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ARTICLE

Probing the utility of palladium complexes supported by morpholine-functionalized *N*-heterocyclic carbene ligands in Buchwald–Hartwig amination

Craig A. Wheaton and Mark Stradiotto

Abstract: Convenient and high-yielding syntheses of two new morpholine-substituted *N*-heterocyclic carbene ligands, 1-Ar-3-{2-(4-morpholinyl)phenyl}imidazolidin-2-ylidene (Ar = Dipp, Mes), are described. An investigation of corresponding palladium complexes reveals hemilability, and examples of both monodentate and bidentate coordination are observed. A preliminary investigation of the activity of these palladium complexes for Buchwald–Hartwig amination catalysis is presented.

Key words: *N*-heterocyclic carbene, palladium, Buchwald–Hartwig amination, ligand design, hemilabile.

Résumé : On décrit les synthèses commodes et à haut rendement de deux nouveaux ligands carbène *N*-hétérocyclique substitués par la morpholine, 1-Ar-3-{2-(4-morpholinyl)phényl}imidazolidin-2-ylidène (Ar = Dipp, Mes). Une étude des complexes de palladium correspondants révèle une hémilabilité et l'on observe des exemples de coordination monodente ainsi que bidente. On présente une étude préliminaire de l'activité de ces complexes de palladium pour la catalyse de la réaction d'amination de Buchwald–Hartwig. [Traduit par la Rédaction]

Mots-clés : carbène *N*-hétérocyclique, palladium, amination de Buchwald–Hartwig, conception de ligands, hémilabile.

Introduction

The combination of a strong and weak donor within a bidentate ligand set can lead to interesting reactivity in the derived metal complexes, owing to the electronic asymmetry and (or) hemilability arising from the secondary donor fragment.[1] Our group recently introduced the P,N ligand Mor-DalPhos (MDP) (Scheme 1),[2] which exhibits remarkable chemoselectivity in a variety of palladium-catalyzed cross-coupling reactions, most notably in C–N coupling[3] and in particular the monoarylation of ammonia[4] and hydrazine.[5] The high chemoselectivity that is achieved by use of MDP has been attributed to the chelating ability of this mixed-donor ligand. Conversely, the use of bulky monodentate *N*-heterocyclic carbene (NHC) ligands[6] such as SIPr (Scheme 1),[7] and the recently reported bulkier variants IPr*[8] and IPent,[9] has been shown to give rise to remarkably active catalysts for Buchwald–Hartwig amination, with efficacy at lower catalyst loadings and under milder conditions than can be achieved with MDP. However, these NHC ligands tend to suffer from inferior chemoselectivity, which may be attributed in part to their monodentate nature. Functionalization of carbene ligands with secondary donors of the group 15 or 16 elements is an active area of research and has been thoroughly reviewed.[10] However, there are only a handful of examples of NHC functionalization with simple tertiary alkylamines,[11] and none of these feature the amine tethered to the NHC through a rigid phenylene linker. In this context, we envisioned that a new and potentially bidentate hybrid ligand framework that incorporates structural features found in both SIPr and MDP by tethering a morpholine donor to a saturated NHC moiety might espouse the desirable reactivity features of each individual ligand type (Scheme 1). We report herein on the preparation of new ligands of this type, the synthesis and structural characterization of palladium derivatives, and a preliminary investigation of their performance in Buchwald–Hartwig amination.

Results and discussion

The diamine compounds **1** and **2** were each prepared via Buchwald–Hartwig amination starting from *N*-(2-bromophenyl) morpholine and using Pd–MDP catalyst mixtures, which gave excellent regioselectivity and high yields for both the Dipp (**1**) and less hindered Mes (**2**) variant (Scheme 2). Conversion to the imidazolidinium salts was then achieved by using triethyl orthoformate as the precarbenic unit, as per the standard protocol,[12] and both variants were conveniently prepared as both the chloride (**3** and **5**) and the BF_4 (**4** and **6**) salts (Scheme 2). Both formulations were isolated in moderate to high yields (69%–88%). Compounds **4** and **6** crystallized readily and their solid-state structures were determined by use of single-crystal X-ray diffraction (Figs. 1 and 2; Table 1), thereby verifying the expected connectivities.

Conversion of the salts to the corresponding free carbenes was carried out under inert atmosphere by reaction with 1 equiv. of NaHMDS base (Scheme 3). Deprotonation of the chloride salt **3** could be carried out in toluene solvent giving moderate yield of **7**, while the analogous reaction with less sterically hindered **5** gave the desired carbene **8** and an additional compound in a 2:1 ratio. The minor product was identified to be the dimer **8b** by determination of the solid-state molecular structure (Fig. 3; Table 1). Deprotonation of the BF_4 salts **4** and **6** was carried out in tetrahydrofuran (THF) solvent due to their poor solubility in toluene. Improved yields of **7** and **8** were achieved using these conditions (88% and 85%, respectively), and no formation of the dimer **8b** was observed in this case. Spectroscopic data for **7** and **8** are consistent with the monomeric carbene structure, including the observation

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C.A. Wheaton and M. Stradiotto. Department of Chemistry, Dalhousie University, 6274 Coburg Road, P.O. Box 15000, Halifax, NS B3H 4R2, Canada.
Corresponding author: Mark Stradiotto (e-mail: mark.stradiotto@dal.ca).

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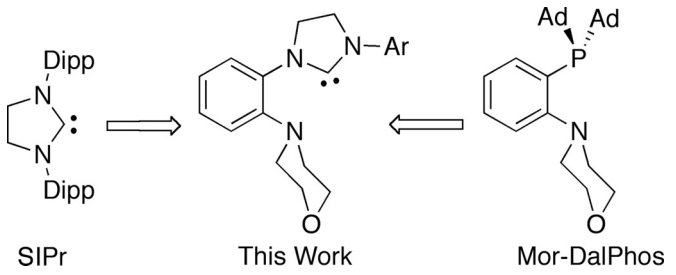
Scheme 1. Design concept for new ligands that are a hybrid of SIPr and Mor-DalPhos (Dipp = 2,6-di*iso*propylphenyl, Ar = Dipp or 2,4,6-trimethylphenyl (Mes), Ad = 1-adamantyl).



of resonances in the $^{13}C\{^1H\}$ NMR spectrum appearing at δ 243.7 and 243.9 for the carbenic carbons of **7** and **8**, respectively.

Having established a high-yielding synthesis of two new morpholine-functionalized NHC compounds, we sought to understand their coordination behaviour as ligands in palladium complexes. Compounds **9** and **10**, which have the general formula (NHC)Pd(η^3-cinnamyl)Cl, were generated quantitatively by reaction of [Pd(η^3-cinnamyl)Cl]$_2$ with a slight excess of **7** or **8** in THF solution (Scheme 4). As is typical for analogous complexes of monodentate NHCs, **9** and **10** are air and moisture stable.[7] The ^{13}C NMR resonances of the metal-bound carbon in **9** and **10** appear at δ 211.9 and 211.4, respectively. Many resonances associated with both the carbene and the cinnamyl moieties exhibit significant broadening in the ^1H NMR spectra at 300 K, which is suggestive of dynamic processes arising from η^3/η^1 exchange involving the cinnamyl co-ligand, restricted C–N bond rotation, and (or) other fluxional processes. Single crystals of **9** were grown from a benzene solution and the X-ray structure is depicted in Fig. 4 (Table 2). A notable feature of this crystal structure is the absence of a bond between the morpholine nitrogen atom and palladium. Instead, the cinnamyl retains the η^3 coordination mode to fill the coordination sphere of the metal. Similar spectroscopic features suggest analogous monodentate coordination behaviour for the less sterically hindered ligand in **10**.

Complexes of the formula (NHC)PdCl$_2$ were then targeted to determine if the NHC ligands **7** and **8** can adopt a k^2-C,N bidentate motif in the absence of the cinnamyl co-ligand. Therefore, complexes **11** and **12** were prepared from the corresponding (NHC)Pd(η^3-cinnamyl)Cl complexes **9** and **10** by protonolysis of the cinnamyl group using HCl according to a previously reported procedure applied to monodentate NHCs.[13] Compounds **11** and **12** are each generated in approximately 80% purity on the basis of NMR data, with a second unidentified compound (20%) formed as a minor product, which we propose may be attributed to protonation of the morpholine nitrogen by HCl. The crystal structure of **11** was determined (Fig. 5; Table 2), confirming a k^2-C,N coordination mode of the ligand (Pd(1)–N(3) = 2.148(1) Å, Pd(1)–C(11) = 1.969(2) Å).[14] Interestingly, the chelation requires a significant reduction in the torsion angle between the plane of the NHC and that of the metal in complex **11** (44°) versus that observed in **9** (89°). This geometric requirement places the coordination site *cis* to the carbene carbon Cl(2) in a much more sterically crowded environment near both isopropyls of the Dipp group. Furthermore, the stronger *trans*-directing ability of the carbene versus the morpholine donor is manifested in a significantly longer Cl(1) distance (2.3451(5) relative to Cl(2) (2.2946(4)).

We have undertaken a preliminary investigation of the efficacy of complexes **9–12** in catalyzing the Buchwald–Hartwig amination of chlorobenzene with a limited series of amines (morpholine, aniline, and octylamine). Additionally, related complexes of SIPr and MDP with the general formula LPd(cinnamyl)Cl (L = SIPr (**13**), MDP (**14**)), prepared according to the literature procedures,[7,15] were examined under analogous conditions for comparison. The results of these studies are presented in Table 3. In general, it is observed that complexes **9–12** featuring morpholine-functionalized NHCs perform poorly in Buchwald–Hartwig amination in comparison with **13** and **14**. Under the standard conditions that have been used successfully with Pd–MDP in previous studies (Table 3, entries 1–6), yields ≤20% were obtained for each of **9–12** for the three amine substrates that were examined. By comparison, complexes of both SIPr and MDP (**13** and **14**) were found to be highly effective catalysts under these conditions (Table 3, entries 5 and 6).

Complexes **9** and **10** were also examined under conditions that have proven favourable for NHC systems (KO^{t}Bu base, DME solvent). This resulted generally in a modest improvement in performance for both, with the bulkier precatalyst **9** affording marginally higher yields in some cases. The best yield was obtained with morpholine as substrate, at 42%. As anticipated, SIPr was found to be highly effective under these conditions for the arylation of morpholine and aniline; however, for octylamine, the chemoselectivity was poor compared with the same reaction performed using the previous conditions, with formation of diarylation product (i.e., Ph$_2$Noctyl) accounting for the reduction in yield of monoarylation product. Conversely, under these conditions, MDP remains effective for arylation of octylamine, while yields are substantially reduced for arylation of morpholine and aniline (34% and 15%, respectively).

Conclusions

We have reported herein a convenient and high-yielding synthesis of two variants of a new morpholine-functionalized NHC ligand. The ligands may be either monodentate or bidentate when bound to palladium, depending on the character of the other co-ligands bound to the metal center. A preliminary study has shown these complexes to be poor catalysts for Buchwald–Hartwig amination of a standard substrate set, despite the close structural relationship between these new ligands and the highly effective ligands SIPr and MDP.

Experimental details

General considerations

Unless otherwise stated, all manipulations were conducted under an inert atmosphere of dinitrogen using standard Schlenk methods or within an mBraun glovebox apparatus using glassware that was oven-dried at 120 °C and evacuated while hot prior to use. Toluene, benzene, hexanes, and pentane were deoxygenated and dried by sparging with dinitrogen gas followed by passage through a double-column solvent purification system purchased from mBraun Inc. THF and 1,4-dioxane were dried over sodium/benzophenone, distilled, and stored over 4 Å molecular sieves. Benzene-d_6 (Cambridge Isotopes) was degassed by using at least three repeated freeze–pump–thaw cycles and stored over 4 Å molecular sieves for 24 h prior to use. Other deuterated solvents ($CDCl_3$, DMSO-d_6, and methanol-d_4) were used with air- and moisture-stable compounds and were used as received. *N*-(2,4,6-trimethylphenyl)-1,2-ethanediamine,[16] *N*-(2,6-di*iso*propylphenyl)-1,2-ethanediamine,[16] *N*-(2-bromophenyl)morpholine,[17] and [Pd(cinnamyl)Cl]$_2$[18] were prepared according to literature procedures. All other materials were obtained from commercial sources (Sigma-Aldrich, Alfa Aesar, and Strem) and used without further purification. NMR spectra were collected on a Bruker instrument at a frequency of 500 MHz for ^1H and 126 MHz for ^{13}C experiments, at ambient temperature, and referenced to residual solvent signals. Peak assignments were made with the aid of COSY, DEPT-135, and HSQC experiments. Mass spectrometric data were acquired by Mr. Xiao Feng (Mass Spectrometry Laboratory, Dalhousie University, Halifax, Nova Scotia). Single-crystal X-ray diffraction data were collected by Dr. Robert McDonald and Dr. Michael Ferguson (X-Ray Crystallography Laboratory, University of Alberta, Edmonton, Alberta).

Scheme 2. Synthesis of morpholine-functionalized NHC precursors. Conditions: (*i*) [Pd(cinnamyl)Cl]$_2$ (2.5 mol%), MDP (7 mol%), ArBr–amine–NaO^{t}Bu = 1:1.1:1.4, [ArBr] = 1 mol L^{-1}; (*ii*) HCl (2 equiv.) or NH_4BF_4 (1.4 equiv.), $CH(OEt)_3$, 110 °C, 30 min.

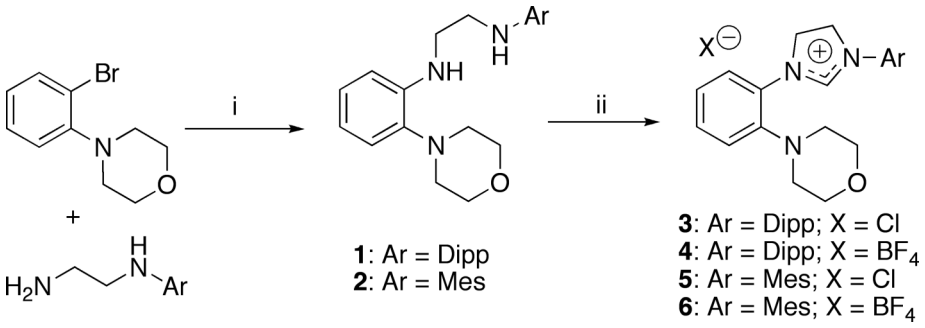


Fig. 1. Molecular structure of **4** with hydrogen atoms omitted for clarity. Thermal ellipsoids are shown at 50% probability.

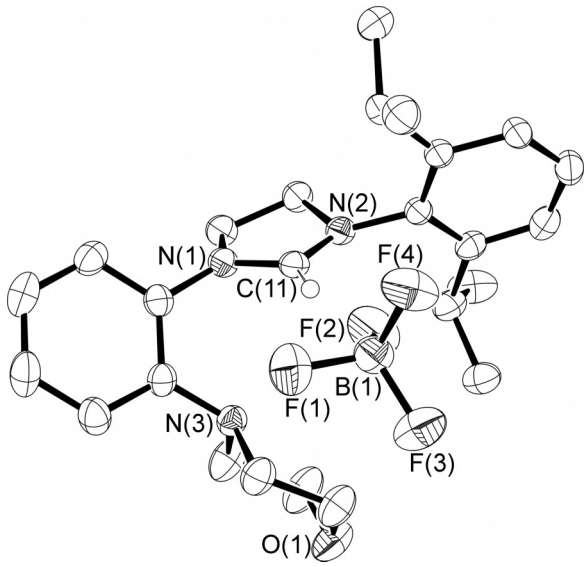
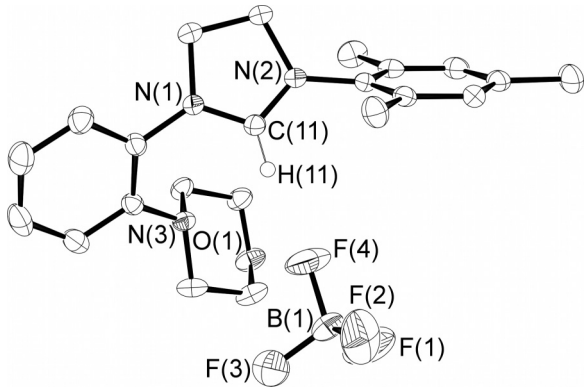


Fig. 2. Molecular structure of **6** with hydrogen atoms omitted for clarity. Thermal ellipsoids are shown at 50% probability.



Elemental analysis data were obtained from Canadian Microanalytical Service, Delta, British Columbia, or by Dr. Kevin Johnson and Dr. Paul Hayes at the University of Lethbridge, Lethbridge, Alberta.

Details of catalytic studies

Stock solutions of each complex were prepared in either toluene or DME at a concentration of 0.01 mol L^{-1}. Catalysis vials (1 dram capacity) were charged with either NaO*t*Bu (33.6 mg, 0.35 mmol, 1.4 equiv.) or KO*t*Bu (33.7 mg, 0.30 mmol, 1.2 equiv.) base and 0.500 mL of catalyst stock solution and stirred for 5 min. Then, chlorobenzene (25.3 μL, 0.25 mmol), amine (0.30 mmol, 1.2 equiv.), and the internal standard dodecane (40.9 μL, 0.18 mmol, 0.72 equiv.) were added and the vials were sealed with caps containing PTFE septa. The vials were removed from the glovebox and heated to 110 °C for between 18 and 24 h (not optimized) with vigorous stirring. An aliquot was then removed from each vial, filtered through a silica plug with approximately 1 mL of CH_2Cl_2, and analyzed by GC. Yields were determined from the GC data by calibration using authentic samples with dodecane as the internal standard.

N^1-*{2-(4-morpholinyl)phenyl}*-N^2-*(2,6-di*iso*propylphenyl)-1,2-ethanediamine (1)*

Within a dinitrogen-filled glovebox, [Pd(cinnamyl)Cl]$_2$ (65 mg, 0.125 mmol) and MDP (140 mg, 0.30 mmol) were combined in a 4 dram vial. Five millilitres of toluene was added and the mixture stirred for 10 min followed by the addition of 1.4 equiv. of NaO^{t}Bu (673 mg, 7 mmol). The vial was capped and removed from the glovebox and the substrates *N*-(2-bromophenyl)morpholine (1.21 g, 5 mmol) and *N*-2,6-di*iso*propylphenyl-(1,2-diaminoethane) (1.21 g, 5.5 mmol) were injected via syringe. The reaction mixture was heated to 110 °C with vigorous stirring for 2.5 h, at which time the reaction was complete as determined by GC. After cooling to ambient temperature, the reaction mixture was added to 50 mL of water and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extracts were dried with Na_2SO_4, filtered, and concentrated in vacuo, giving the crude product as a dark brown oil. Flash chromatography (5:1 hexanes – ethyl acetate) gave the purified product as a pale orange oil in 95% yield (1.807 g, 4.74 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.12–7.04 (m, 5H, 5,6-Ph + *m*,*p*-Dipp C*H*), 6.76–6.70 (m, 2H, 3-Ph + 4-Ph), 5.13 (s, 1H, N*H*), 3.86 (s, 4H, OCH_2 Morph), 3.43 (q, *J* = 4.9 Hz, 2H, NCH_2), 3.26 (7, *J* = 6.9 Hz, 2H, $CH(CH_3)_2$), 3.16 (t, *J* = 5.6 Hz, 2H, NCH_2), 2.93 (t, *J* = 4.6 Hz, 4H, NCH_2 Morph), 1.21 (d, *J* = 6.9 Hz, 12H, $CH(CH_3)_2$). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 143.2, 142.9, 142.7, 138.8, 125.4 (5-Ph), 124.2 (*p*-Dipp), 123.7 (*m*-Dipp), 119.7 (6-Ph), 117.3 (4-Ph), 110.5 (3-Ph), 67.8 (OCH_2 Morph), 51.9 (NCH_2 Morph), 51.0 (NCH_2), 44.7 (NCH_2), 27.7 ($CH(CH_3)_2$), 24.5 ($CH(CH_3)_2$). HRMS (ESI/[M + H]$^+$) calcd. for $C_{24}H_{36}N_3O$: 382.2853; found: 382.2853.

N^1-*{2-(4-morpholinyl)phenyl}*-N^2-*(2,4,6-trimethylphenyl)-1,2-ethanediamine (2)*

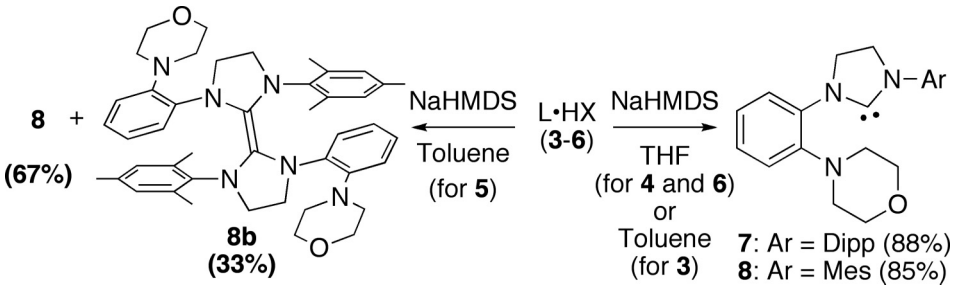
This was prepared similarly to **1** on a 5 mmol scale using a reduced catalyst loading of 2 mol% Pd. Purification by flash chromatography (1000:10:1 CH_2Cl_2–MeOH–NH_4OH) gave the purified product in 77% yield (1.312 g, 3.86 mol). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.99–6.93 (ov m, 2H, 5,6-Ph), 6.75 (s, 2H, *m*-Mes), 6.64 (td, *J* = 7.6, 1.4 Hz, 1H, 4-Ph), 6.59 (dd, *J* = 7.9, 1.2 Hz, 1H, 3-Ph), 5.01 (br s, 1H, N*H*), 3.74 (br s, 4H, OCH_2 Morph), 3.25 (br s, 2H, NCH_2), 3.13 (dd, *J* = 6.5, 4.7 Hz, 2H, NCH_2), 2.81 (t, *J* = 4.6 Hz, 4H, NCH_2 Morph), 2.17 (s, 6H,

Table 1. Crystal data and structure refinement details for **4**, **6**, and **8b**.

Compound	**4**	**6**	**8b**
Empirical formula	$C_{25}H_{34}BF_4N_3O$	$C_{22}H_{28}BF_4N_3O$	$C_{22}H_{27}N_3O$
Formula weight	479.36	437.28	349.47
Temperature (K)	173(2)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073	1.54178
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	*P*1	*Cc*	$P2_1/c$
a (Å)	9.0782(6)	15.2294(7)	9.1727(1)
b (Å)	9.7972(7)	10.0838(4)	17.2446(2)
c (Å)	16.209(1)	15.2480(7)	23.8059(3)
α (°)	84.141(1)	90	90
β (°)	74.065(1)	110.833(1)	98.283(1)
γ (°)	64.483(1)	90	90
V (Å^3)	1250.8(2)	2188.5(2)	3726.33(8)
Z	2	4	8
ρ_{calc} (Mg m^{-3})	1.273	1.327	1.246
μ (mm^{-1})	0.098	0.105	0.605
Crystal size (mm^3)	0.33 × 0.28 × 0.12	0.53 × 0.36 × 0.27	0.21 × 0.08 × 0.07
θ range (°)	1.31–26.39	2.48–28.27	3.18–69.94
Reflections collected	17281	9872	54370
Independent reflections	5123 (R_{int} = 0.0380)	5266 (R_{int} = 0.0126)	6902 (R_{int} = 0.0365)
Goodness-of-fit on F^2	1.064	1.043	1.042
Final *R* indices	R_1 = 0.0442,	R_1 = 0.0364,	R_1 = 0.0365,
$[I > 2\sigma(I)]^a$	wR_2 = 0.1154	wR_2 = 0.0938	wR_2 = 0.0981
R indices (all data)^a	R_1 = 0.0725	R_1 = 0.0380,	R_1 = 0.0408,
	wR_2 = 0.1410	wR_2 = 0.0954	wR_2 = 0.1013
Largest peak and hole (e Å^{-3})	0.203 and –0.217	0.279 and –0.309	0.219 and –0.162

$^aR_1 = \Sigma| (|F_o| - |F_c|)|/\Sigma|F_o|$. $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (mP)^2 + nP]$, where $P = (F_o^2 + 2F_c^2)/3$.

Scheme 3. Generation of free NHCs **7** and **8** and the dimer **8b**.

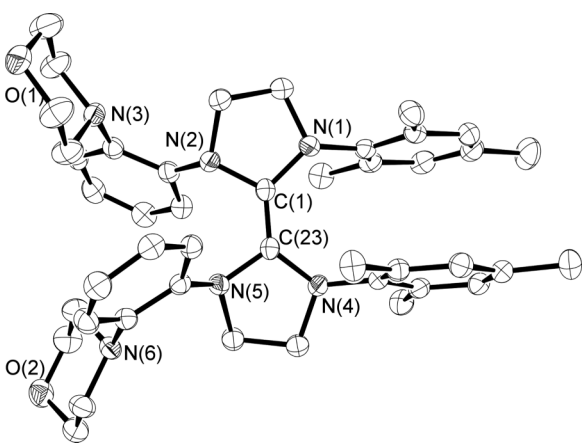


o-CH_3 Mes), 2.15 (s, 3H, *p*-CH_3 Mes). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ: 143.3, 143.1, 138.8, 130.1, 129.6 (*m*-Mes), 125.5 (5-Ph), 119.8 (6-Ph), 117.2 (4-Ph), 110.5 (3-Ph), 67.8 (OCH_2 Morph), 51.9 (NCH_2 Morph), 48.0 (NCH_2), 44.7 (NCH_2), 20.7 (*p*-CH_3 Mes), 18.4 (*m*-CH_3 Mes). HRMS (ESI/[M + H]$^+$) calcd. for $C_{21}H_{30}N_3O$: 340.2384; found: 340.2383.

[1-Dipp-3-{2-(4-morpholinyl)phenyl}imidazolidin-2-ylium][Cl] (3)

Under an ambient atmosphere, diamine **1** (1.29 g, 3.38 mmol) was dissolved in 40 mL of diethyl ether and cooled to 0 °C. With vigorous stirring, 3.4 mL of 4 mol L^{-1} HCl in 1,4-dioxane was added dropwise. The resulting white precipitate was collected by filtration, washed with diethyl ether (3 × 10 mL), and dried in vacuo. This material was then placed in a 4 dram vial with 10 mL of triethylorthoformate, and the resulting suspension was heated to 110 °C with vigorous stirring for 30 min, giving a clear solution. Cooled to ambient temperature, added 5 mL of ether, and let stand at ambient temperature overnight to allow crystallization of the product. The resulting white crystalline material was collected by filtration, washed copiously with diethyl ether, and dried in vacuo, giving the product as an analytically pure white solid in 85% yield (1.226 g, 2.86 mmol). ^1H NMR (500 MHz, $CDCl_3$) δ: 9.44 (s, 1H, NC*H*N), 7.71 (d, *J* = 7.6 Hz, 1 H, 6-Ph), 7.44 (t, *J* = 7.8 Hz, 1H, *p*-Dipp), 7.38 (t, *J* = 7.7 Hz, 1 H, 4-Ph), 7.26–7.22 (ov m, 4H, *m*-Dipp +

Fig. 3. Molecular structure of **8b** with hydrogen atoms omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths (Å) and angles (°) and torsion angles (°): C(1)–C(23) 1.354(2), C(1)–N(1) 1.425(2), C(1)–N(2) 1.430(2), N(1)–C(1)–C(23) 129.6(1), N(2)–C(1)–C(23) 121.0(1), N(1)–C(1)–C(23)–N(5) 166.5(1).



Scheme 4. Preparation of monodentate (NHC)Pd(η^3-cinnamyl)Cl and bidentate (NHC)$PdCl_2$ complexes.

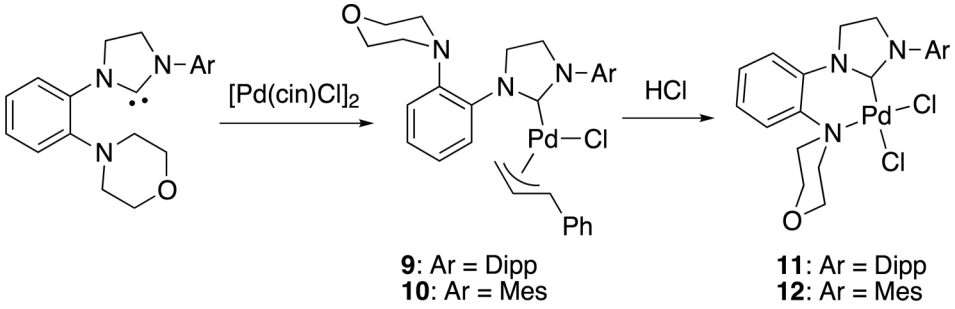
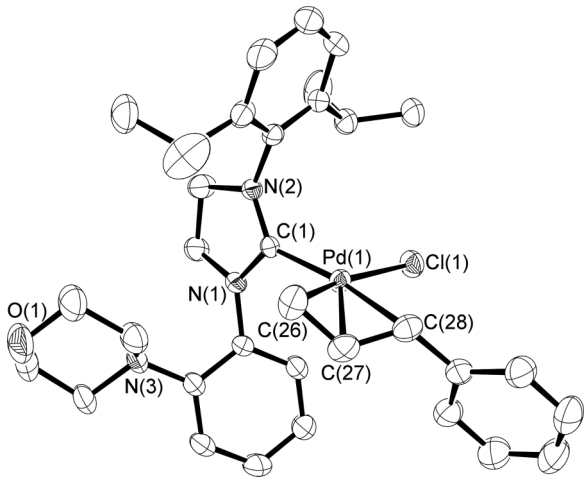


Fig. 4. Molecular structure of **9** with hydrogen atoms omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths (Å) and angles (°): Pd(1)–C(1) 2.021(2), Pd(1)–Cl(1) 2.3500(6), Pd(1)–C(26) 2.116(3), Pd(1)–C(27) 2.117(2), Pd(1)–C(28) 2.248(3), C(1)–Pd(1)–Cl(1) 94.42(6), C(1)–Pd(1)–C(26) 101.0(1), Cl(1)–Pd(1)–C(28) 97.20(7).



3,5-Ph), 5.04 (t, J = 10.4 Hz, 2H, NCH_2), 4.52 (t, J = 10.4 Hz, 2H, NCH_2), 3.80 (t, J = 4.2 Hz, 4H, OCH_2 Morph), 3.03 (sp, J = 6.7 Hz, 2H, CH(CH_3)$_2$), 2.98 (t, J = 4.3 Hz, 4H, NCH_2 Morph), 1.31 (d, J = 6.7 Hz, 6H, CH(CH_3)$_2$), 1.27 (d, J = 6.7 Hz, 6H, CH(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ: 158.4, 146.4, 131.5 (*p*-Dipp), 130.5 (4-Ph), 130.2, 130.0, 126.4 (6-Ph), 126.3 (3-Ph), 125.2 (*m*-Dipp), 122.0 (5-Ph), 67.1 (OCH_2 Morph), 54.4 (NCH_2), 52.9 (NCH_2 Morph), 51.7 (NCH_2), 29.0 (CH(CH$_3$)$_2$), 25.1 (CH(CH_3)$_2$), 24.6 (CH(CH_3)$_2$). The high purity of the material is demonstrated by the spectra presented below and comparison with spectra for **4**, which is shown to be pure by elemental analysis.

[1-Dipp-3-{2-(4-morpholinyl)phenyl}imidazolidin-2-ylium][BF_4] (4)

Under an ambient atmosphere, compound **1** (1.711 g, 4.48 mmol) was combined with 1.2 equiv. of NH_4BF_4 (564 mg, 5.38 mmol) and 5 mL of triethylorthoformate in a 4 dram vial. The resulting mixture was stirred vigorously at 110 °C for 30 min. Upon cooling to ambient temperature, the resulting white precipitate was collected by filtration and washed with diethyl ether (3 × 15 mL). The product was taken up in CH_2Cl_2 and filtered to remove unreacted NH_4BF_4. Evaporation of the solvent afforded the product as an analytically pure white powder in 84% yield (1.798 g, 3.75 mmol). ^1H NMR (500 MHz, $CDCl_3$) δ: 8.47 (s, 1H, NCHN), 7.54 (d, J = 8.2 Hz, 1H, 6-Ph), 7.50 (t, J = 7.8 Hz, 1H, *p*-Dipp), 7.43 (td, J = 7.8, 1.1 Hz, 1H, 5-Ph), 7.30 (ov m, 4H, m-Dipp + 3,4-Ph), 4.92 (dd, J = 12.1, 9.6 Hz, 2H, N-CH_2), 4.49 (dd, J = 12.0, 9.7 Hz, 2H, N-CH_2), 3.83 (t, J = 4.5 Hz, 4H, *o*-CH_2 Morph), 3.04 (sp, J = 6.8 Hz, 2H, CH(CH$_3$)$_2$), 2.99 (t, J = 4.6 Hz, 4H, N-CH_2 Morph), 1.35 (d, J = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.28 (d, J = 6.8 Hz, 6H, CH(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (126 MHz, 1:1 $CDCl_3$:CD_3OD) δ: 146.8, 146.1, 131.4 (*p*-Dipp), 130.8 (5-Ph), 129.9, 129.6, 125.7 (6-Ph), 125.6 (4-Ph), 124.9 (*m*-Dipp), 122.0 (3-Ph), 66.8 (*o*-CH_2 Morph), 53.7 (N-CH2), 52.4 (N-CH_2 Morph), 50.6 (N-CH_2), 28.7 (CH(CH$_3$)$_2$), 24.3 (CH(CH_3)$_2$), 23.9 (CH(CH_3)$_2$). Anal. calcd. (%) for $C_{25}H_{34}BF_4N_3O$: C 62.64, H 7.15, N 8.77; found: C 62.30, H 7.23, N 8.78.

Table 2. Crystal data and structure refinement details for **9**·C_6H_6 and **11**.

Compound	**9**·C_6H_6	**11**
Empirical formula	$C_{40}H_{48}ClN_3OPd$	$C_{25}H_{33}Cl_2N_3OPd$
Formula weight	728.66	568.84
Temperature (K)	173(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	$P2_1/c$
a (Å)	42.033(1)	19.6306(5)
b (Å)	10.1353(3)	7.6529(2)
c (Å)	17.4060(6)	19.0873(5)
α (°)	90	90
β (°)	101.48	117.69
γ (°)	90	90
V (Å^3)	7266.9(4)	2539.1(1)
Z	8	4
ρ_{calc} (Mg m^{-3})	1.332	1.488
μ (mm^{-1})	0.619	0.963
Crystal size (mm^3)	0.27 × 0.21 × 0.15	0.46 × 0.34 × 0.17
θ range (°)	0.99–27.52	1.17–27.39
Reflections collected	77163	36679
Independent reflections	8365 (R_{int} = 0.0455)	5743 (R_{int} = 0.0161)
Goodness-of-fit on F^2	1.048	1.194
Final *R* indices	R_1 = 0.0320,	R_1 = 0.0191,
[$I > 2\sigma(I)$][a]	wR_2 = 0.0733	wR_2 = 0.0565
R indices (all data)[a]	R_1 = 0.0424,	R_1 = 0.0208,
	wR_2 = 0.0812	wR_2 = 0.0652
Largest peak and hole (e Å^{-3})	1.554 and –1.090	0.691 and –0.688

[a] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (mP)^2 + nP]$, where $P = (F_o^2 + 2F_c^2)/3$.

[1-Mesityl-3-{2-(4-morpholinyl)phenyl}imidazolidin-2-ylium][Cl] (5)

This was prepared similarly to **3** from diamine **2** (1.303 g, 3.84 mmol), giving the product as an analytically pure white powder in 69% yield (1.02 g, 2.64 mmol). ^1H NMR ($CDCl_3$) δ: 9.45 (s, 1H, NCHN), 7.70 (d, 1H, 6-Ph), 7.27 (td, 1H, 4-Ph), 7.17–7.12 (ov m, 2H, 3,5-Ph), 6.87 (s, 2H, *m*-Mes), 4.90 (dd, 2H, NCH_2), 4.41 (dd, 2H, NCH_2), 3.70 (m, 4H, OCH_2 Morph), 2.90 (m, 4H, NCH_2 Morph), 2.31 (s, 6H, *o*-CH_3 Mes), 2.20 (s, 3H, *p*-CH_3 Mes). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 158.6 (NCHN), 146.0, 140.8, 135.1, 130.6, 130.3 (overlapping; 4-Ph + *m*-Mes), 130.3, 129.8, 126.3 (5-Ph), 126.0 (6-Ph), 122.1 (3-Ph), 67.2 (NCH_2), 52.8 (NCH_2), 51.7 (OCH_2 Morph), 51.5 (NCH_2 Morph), 21.2 (*o*-CH_3 Mes), 18.3 (*p*-CH_3 Mes). Anal. calcd. (%) for $C_{22}H_{28}ClN_3O$: C 68.47, H 7.31, N 10.98; found: C 68.22, H 7.16, N 10.82.

Fig. 5. Molecular structure of **11** with hydrogen atoms omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths (Å])and angles (°): Pd(1)–C(11) 1.969(2), Pd(1)–N(3) 2.148(1), Pd(1)–Cl(1) 2.3451(5), Pd(1)–Cl(2) 2.2946(4), C(11)–Pd(1)–N(3) 86.60(6), C(11)–Pd(1)–Cl(2) 91.53(5), Cl(1)–Pd(1)–Cl(2) 87.18(2), Cl(1)–Pd(1)–N(3) 94.60(4).

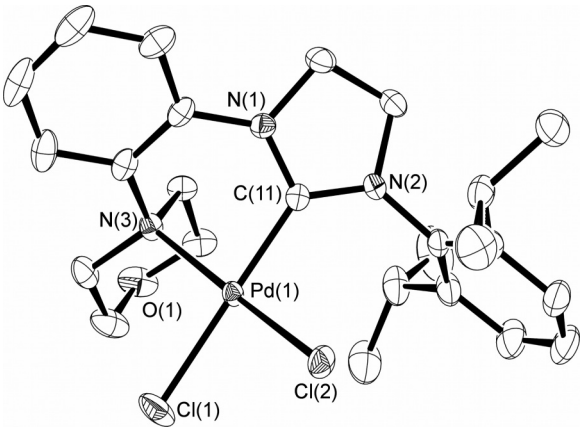
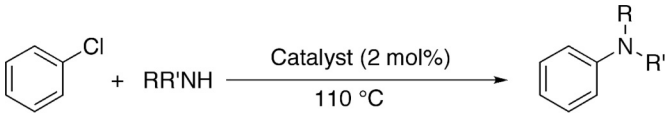


Table 3. GC yields for the arylation of various amines with chlorobenzene employing **9–14** as catalysts.



Entry	Catalyst	Morpholine yield (%)	Aniline yield (%)	Octylamine yield (%)
1	**9**	18	14	20
2	**10**	11	4	6
3	**11**	13	8	8
4	**12**	11	1	8
5	**13**	95	>99	>99
6	**14**	86	>99	>99
7	**9**[a]	42	10	28
8	**10**[a]	35	9	25
9	**13**[a]	>99	>99	66[b]
10	**14**[a]	34	15	>99

Note: Conditions: 2 mol% Pd, PhCl/amine/NaO^{t}Bu = 1:1.2:1.4, [ArCl] = 0.5 mol L^{-1}, toluene. Reactions were performed on a 0.25 mmol scale with reaction times of 18–24 h (unoptimized). Yields were determined from GC data calibrated using authentic samples with dodecane as the internal standard.

[a]1.2 equiv. of KO^{t}Bu, DME solvent.

[b]Complete consumption of starting material was observed. The low yield is attributed to formation of diarylation product.

[1-Mesityl–3-{2-(4-morpholinyl)phenyl}imidazolidin–2-ylium][BF$_4$] (6)

This was prepared similarly to **4** from diamine **2** (819 mg, 2.41 mmol) and 1.4 equiv. of NH_4BF_4 (354 mg, 3.38 mg), giving the product as an analytically pure white powder in 88% yield (932 mg, 2.13 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.56 (s, 1H, NC*H*N), 7.53 (dd, *J* = 7.9, 1.3 Hz, 1H, 6-Ph), 7.40 (t, *J* = 7.8 Hz, 1H, 4-Ph), 7.31–7.27 (ov m, 2H, 3,5-Ph), 7.01 (s, 2H, *m*-Mes), 4.86 (dd, *J* = 11.9, 9.7 Hz, 2H, NCH_2), 4.45 (dd, *J* = 12.0, 9.6 Hz, 2H, NCH_2), 3.80 (t, *J* = 4.6 Hz, 4H, OCH_2 Morph), 2.98 (t, *J* = 4.6 Hz, 4H, NCH_2 Morph), 2.38 (s, 6H, *o*-CH_3 Mes), 2.33 (s, 3H, *p*-CH_3 Mes). ^{1}H NMR (500 MHz, DMSO-d_6) δ: 9.22 (s, 1H, NC*H*N), 7.60 (dd, *J* = 7.9, 1.4 Hz, 1H, 6-Ph), 7.49 (ddd, *J* = 8.0, 7.4, 1.4 Hz, 1H, 4-Ph), 7.41 (dd, *J* = 8.1, 1.3 Hz, 1H, 3-Ph), 7.30 (td, *J* = 7.6, 1.1 Hz, 1H, 5-Ph), 7.11 (s, 2H, *m*-Mes), 4.72 (dd, *J* = 12.0, 9.3 Hz, 2H, NCH_2), 4.41 (dd, *J* = 11.9, 9.5 Hz, 2H, NCH_2), 3.78 (t, *J* = 4.5 Hz, 4H, OCH_2 Morph), 2.94 (t, *J* = 4.5 Hz, 4H, NCH_2 Morph), 2.35 (s, 6H, *o*-CH_3 Mes), 2.30 (s, 3H, *p*-CH_3 Mes). ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) δ: 159.3 (N*C*HN), 146.8, 139.7, 135.3, 131.1, 130.6 (4-Ph), 130.1, 129.5 (*m*-Ph), 126.0 (6-Ph), 124.8 (5-Ph), 122.0 (3-Ph), 66.3 (OCH_2 Morph), 51.8 (NCH_2 Morph), 50.9 (NCH_2), 50.1 (NCH_2), 20.6 (*p*-CH_3 Mes), 17.3 (*m*-CH_3 Mes). Anal. calcd. (%) for $C_{22}H_{28}BF_4N_3O$: C 60.43, H 6.45, N 9.61; found: C 60.21, H 6.42, N 9.56.

1-Dipp-3-{2-(4-morpholinyl)phenyl}imidazolidin-2-ylidene (7)

Within a dinitrogen-filled glovebox, compound **5** (400 mg, 0.834 mmol) was combined with 1 equiv. of NaHMDS (153 mg, 0.834 mmol) in a 4 dram vial. To the vial was added 5 mL of THF and the mixture was stirred for 1 h. Filtration through a plug of celite gave a clear solution, which was concentrated to approximately 1 mL. To this material was added 5 mL of hexanes and the resultant mixture was cooled to –35 °C for 18 h, resulting in crystallization of **7**. The supernatant was decanted and the crystals were washed with cold hexanes (3 × 3 mL) and dried in vacuo, giving 245 mg of the product. A second crop of 43 mg was obtained from the combined supernatant and washings after cooling to –35 °C for an additional 48 h, giving a total yield of 88% (288 mg, 0.736 mmol). ^{1}H NMR (500 MHz, C_6D_6) δ: 7.80 (dd, *J* = 7.8, 1.6 Hz, 1H, 6-Ph), 7.26 (dd, *J* = 8.3, 7.1 Hz, 1H, *p*-Dipp), 7.17 (d, *J* = 8.1 Hz, 2H, *m*-Dipp), 7.09 (ddd, *J* = 8.0, 7.4, 1.7 Hz, 1H, 4-Ph), 6.97 (td, *J* = 7.6, 1.4 Hz, 1H, 5-Ph), 6.79 (dd, *J* = 8.0, 1.4 Hz, 1H, 3-Ph), 3.94 (dd, *J* = 11.0, 9.0 Hz, 2H, NCH_2), 3.68 (t, *J* = 4.6 Hz, 4H, OCH_2 Morph), 3.47 (dd, *J* = 11.0, 9.0 Hz, 2H, NCH_2), 3.17 (sp, *J* = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 2.85 (t, *J* = 4.6 Hz, 4H, NCH_2 Morph), 1.29 (d, *J* = 6.9 Hz, 6H), 1.23 (d, *J* = 6.9 Hz, 6H). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ: 243.68 (carbene), 147.2, 147.0, 139.5, 138.6, 129.8 (6-Ph), 128.4 (*p*-Dipp), 127.1 (4-Ph), 124.1 (*m*-Dipp), 123.8 (5-Ph), 118.9 (3-Ph), 67.4 (NCH_2 Morph), 54.6 (NCH_2), 51.6 (OCH_2 Morph), 48.6 (NCH_2), 29.0 (*C*H(CH$_3$)$_2$), 25.2 (CH(*C*H$_3$)$_2$), 23.7 (CH(*C*H$_3$)$_2$). Anal. calcd. (%) for $C_{25}H_{33}N_3O$: C 76.69, H 8.49, N 10.73; found: C 76.51, H 8.30, N 10.61.

1-Mesityl-3-{2-(4-morpholinyl)phenyl}imidazolidin-2-ylidene (8)

This was prepared similarly to **7** from compound **6** (400 mg, 0.915 mmol), giving a crystalline white solid in 85% yield (272 mg, 0.778 mmol). ^{1}H NMR (500 MHz, C_6D_6) δ: 7.87 (dt, *J* = 7.8, 1.2 Hz, 1H, 6-Ph), 7.09 (ddd, *J* = 8.0, 7.4, 1.7 Hz, 1H, 4-Ph), 6.98 (td, *J* = 7.6, 1.4 Hz, 1H, 5-Ph), 6.84 (s, 2H, *m*-Mes), 6.81 (dd, *J* = 8.0, 1.4 Hz, 1H, 3-Ph), 3.92 (m, 2H, NCH_2), 3.64 (m, 4H, OCH_2 Morph), 3.34 (m, 2H, NCH_2), 2.84 (t, *J* = 4.6 Hz, 4H, NCH_2 Morph), 2.25 (s, 6H, *o*-CH_3 Mes), 2.17 (s, 3H, *p*-CH_3 Mes). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ: 243.9 (carbene), 146.8, 139.7, 138.7, 136.5, 136.0, 129.6 (6-Ph), 129.5 (*m*-Mes), 126.9 (4-Ph), 123.8 (5-Ph), 118.9 (3-Ph), 67.4 (OCH_2 Morph), 51.7 (NCH_2), 51.6 (NCH_2 Morph), 48.5 (NCH_2), 21.1 (*p*-CH_3 Mes), 18.2 (*m*-CH_3 Mes). Anal. calcd. (%) for $C_{22}H_{27}N_3O$: C 75.61, H 7.79, N 12.02; found: C 75.92, H 8.22, N 12.01.

Pd(1-Dipp-3-{2-(4-morpholinyl)phenyl}imidazolidin-2-ylidene) (cinnamyl)Cl (9)

Within a dinitrogen-filled glovebox, a slight excess of carbene **7** (300 mg, 0.766 mmol) in 2 mL of THF was added dropwise to a rapidly stirring suspension of [Pd(cinnamyl)Cl]$_2$ (191 mg, 0.369 mmol) in 2 mL of THF in a 4 dram vial, resulting in a pale yellow solution. The reaction mixture was stirred for 30 min and then removed from the glovebox and worked up under ambient atmosphere. The reaction mixture was filtered through a short plug of silica, which was washed down with THF (5 mL). Evaporation of the solvent afforded the product as a light yellow powder in >99% yield (479 mg, 0.736 mmol). ^{1}H NMR (500 MHz, C_6D_6) δ: 8.78 (br s, 1H, 6-Ph), 7.20–7.18 (ov m, 2H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.09–6.98 (m, 7H), 6.69 (dd, *J* = 7.9, 1.3 Hz, 1H, 3-Ph), 5.04 (dt, *J* = 12.4, 9.3 Hz, 1H, cinnamyl C*H*), 4.37 (br d, *J* = 12.8 Hz, 1H, cinnamyl C*H*), 3.72 (t, *J* = 4.5 Hz, 4H, OCH_2 Morph), 3.7–3.3 (br ov m, 6H, NCH_2 Morph + C*H*(CH$_3$)$_2$), 3.02 (br s, 2H, NCH_2), 2.91 (br s, 1H, cinnmyl CH_2), 2.81 (br s, 2H, NCH_2), 1.75 (br d, *J* = 8.5 Hz, 1H, cinnamyl CH_2), 1.44 (br s, 6H, CH(CH_3)$_2$), 1.09 (d, *J* = 6.8 Hz, 6H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ: 211.9 (carbene), 146.9, 138.5, 136.4, 135.5, 131.7 (6-Ph), 129.6, 128.8, 128.4, 128.0, 126.8, 124.7, 123.5, 119.1 (3-Ph), 109.1 (cinnamyl CH), 90.6 (cinnamyl CH), 67.5 (OCH_2 Morph), 55.0

(NCH$_2$ Morph), 51.9 (NCH$_2$), 48.8 (NCH$_2$), 45.5 (cinnamyl CH$_2$), 28.6 (CH(CH$_3$)$_2$), 26.7 (CH(CH$_3$)$_2$), 24.0 (CH(CH$_3$)$_2$). One quaternary C is not observed due to obscuring solvent signals. Anal. calcd. (%) for $C_{34}H_{42}ClN_3OPd$: C 62.77, H 6.51, N 6.46; found: C 62.82, H 6.58, N 6.42.

Pd(1-Mesityl-3-{2-(4-morpholinyl)phenyl}imidazolidin-2-ylidene)(cinnamyl)Cl (10)

This was prepared similarly to **9** from carbene **8** (250 mg, 0.715 mmol) and [Pd(cinnamyl)Cl]$_2$ (178 mg, 0.344 mmol), giving the complex as a light yellow powder in >99% yield (416 mg, 0.684 mmol). ^{1}H NMR (500 MHz, C_6D_6) δ: 8.54 (br s, 1H, 6-Ph), 7.13 (d, J = 7.4 Hz, 2H, *o*-Ph cinnamyl), 7.07 (t, J = 7.7 Hz, 1H, 4-Ph), 7.04–6.98 (ov m, 3H, *m*-Ph cinnamyl + 5-Ph), 6.96 (t, J = 7.1 Hz, 1H, *p*-Ph cinnamyl), 6.78 (br s, 2H, *m*-Mes), 6.68 (d, J = 7.9 Hz, 1H, 3-Ph), 5.04 (m, 1H, cinnamyl), 4.31 (d, J = 12.4 Hz, 1H, cinnamyl), 3.94 (br s, 2H, NCH$_2$), 3.68 (t, J = 4.1 Hz, 4H, OCH$_2$ Morph), 3.33 (br m, 2H, NCH$_2$), 3.01–2.86 (br ov m, 5H, NCH$_2$ Morph + cinnamyl), 2.28 (br s, 6H, *m*-CH$_3$ Mes), 2.10 (s, 3H, *p*-CH$_3$ Mes), 1.90 (d, J = 10.9 Hz, 1H, cinnamyl). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ: 211.4 (s, PdC), 147.1, 138.7, 138.2, 136.8, 135.4, 131.5 (6-Ph), 129.5 (*m*-Mes), 128.7 (4-Ph), 126.8 (s), 128.2 (*m*-Ph cinnamyl), 128.0 (*o*-Ph cinnamyl), 126.8 (*p*-Ph cinnamyl), 123.4 (5-Ph), 119.2 (3-Ph), 109.5 (cinnamyl), 90.6 (cinnamyl), 67.5 (OCH$_2$ Morph), 51.8 (NCH$_2$ Morph), 51.5 (NCH$_2$), 49.2 (NCH$_2$), 45.5 (cinnamyl CH$_2$), 21.1 (br s, *p*-CH$_3$ Mes), 18.4 (*m*-CH$_3$ Mes). The signal for one quaternary C is not observed. Anal. calcd. (%) for $C_{31}H_{36}ClN_3OPd$: C 61.19, H 5.96, N 6.91; found: C 61.17, H 6.00, N 6.70.

Pd(1-Dipp-3-{2-(4-morpholinyl)phenyl}imidazolidin-2-ylidene)Cl$_2$ (11)

Under an ambient atmosphere, compound **9** (106 mg, 0.163 mmol) was dissolved in 1 mL of THF in a 1 dram vial, to which was added 1 mL of a 4 mol L^{-1} HCl solution in 1,4-dioxane with stirring. The product immediately began to precipitate as a light yellow solid, and the reaction mixture was stirred for a total of 15 min. The product was collected by filtration, washed with diethyl ether (3 × 5 mL), and dried in vacuo, giving **11** as a light yellow powder that is approximately 80% pure on the basis of NMR data in an overall yield of 80% (74 mg, 0.13 mmol). ^{1}H NMR (500 MHz, DMSO-d_6) δ: 8.77 (d, J = 7.6 Hz, 1H, 6-Ph), 7.47 (t, J = 7.7 Hz, 1H, *p*-Dipp), 7.40 (td, J = 7.7, 1.1 Hz, 1H, 4-Ph), 7.35 (d, J = 7.7 Hz, 2H, *m*-Dipp), 7.25 (td, J = 7.6, 0.9 Hz, 1H, 5-Ph), 7.19–7.18 (m, 1H, 3-Ph), 6.00 (s, 4H, NCH$_2$ Morph), 4.01 (t, J = 9.8 Hz, 2H, NCH$_2$), 3.78–3.75 (m, 4H, OCH$_2$ Morph), 3.30 (sp, J = 6.5 Hz, 2H, CH(CH$_3$)$_2$), 3.24–3.11 (br s, 2H, NCH$_2$), 1.34 (d, J = 6.5 Hz, 6H, CH(CH$_3$)$_2$), 1.13 (d, J = 6.9 Hz, 6H, CH(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) δ: 147.9, 146.8, 135.2, 134.5, 130.2 (6-Ph), 129.9 (*p*-Dipp), 129.0 (4-Ph), 124.8 (*m*-Dipp), 123.0 (5-Ph), 120.3 (3-Ph), 66.8 (OCH$_2$ Morph), 55.0 (NCH$_2$), 51.8 (NCH$_2$ Morph), 48.8 (NCH$_2$), 28.4 (CH(CH$_3$)$_2$), 27.1 (CH(CH$_3$)$_2$). The signal associated with the carbenic C is apparently too broad to be observed.

Pd(1-Mesityl-3-{2-(4-morpholinyl)phenyl}imidazolidin-2-ylidene)Cl$_2$ (12)

This was prepared similarly to **11** from complex **10** (90 mg, 0.15 mmol), giving a light yellow powder that is approximately 75% pure on the basis of NMR data in overall 94% yield (73 mg, 0.14 mmol). ^{1}H NMR (500 MHz, DMSO-d_6) δ: 8.70 (d, J = 7.6 Hz, 1H, 6-Ph), 7.99 (br m, 2H, NCH$_2$), 7.38 (t, J = 7.7 Hz, 1H, 4-Ph), 7.22 (t, J = 7.6 Hz, 1H, 5-Ph), 7.17 (d, J = 7.4 Hz, 1H, 3-Ph), 7.01 (s, 2H, *m*-Mes), 4.43 (br s, 2H, NCH$_2$), 4.00 (t, J = 10.0 Hz, 2H, NCH$_2$), 3.75 (m, 4H, OCH$_2$ Morph), 3.11 (br m, 4H, NCH$_2$ Morph), 2.38 (6H, *m*-CH$_3$ Mes), 2.30 (s, 3H, *p*-CH$_3$ Mes). ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) δ: 146.6 (s), 137.8 (s), 137.0 (s), 134.9 (s), 133.8 (s), 129.9 (6-Ph), 129.2 (*m*-Mes), 128.5 (4-Ph), 122.6 (5-Ph), 119.9 (3-Ph), 66.4 (OCH$_2$ Morph), 51.2 (NCH$_2$ Morph), 20.6 (p-CH$_3$ Mes), 18.7 (*m*-CH$_3$ Mes). The signals associated with the carbenic C and two aliphatic CH$_2$ groups are too broad to be observed.

Details of crystallographic studies

Crystals of **4** and **6** were grown by slow diffusion of ether into CH$_2$Cl$_2$ solutions of the compounds. Crystals of **8b** were grown at –35 °C from a solution of the compound and **8** in a mixture of THF and pentane. Crystals of **9**·C$_6$H$_6$ were grown by slow diffusion of pentane into a solution of the compound in benzene. Crystals of **11** were grown by slow evaporation of a dilute CH$_2$Cl$_2$–MeOH solution. Crystallographic data were obtained at 173(2) K for **4**, **6**, **8b**, and **9**·C$_6$H$_6$ and at 296(2) K for **11** on either a Bruker PLATFORM/SMART 1000 CCD diffractometer or a Bruker D8/APEX II CCD diffractometer using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation for **4**, **6**, **9**, and **11** or Cu Kα (λ = 1.54178 Å) for **8b**. Unit cell parameters were determined and refined on all reflections. Data reduction and correction for Lorentz polarization were performed using Saint-plus,[19] and scaling and absorption correction were performed using the SADABS software package.[20] Structure solution by direct methods and least-squares refinement on F^2 was performed using the SHELXTL software suite.[21] Nonhydrogen atoms were refined with anisotropic displacement parameters, while hydrogen atoms were placed in calculated positions and refined with a riding model. Multiscan absorption correction was employed in all cases. Structural figures were generated with ORTEP-3.[22] Crystallographic data are given in Tables 1 and 2.

Supplementary material

Supplementary data containing NMR spectra of all reported compounds are available with the article through the journal Web site at http://nrcresearchpress.com/doi/suppl/10.1139/cjc-2013-0132. CCDC 931142–931146 contain the supplementary crystallographic data for this paper. These data can be obtained, free of charge, via http://www.ccdc.cam.ac.uk/products/csd/request/ (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: 44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

Notes

The authors declare the following competing financial interest(s): Dalhousie University holds patents on the MDP ligand used during the course of this research, from which M.S. receives royalty payments.

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