7.5$, 3.0 Hz, 1H; ArH), 7.80–7.72 (m, 2H; ArH), 7.57–7.52 (m, 3H; 2Pd–Ph + ArH), 7.14–7.11 (m, 2H; Pd–Ph), 7.08–7.06 (m, 1H; Pd–Ph), 4.61–4.56 (m, 2H; morph CH_2), 4.27–4.22 (m, 2H; morph CH_2), 3.87–3.85 (m, 2H; morph CH_2), 3.72 (brs, 2H; morph CH_2), 2.29–2.26 (m, 6H; 1-Ad CH_2), 2.03 (brs, 12H,; 1-Ad CH/CH_2), 1.72 ppm (brs, 12H; 1-Ad CH_2); $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): δ 154.6 (aryl C_{quat}), 145.3 (Pd–Ph C_{quat}), 136.5 (Pd–Ph CH), 135.7 (aryl CH), 134.2 (aryl CH), 128.7 (d, $J_{PC} = 5.0$ Hz; aryl CH), 128.4 (d, $J_{PC} = 32.9$ Hz; aryl C_{quat}), 127.8 (Pd–Ph CH), 127.1 (d, $J_{PC} = 7.5$ Hz; ArH), 125.2 (Pd–Ph CH), 68.1 (morph CH_2), 54.7 (morph CH_2), 43.9 (d, $J_{PC} = 15.9$ Hz; 1-Ad C_{quat}), 41.0 (1-Ad CH_2), 36.1 (1-Ad CH_2), 28.5 ppm (d, $J_{PC} = 9.6$ Hz; 1-Ad CH); $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$): $\delta = 78.8$ ppm (brs); elemental analysis calcd (%) for $C_{37}H_{47}F_3NO_4PPdS$ (796.2279 g mol^{-1}): C, 55.81; H, 5.95; N, 1.76; found: C, 55.74; H, 5.92; N, 1.92.

Representative protocol for room temperature ammonia monoarylation: A vial containing a magnetic stir bar, **1a** (17.1 mg, 0.0025 mmol, 5.0 mol%), NaO*t*Bu (96.1 mg, 1.00 mmol, 2.0 equiv), and 1,4-dioxane (2.00 mL) was charged with 3-chloro-5-fluoroanisole (0.0635 mL, 0.50 mmol, 1.0 equiv). The resulting cloudy solution was stirred briefly, sealed with a cap containing a PTFE septum, and removed from the glovebox. This was followed by the addition of NH_3 (0.5 M solution in 1,4-dioxane, 3.00 mL, 1.5 mmol). The solution was stirred magnetically at room temperature overnight (14–20 h) and the reaction progress was monitored by the use of TLC or GC methods. After complete consumption of the aryl halide, the reaction was filtered over Celite, concentrated, and silica powder (0.5–1.0 g) was added to the crude material. The solvent was removed from the silica–product mixture and the compound was purified by column chromatography with 15–20% EtOAc/hexanes and allowed to dry on the benchtop overnight to afford 3-fluoro-5-meth<->oxyaniline (**6q**) as an orange oil in 65% yield (46 mg, 0.33 mmol). ^1H NMR (500.1 MHz, $CDCl_3$): $\delta = 6.04$ (dt, $J = 11.0$, 2.3 Hz, 1H), 6.02–5.99 (m, 2H), 3.77–3.74 ppm (m, 5H); $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): $\delta = 164.7$ (d, $J_{CF} = 241.5$ Hz), 161.8 (d, $J_{CF} = 13.8$ Hz), 148.7 (d, $J_{CF} = 13.8$ Hz), 96.7, 95.0 (d, $J_{CF} = 23.9$ Hz), 92.0 (d, $J_{CF} = 25.1$ Hz), 55.5 ppm. Agrees with data previously reported in the literature.[21]

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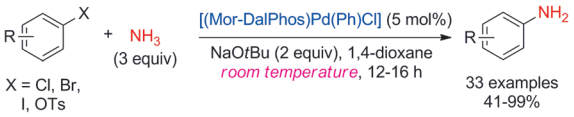
Amination

P. G. Alsabeh, R. J. Lundgren, R. McDonald, C. C. C. Johansson Seechurn, T. J. Colacot, M. Stradiotto . . ■■■–■■■*

An Examination of the Palladium/Mor-DalPhos Catalyst System in the Context of Selective Ammonia Monoarylation at Room Temperature



More and Mor-DalPhos: Investigations into the Pd/Mor-DalPhos catalyst system enabled the development of an effective precatalyst for the Buchwald–Hartwig amination of (hetero)aryl (pseudo)halides employing ammonia at room temperature (see scheme; Mor-DalPhos = di(1-adamantyl)-2-morpholinophenylphosphine).