P-C Bond Activation and Transfer of a Diphenylphosphino Unit from 1,1'-*Bis*(diphenylphosphino)ferrocene: Unexpected Templated Synthesis of an *N^N⁻^P* Pincer Ligand Palladium Complex

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ABSTRACT

The Pd-catalyzed Buchwald-Hartwig amination of 2-bromo-1-iodobenzene with (4-amino-2-*tert*-butyl)phenanthridine using 1,1'-*bis*(diphenylphosphino)ferrocene (dppf) results in a side-reaction involving the first reported example of P-C bond activation of dppf and the templated formation of an *N^N-^P*-supported Pd(II) coordination complex. The full characterization of this complex along with a proposed mechanism for a rare example of unstrained P-C(cyclopentadienyl) bond activation are described.

INTRODUCTION

Palladium-catalyzed formation of C(sp^2)-N bonds via the selective coupling of aryl halides and pseudo-halides with amines, the so-called 'Buchwald-Hartwig amination' reaction,[1] is by now a well-established methodology with wide-ranging applications.[2] Of the myriad ligands reported for this transformation,[3,4] '2nd generation' chelating, aromatic *bis*(phosphines) such as 2,2'-*bis*(diphenylphosphino)-1,1'-binaphthyl (BINAP)[5] and 1,1'-*bis*(diphenylphosphino)ferrocene (dppf)[6] still remain in widespread use for Buchwald-Hartwig aminations and related Pd-catalyzed reactions, with high yields ascribed to the promotion of reductive elimination of the coupled product[7] and stable, bidentate coordination. For the most part, such phosphine ligands remain faithful spectators in catalysis. However, given the central role of electron-rich, low-coordinate Pd(0) species in Buchwald-Hartwig amination catalytic cycles,[8–10] ligand decomposition through ligand bond activation is possible and can complicate reactivity.

Activation of arylphosphine ligands most commonly involves β-metallation by means of metal insertion into a C-H bond to form a four-membered cyclometallated ring (Figure 1a).[11,12] P-C bond activation and aryl group transfer have also been reported,[13] in some cases leading to the formation of novel, catalytically active species.[14,15] P-C activation has historically been associated with the formation of multimetallic, phosphide-bridged (e.g., μ^2-PPh$_2$) clusters (Figure 1b),[16] or observation of substituents rearranging between different phosphines (Figure 1c),[17,18] and largely studied in the context of catalyst deactivation.[19] Recently, aryl group exchange has been exploited in the development of novel cross-metathesis methodologies that enable preparation of a host of novel phosphines[20] and phospholes[21], *inter alia*. These are examples of catalytic isofunctional reactions[22] that demonstrate how interesting applications can emerge from fundamental studies of 'side reactions'.[20]
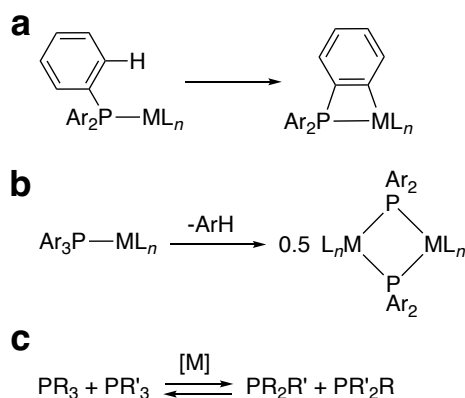
Figure 1. C-H/P-C reactivity of metal-coordinated arylphosphines: (a) C-H activation and cyclometallation; (b) P-C activation and bridging phosphide formation; and (c) phosphine aryl group scrambling.

In the context of multidentate phosphines, numerous examples of P-C(sp^2) activation of chelating alkylenyl-bridged diphosphines [$e.g.$, $Ar_2P(CH_2)_nPAr_2$] and related species have been reported.[20,23,24] To our knowledge, similar reactivity with dppf has not been observed. For example, [(dppf)Pd(diphenyl-2-(6-methyl-pyridyl)phosphine)]$^{2+}$ undergoes P-C bond cleavage to form a palladium aryl complex upon treatment with H_2 but with activation of the phosphorus-pyridyl P-C bond; the dppf remains intact.[25] When P-C(cyclopentadienyl) bond cleavage has been reported, it is usually driven by release of ring-strain, as in phospha[1]ferrocenophanes.[26,27] In addition, examples of P-C bond activation leading directly to formation of multidentate ligand-metal coordination complexes are rare. Chelation-assisted P-C activation has provided access to 'pincer'-type complexes of phosphine/phosphine oxide ligands,[28] while thermal rearrangement and P-C bond cleavage in a preformed tridentate diphosphine/*N*-heterocyclic carbene-supported *P^C^P* rhodium complex was used to form a ring-contracted *C^C^P*-bound species.[29] Metal templated synthesis[30] can facilitate assembly of otherwise difficult to access ligand scaffolds.[31–34] Here, we report the unexpected rearrangement of dppf during Buchwald-Hartwig amination catalysis

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leading to the formation of a novel benzannulated *P^N^N*-chelating pincer-type ligand-metal complex.

RESULTS AND DISCUSSION

As part of our work developing synthetic routes to incorporating benzannulated *N*-heterocycles into multidentate ligand platforms, we became interested in pincer-type scaffolds which combine amido donors with strongly π-accepting groups such as phenanthridine (3,4-benzoquinoline). These sorts of architectures have allowed construction of unusually deep-red emitting phosphorescent materials,[35,36] coordination complexes with promising anti-cancer activity,[37] and iron(II) compounds with panchromatic absorption and exceptionally long-lived charge-transfer excited states.[38] In order to expand our library of synthetically available analogs, we targeted the formation of secondary *N,N*-(2-bromophenyl)(phenanthridinyl)amines that might be further elaborated into tridentate, pincer-like scaffolds via functionalization of the arylbromide, as has been demonstrated for related *P^N^N*-diarylamido ligands.[39] To do so, we attempted the Pd-catalyzed Buchwald-Hartwig amination of 2-bromo-1-iodobenzene with (4-amino-2-*tert*-butyl)phenanthridine (Scheme 1).
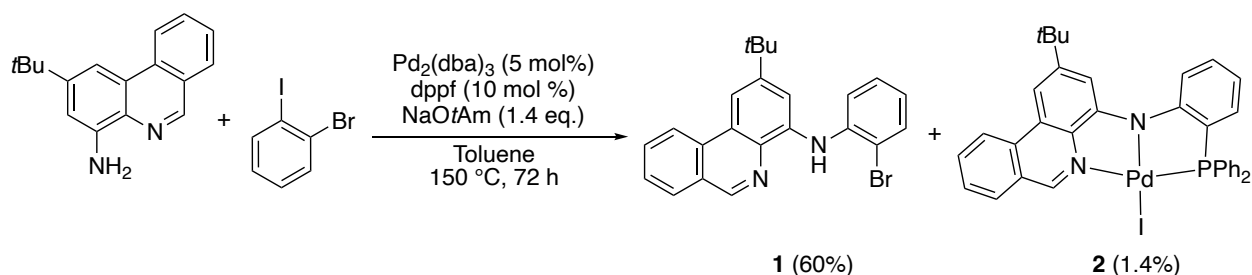

Scheme 1. Synthesis of **1** and unexpected formation of **2** with isolated yields in parentheses.

The two reagents were heated in the presence of 5 mol% $Pd_2(dba)_3$ (dba = dibenzylideneacetone), a source of Pd(0), 10 mol% dppf and a base (sodium *tert*-amoxide, NaO*t*Am; 1.4 equivalents) in toluene. Preliminary experiments indicated that appreciable conversion was only observed following extended heating, so the mixture was heated in an oil bath set to 150 °C for 72 h. Following work-up and column chromatography, the target compound **1** was isolated in moderate yield (60%) as a light-yellow solid (R_f = 0.567). Compound **1** was fully characterized by multi-nuclear NMR spectroscopy and high-resolution mass spectrometry (HRMS). A downfield shifted ^{1}H NMR signal characteristic of the 'imine-like' *H*C=N subunit of the phenanthridinyl ring[40] is evident at 9.19 ppm [δ(^{13}C) = 150.5 ppm]. The rest of the spectroscopic data is similarly consistent with the proposed structure. We were also able to isolate a dark purple-red material in limited yield with a smaller retention factor (R_f = 0.333). A UV-Vis absorption spectrum of the material (Figure S1) exhibited a broad peak in the typical range for metal-to-ligand-charge-transfer (MLCT) of Group 10 metal complexes of diarylamido ligands (λ_{max} = 482 nm).[41] Assuming formation of a metal adduct of a secondary phenanthridinyl/aryl amine,[42] we were surprised to find a ^{31}P NMR signal for the isolated solid (δ_P = 47.3 ppm), consistent with a metal-bound phosphine.[43] The ^{1}H NMR signal for the phenanthridinyl *H*C=N subunit in this product was shifted further downfield to 9.84 ppm, also indicative of metal-coordination,[44] with coupling evident to [31]P ($^4J_{HP}$ = 6 Hz). The total number of hydrogen nuclei determined via integration of the spectrum indicated an extra 10 H atoms, consistent with installation of a PPh_2 fragment. HRMS supported formation of a complex additionally containing a palladium and iodide.

Single-crystals suitable for X-ray diffraction confirmed the construction of a *P^N^N*-supported palladium species (Figure 2). In it, the bromide *ortho* to the amine nitrogen in **1** has been

replaced with a PPh$_2$ fragment and the Pd center sits in a distorted square planar geometry (τ_4 = 0.123)[45] formed by the tridentate ligand, with an iodide occupying the fourth coordination site. The bond distances about the metal are typical for such complexes, with a slightly longer Pd-N distance to the *N*-heterocyclic donor [2.099(3) Å] compared with the amido nitrogen [2.017(3) Å]. The N$_{amido}$-Pd-I vector is nearly linear [178.22(10)°], while the constrained geometry of the ligand enforces a less obtuse N$_{phenanthridine}$-Pd-P angle [164.37(10)°]. As is usual for such ligands, intraligand repulsion between aromatic CH units of the diarylamido backbone causes a staggering of the two aryl rings, with ~33° angle between the plane of the phenanthridinyl and that of the phenylenyl ring, and C_s symmetry. The tricyclic phenanthridinyl unit resists bending out of the coordination plane more so than the phenylenyl ring (interplanar angle to least-squares plane containing P1-N2-N1-Pd1-I1 of 11° vs 25°).
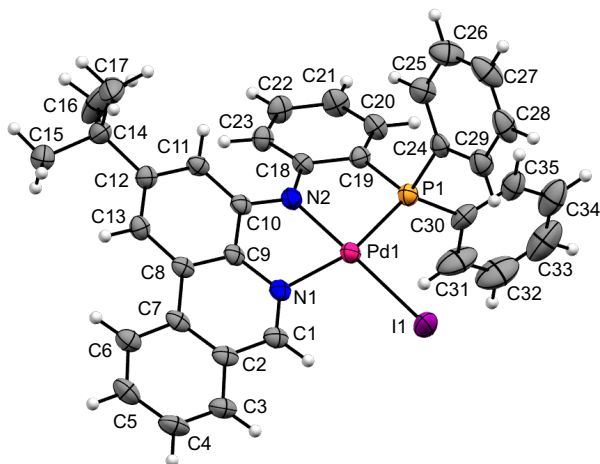
Figure 2. Solid-state structure of **2** with thermal ellipsoids shown at 50% probability levels. Selected bond distances (Å) and angles (°): Pd1-I1 2.5991(6), Pd1-N1 2.099(3), Pd1-N2 2.017(3), Pd1-P1 2.208(1); N1-Pd1-P1 164.4(1), N2-Pd1-I1 178.2(1), N1-Pd1-N2 81.0(1), P1-Pd1-N2 83.6(1), N1-Pd1-I1 98.77(9), P1-Pd1-I1 96.70(3).

To gain insight into the mechanism of the reaction, a small-scale reaction was performed inside a sealed J-Young tube and monitored via $^{31}P\{^1H\}$ NMR spectroscopy. Combining dppf (δ_P = -17.3 ppm) and Pd$_2$(dba)$_3$ at catalytically relevant concentrations gave rise to new ^{31}P signals at 31.8 ppm (singlet), 19.3 ppm (doublet, $^3J_{PP}$ = 8 Hz) and 18.0 ppm (doublet, $^3J_{PP}$ = 8 Hz; Figure S2). The singlet is consistent with the formation of (dppf)$_2$Pd, which has been previously reported at 25.91 ppm in a different solvent mixture (THF/d$_6$-acetone);[46] we do note that (dppf)PdCl$_2$ has been reported at δ_P = 34.0 ppm in CH$_2$Cl$_2$.[47] The two doublets at 19.3 ppm and 18.0 ppm arise from the formation of (dppf)Pd(dba), with weak coupling (8 Hz) between magnetically inequivalent, *cis*-disposed phosphines.[46] Upon addition of 2-bromo-1-iodobenzene, there is a slight shift to the ^{31}P singlet to 32.1 ppm (assigned to residual Pd(dppf)$_2$) and the new major product is represented by doublets at 24.6 and 7.7 ppm ($^3J_{PP}$ = 32 Hz) indicating the formation of (dppf)Pd(X)(PhY) (X/Y = Br or I).[46] This remains the major species in solution following the addition of (4-amino-2-*tert*-butyl)phenanthridine and base. Prolonged heating (24-48 h) complicates the $^{31}P\{^1H\}$ NMR spectra of the mixture, which retain broad peaks at ~25 and -15 ppm as the major species in solution. After 72 h, a signal attributable to **2** cannot be conclusively assigned; however, performing the reaction at the same scale in a 10 mL Teflon-stoppered flask and heating consistently for 3 d, the $^{31}P\{^1H\}$ NMR signal for **2** is clearly evident in the crude mixture prior to work-up (δ_P = 47.3 ppm, ~10% of the observable phosphorus-containing species; Figure 3a). The ^1H NMR spectrum of both crude mixtures showed the formation of **1**, confirming that the catalysis had proceeded in each case.
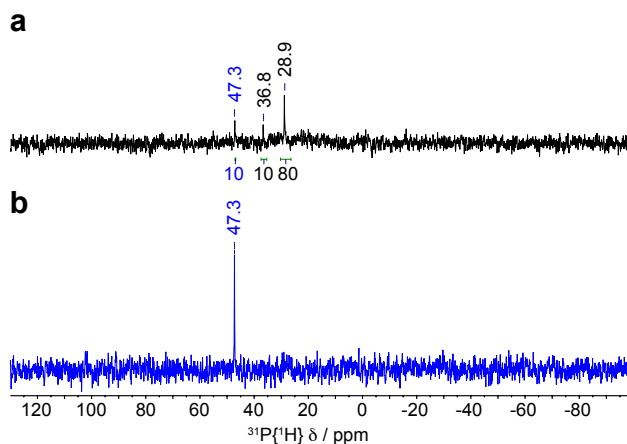
Figure 3. $^{31}P\{^1H\}$ NMR (CDCl$_3$, 121 MHz, 25 °C) of (a) the crude mixture showing the presence of **2** and (b) an isolated sample of **2**.

A tentative mechanism for the formation of both **1** and **2** is proposed in Figure 4. Following the generally accepted mechanism for Buchwald-Hartwig amination,[8–10] ligand substitution with dppf produces the active catalyst (dppf)Pd(dba) (**A**). In the dominant catalytic cycle forming **1**, this Pd(0) species undergoes dissociation of dba and oxidative addition of the more reactive C-I bond to form **B**. Both (dppf)Pd(dba) and a putative (dppf)Pd(Ar)(X) species are identifiable by ^{31}P NMR spectroscopy. Halide-amine ligand exchange/deprotonation installs the phenanthridinyl amine on Pd, forming Pd(II) amido/aryl species **C**. This intermediate can then undergo reductive elimination and ligand substitution to release **1** via **D** as the major reaction pathway. In a minor pathway, we propose that aryl bromide oxidative addition may form the bromo/aryl Pd(II) species **E** instead of iodo/aryl intermediate **B**. Subsequent amine association/deprotonation forms **F**, followed by C-N bond formation to produce **G** bearing the iodo analog of **1** in the Pd coordination sphere. A second, rapid, intramolecular aryl iodide oxidative addition could form intermediate **H**. Intramolecular Ar-I oxidative addition may be more facile for **G** than the corresponding Ar-Br

oxidative addition for **D** due to the predilection of dppf for bidentate coordination and the preference of bromoarenes to react with lower coordinate Pd(0).[48]
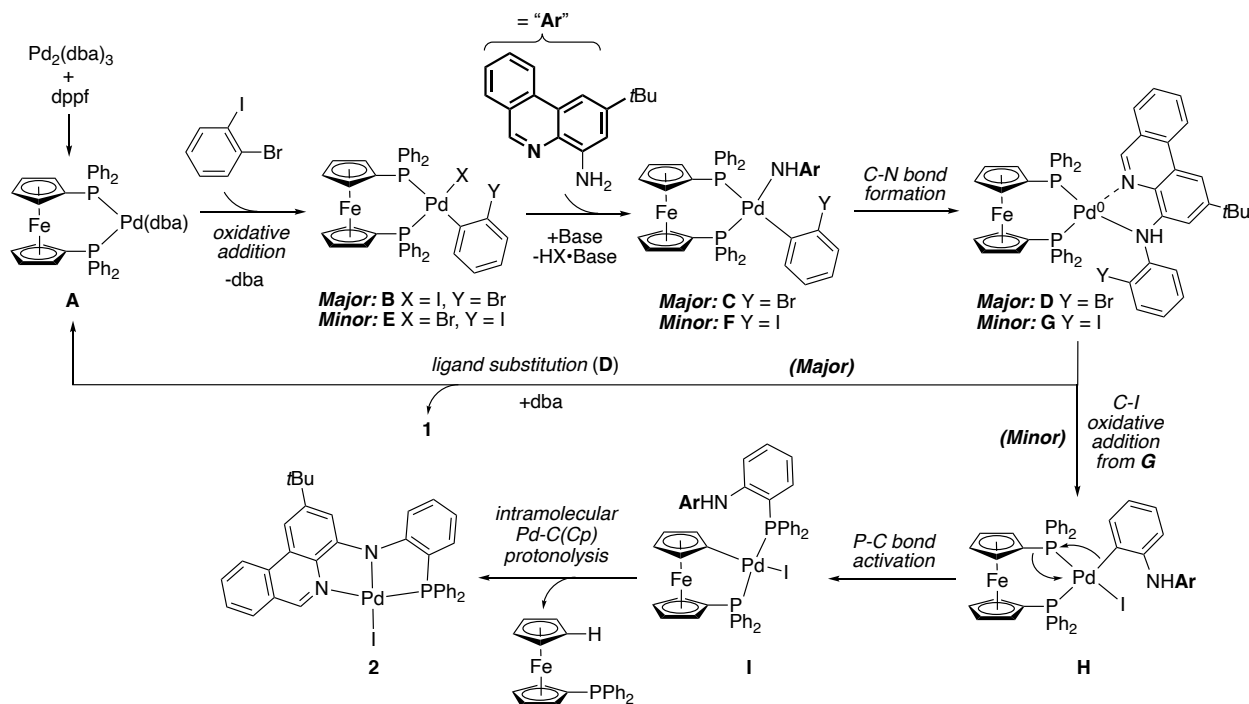
Figure 4. Proposed mechanism for formation of **1** and **2**.

Intermediate **H** then undergoes P-C bond activation to form **I**. It is not clear why this intermediate alone undergoes P-C bond rupture. It may be due to the electron-richness of the Pd-C moiety thanks to the presence of the ortho-amino substituent. However, it may also be that this intermediate is the sole species to undergo P-C bond cleavage leading to *irreversible* formation of a product (**2**). Three mechanistic steps can be considered here: direct oxidative addition of the P-C(Cp) (Cp = cyclopentadienyl) bond; migration of the aryl to P with formation of a metallophosphorane intermediate; and internal nucleophilic attack and formation of a Pd-C(Cp) bond.[24] While we have no direct evidence supporting any one particular pathway, we discount P-

C oxidative addition as no bridging phosphide species are formed.[25] We furthermore rule out metallophosphorane formation, as such species are typically associated with strongly electron-withdrawing groups such as fluorides.[49] Intramolecular protonolysis of **I** would then install the amido moiety on Pd while eliminating (diphenylphosphino)ferrocene. Signals in the range expected for the monophosphine were not observed;[26] however, the major species ($\delta_P = 28.9$ ppm, ~80%) observed by ^{31}P NMR spectroscopy in the crude reaction mixture aside from **2** has a chemical shift consistent with Lewis acid adducts of (diphenylphosphino)ferrocenes,[50] though we cannot exclude formation of dppf dioxide ($\delta_P = 28.2$ ppm).[51] Cleavage of unstrained P-C bonds to η^6-coordinated arene rings has been previously reported.[52] Catalysis of Buchwald-Hartwig amination using (1-diphenylphosphino)ferrocene supported Pd has also been described.[53]

To test the hypothesis that intramolecular Ar-I oxidative addition may be more facile for **G** than the corresponding Ar-Br oxidative addition for **D**, we investigated the reactivity of two alternative aryl halides – 1,2-diiodobenzene and 1,2-dibromobenzene. Using 1,2-diiodobenzene in place of 2-bromo-1-iodobenzene roughly trebled the crude yield of **2** based on integration of the [31]P{[1]H} spectrum (~34%; Figure S10). In comparison, the bromo analog of **2** was not observed to form from 1,2-dibromobenzene (Figure S11). Formation of **2** thus apparently requires the exclusive involvement of **G**, precluding a significant role for I/Br halide exchange from the bromo analog of **2**. In addition, when 1,2-diiodobenzene is used in place of 2-bromo-1-iodobenzene, the hydro-dehalogenated product (*N*-phenyl-4-amino-2-*tert*-butyl)phenanthridine[42] (**3**) is formed in place of the expected (*N*-(2-iodophenyl)-4-amino-2-*tert*-butyl)phenanthridine (*i.e.*, the iodo analog of **1**), consistent with more reactive Ar-I bonds.

To probe the possibility that impurities present in commercially available dppf were responsible for the formation of **2**, dppf was purified by three successive recrystallizations which

afforded spectroscopically pure compound as evidenced by ^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectroscopy, elemental analysis and high-resolution mass spectrometry (see Supporting Information). Using thrice-recrystallized dppf resulted in the formation of **2** with approximately the same crude yield as with the as-received phosphine (~8% of the phosphorous-containing species observable in solution; Figure S21). This strongly supports formation of **2** from dppf rather than an impurity. Indeed, ^{31}P{^{1}H} NMR spectroscopic analysis of the reaction mixture resulting from the stoichiometric reaction of Pd$_2$(dba)$_3$, as-received dppf, (4-amino-2-*tert*-butyl)phenanthridine and 2-bromo-1-iodobenzene showed **2** had formed in more appreciable amounts (~20% of the phosphorus-containing species observable in solution; Figure S12). Reaction of a stoichiometric mixture of 1,2-diiodobenzene, (4-amino-2-*tert*-butyl)phenanthridine, Pd$_2$(dba)$_3$ and thrice-recrystallized dppf enabled isolation of **2** in higher yield (10.3%) alongside **3** (28% isolated yield; Scheme 2).
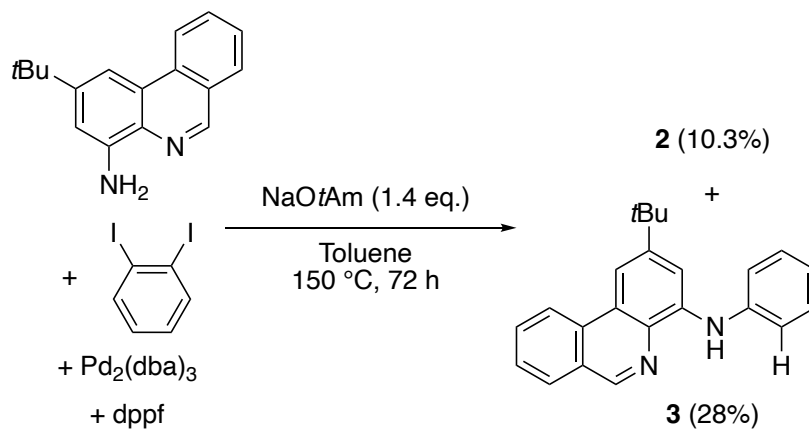
Scheme 2. Stoichiometric reaction conditions for formation of **2** and **3** with isolated yields in parentheses.

Conclusions

An unexpected PPh$_2$ group migration was observed during the Pd-catalyzed Buchwald-Hartwig amination of 2-bromo-1-iodobenzene with (4-amino-2-*tert*-butyl)phenanthridine, arising from P-C(Cp) bond activation of dppf. To our knowledge, this is the first such reported example arising from this commonly used bidentate ligand and is a rare example of P-C(Cp) bond cleavage not driven by ring-strain. The product, **2**, incorporated the new phosphine into a novel tridentate, pincer-like *P^N-^N* ligand framework which was isolated as a Pd(II) complex with an iodide occupying the fourth coordination site. The selective incorporation of iodide suggests a role for C-Br vs. C-I oxidative addition in the specific formation of this minor product. Efforts to further probe the mechanism of P-C(Cp) activation and elaborate the observed side-reaction into a templated synthesis of *P^N^N*-chelating pincer-type ligands[32] of phenanthridines is presently underway.

Experimental Section

Air-sensitive manipulations were carried out either in a N$_2$ filled glove box or using standard Schlenk techniques under Ar. *Tris*(dibenzylideneacetone)dipalladium(0) (Millipore Sigma), sodium *tert*-amoxide (Millipore Sigma) and 2-bromo-1-iodobenzene (Alfa Aesar) were purchased and used without any further purification. (4-Amino-2-*tert*-butyl)phenanthridine was prepared as previously reported.[38] 1,1'-*bis*(diphenylphosphino)ferrocene (Millipore Sigma) was purchased and used both as-received and following repeated recrystallization (3x) via slow diffusion of pentane layered over a concentrated solution of dppf in CH$_2$Cl$_2$ at -35 °C under inert conditions (see Supporting Information for further discussion of purification of dppf). Organic solvents used for absorption measurements were dried and distilled using appropriate drying agents prior to use. 1-

and 2D NMR spectra were recorded on Bruker Avance 300 MHz spectrometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to residual solvent peaks. Mass spectrometry (ESI-TOF/MS), was performed at the University of Manitoba on a Bruker Compact LC-ESI-TOF/MS analyzer. Elemental analysis was carried out at Intertek (Burnaby, BC). Electronic absorption spectra were recorded on an Agilent Technologies Cary 5000 Series UV-Vis-NIR spectrophotometer in dual beam mode.
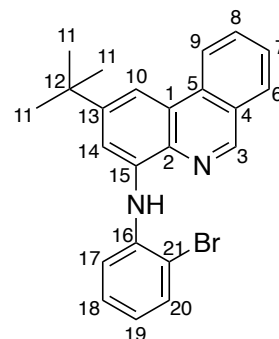
Synthesis of 1 and 2: Inside a N$_2$-filled glovebox, *tris*(dibenzylideneacetone)dipalladium(0) (0.175 g, 0.191 mmol) and 1,1'-*bis*(diphenylphosphino)ferrocene (0.232 g, 0.418 mmol; as-received) were combined in a 100 mL Teflon-stoppered flask and dissolved in 25 mL of anhydrous toluene. In a second 100 mL Schlenk flask, sodium *tert*-amoxide (0.634 g, 5.76 mmol) was dissolved in 25 mL of toluene. The flasks were brought out of the glovebox and connected to a Schlenk line. 1-Bromo-2-iodobenzene (513 μL, 4.09 mmol) was added to the Teflon-stoppered flask and after letting the mixture stir for 5 min, (4-amino-2-*tert*-butyl)phenanthridine (1.00 g, 4.01 mmol) was added. Then the toluene solution of sodium *tert*-amoxide was transferred from the Schlenk flask to the reaction mixture via cannula, and the flask sealed and heated in an oil bath set to 150 °C for 3 d. At that point, the flask was cooled to room temperature and the solvent removed under reduced pressure using a rotary evaporator. The crude mixture was dissolved in dichloromethane (100 mL) and washed with brine (3 x 100 mL). The organic layer was separated and dried under reduced pressure. ^{31}P{^{1}H} NMR spectroscopic analysis of the crude material obtained at this point showed **2** was ~10% of the phosphorus-containing species observable in solution, based on integration of the spectrum. The crude material was purified via flash column chromatography on silica gel using 1:9 mixture of ethyl acetate:hexanes as eluent. (*N*-(2-bromophenyl)-4-amino-2-*tert*-butyl)phenanthridine (**1**) was obtained as a brown oil (R$_f$ = 0.567).

Isolated yield = 0.971 g (60%). Pd(PNN)I (**2**) (R_f = 0.333) was obtained as a dark purple-red solid. Isolated yield = 0.0041 g (1.4% based on $Pd_2(dba)_3$).
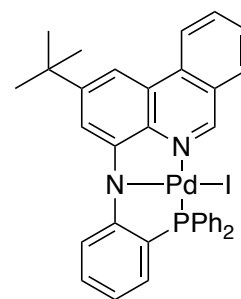
(*N*-(2-bromophenyl)-4-amino-2-*tert*-butyl)phenanthridine (1): ^{1}H NMR (CDCl$_3$, 300 MHz, 22 °C): δ 9.19 (s, 1H; C$_3$-*H*), 8.66 (d, 1H, J_{HH} = 8.4 Hz; C$_{20}$-*H*), 8.55 (br s, 1H; N*H*), 8.08-8.05 (m, 2H; C$_{10}$-*H* and C$_6$-*H*), 7.89-7.84 (m, 1H; C$_{19}$-*H*), 7.73-7.64 (overlapped m, 4H; C$_{14}$-*H*, C$_7$-*H*, C$_{17}$-*H* and C$_{18}$-*H*), 7.34-7.28 (m, 1H; C$_9$-*H*), 6.90-6.84 (m, 1H; C$_8$-*H*), 1.47 ppm (s, 9H; C$_{11}$-*H*). ^{13}C {^{1}H} NMR (CDCl$_3$, 75 MHz, 25 °C): δ 150.53 (*C$_3$*), 150.47 (*C$_2$*), 140.68 (*C$_4$*), 139.34 (*C$_{16}$*), 133.55 (*C$_7$*), 133.03 (*C$_5$*), 130.81 (*C$_{19}$*), 129.38 (*C$_{13}$*), 128.92 (*C$_6$*), 128.13 (*C$_9$*), 127.39 (*C$_{21}$*), 127.06 (*C$_1$*), 124.36 (*C$_{18}$*), 122.37 (*C$_{20}$*), 122.22 (*C$_8$*), 118.09 (*C$_{14}$*), 115.38 (*C$_{15}$*), 109.60 (*C$_{17}$*), 108.83 (*C$_{10}$*), 35.63 (*C$_{12}$*), 31.62 ppm (*C$_{11}$*). HRMS (ESI-TOF/MS, m/z) calcd. for $C_{23}H_{21}BrN_2$ [M]$^+$, 404.0883; found 404.0843. HRMS (ESI-TOF/MS, m/z) calcd. for $C_{23}H_{21}BrN_2$ [M+H]$^+$, 405.0961; found 405.0969.

Pd(PNN)I (2): ^{1}H NMR (CDCl$_3$, 300 MHz, 22 °C): δ 9.84 (d, 1H, $^4J_{HP}$ = 6 Hz; N=C*H*), 8.61 (d, 1H, J_{HH} = 9 Hz; Ar C*H*), 8.12 (d, 1H, J_{HH} = 9 Hz; Ar C*H*), 7.99 (d, 1H, J_{HP} = 3 Hz; Ar C*H*), 7.94-7.87 (overlapped m, 6H; Ar C*H*), 7.78 (s, 1H; Ar C*H*), 7.71 (t, 1H, J_{HH} = 7.5 Hz; Ar C*H*), 7.50-7.41 (overlapped m, 6H; Ar C*H*), 7.33-7.30 (m, 1H; Ar C*H*), 7.05-6.98 (m, 1H, Ar C*H*), 6.67 (t, 1H, J_{HH} = 7.5 Hz; Ar C*H*), 1.49 ppm (s, 9H; *t*Bu). ^{1}H{^{31}P} NMR (CDCl$_3$, 300 MHz, 22 °C): δ 9.84 (s, 1H; N=C*H*), 8.61 (d, 1H, J_{HH} = 8.8 Hz; Ar C*H*), 8.12 (d, 1H, J_{HH} = 8.2 Hz; Ar C*H*), 7.98 (s, 1H; Ar C*H*), 7.94-7.89 (overlapped m, 6H; Ar C*H*), 7.78 (s, 1H; Ar C*H*), 7.71 (t, 1H, J_{HH} = 7.8 Hz; Ar C*H*), 7.53-7.42 (overlapped m, 6H; Ar C*H*), 7.33-7.30 (m, 1H; Ar C*H*), 7.01 (d, 1H, J_{HH} =

7.2 Hz; Ar CH), 6.67 (t, 1H, J_{HH} = 7.5 Hz; Ar CH), 1.49 ppm (s, 9H; tBu). ^{31}P{^{1}H} NMR (CDCl$_3$, 121 MHz, 25 °C): δ 47.3 ppm (PPh$_2$). HRMS (ESI-TOF/MS, m/z) calcd. for C$_{35}$H$_{30}$IN$_2$PPd [M]$^+$, 742.0234; found 742.0213. UV-Vis (CH$_2$Cl$_2$, 22 °C): λ (ε) 482 (4 790), 401 (9 760), 323 nm (21 470 M^{-1} cm^{-1}).

Synthesis of 1 and 2 using thrice-recrystallized dppf: Inside a N$_2$-filled glovebox, *tris*(dibenzylideneacetone)dipalladium(0) (0.00370 g, 0.00401 mmol), 1,1'-*bis*(diphenylphosphino)ferrocene (0.00460 g, 0.00802 mmol; purified via repeated recrystallization), 2-bromo-1-iodobenzene (10.3 μL, 0.0818 mmol), (4-amino-2-*tert*-butyl)phenanthridine (0.0200 g, 0.0802 mmol) and sodium *tert*-amoxide (0.0130 g, 0.118 mmol) were added to a 10 mL Teflon-stoppered flask, followed by the addition of 1 mL toluene. The flask was sealed, removed from the glovebox and heated in an oil bath set to 150 °C for 3 d. At that point, the flask was cooled to room temperature and the solvent removed under reduced pressure using a rotary evaporator. ^{31}P{^{1}H} NMR spectroscopic analysis of the crude material obtained at this point showed **2** was ~10% of the phosphorus-containing species observable in solution, based on integration of the spectrum.

Synthesis of 2 using 1,2-diiodobenzene as the aryl halide: Inside a N$_2$-filled glovebox, *tris*(dibenzylideneacetone)dipalladium(0) (0.00370 g, 0.00401 mmol), 1,1'-*bis*(diphenylphosphino)ferrocene (0.00460 g, 0.00802 mmol; as-received), 1,2-diiodobenzene (10.6 μL, 0.0818 mmol), (4-amino-2-*tert*-butyl)phenanthridine (0.0200 g, 0.0802 mmol), and sodium *tert*-amoxide (0.0130 g, 0.120 mmol) were added to a 10 mL Teflon-stoppered flask, followed by the addition of 1 mL toluene. The flask was then sealed, removed from the glovebox and heated in an oil bath set to 150 °C for 3 d. At that point, the flask was cooled to room temperature and the solvent removed under reduced pressure using a rotary evaporator. ^{31}P{^{1}H}

NMR spectroscopic analysis of the crude material obtained at this point showed **2** was ~34% of the phosphorus-containing species observable in solution, based on integration of the spectrum.

Attempted synthesis of 2 using 1,2-dibromobenzene as the aryl halide: Inside a N_2-filled glovebox, *tris*(dibenzylideneacetone)dipalladium(0) (0.00370 g, 0.00401 mmol), 1,1'-*bis*(diphenylphosphino)ferrocene (0.00460 g, 0.00802 mmol; as-received), 1,2-dibromobenzene (10.0 µL, 0.0818 mmol), (4-amino-2-*tert*-butyl)phenanthridine (0.0200 g, 0.0802 mmol), and sodium *tert*-amoxide (0.0130 g, 0.120 mmol) were added to a 10 mL Teflon-stoppered flask, followed by the addition of 1 mL toluene. The flask was then sealed and brought out of the glovebox, and heated in an oil bath set to 150 °C for 3 d. At that point, the flask was cooled to room temperature and the solvent removed under reduced pressure using a rotary evaporator. $^{31}P\{^1H\}$ NMR spectroscopic analysis of the crude material obtained at this point did not indicate formation of the bromo analog of **2**.

Synthesis of 2 using stoichiometric amounts of Pd₂(dba)₃ and dppf: Inside a N_2-filled glovebox, *tris*(dibenzylideneacetone)dipalladium(0) (0.0370 g, 0.0401 mmol), 1,1'-*bis*(diphenylphosphino)ferrocene (0.0460 g, 0.0802 mmol; as-received), 2-bromo-1-iodobenzene (10.3 µL, 0.0818 mmol), (4-amino-2-*tert*-butyl)phenanthridine (0.0200 g, 0.0802 mmol), and sodium *tert*-amoxide (0.0130 g, 0.118 mmol) were added to a 10 mL Teflon-stoppered flask, followed by the addition of 1 mL toluene. The flask was then sealed and brought out of the glovebox, and heated in an oil bath set to 150 °C for 3 d. At that point, the flask was cooled to room temperature and the solvent removed under reduced pressure using a rotary evaporator. $^{31}P\{^1H\}$ NMR spectroscopic analysis of the crude material obtained at this point showed **2** was ~20% of the phosphorus-containing species observable in solution, based on integration of the spectrum.

Synthesis of 2 using 1,2-diiodobenzene, stoichiometric amounts of Pd₂(dba)₃ and thrice-recrystallized dppf: Inside a N_2-filled glovebox, *tris*(dibenzylideneacetone)dipalladium(0) (0.150 g, 0.164 mmol), 1,1'-*bis*(diphenylphosphino)ferrocene (0.182 g, 0.328 mmol; purified via recrystallization), 1,2-diiodobenzene (44.0 μL, 0.335 mmol), (4-amino-2-*tert*-butyl)phenanthridine (0.082 g, 0.328 mmol), and sodium *tert*-amoxide (0.054 g, 0.492 mmol) were added to a 10 mL Teflon-stoppered flask, followed by the addition of 5 mL toluene. The flask was then sealed and brought out of the glovebox, and heated in an oil bath set to 150 °C for 3 d. At that point, the flask was cooled to room temperature and the solvent removed under reduced pressure using a rotary evaporator. $^{31}P\{^1H\}$ NMR spectroscopic analysis of the crude material obtained at this point showed **2** was ~13% of the phosphorus-containing species observable in solution, based on integration of the spectrum. The crude material was purified via flash column chromatography on silica gel using 1:9 mixture of ethyl acetate:hexanes as eluent. (*N*-phenyl-4-amino-2-*tert*-butyl)phenanthridine (**3**) was obtained as a brown oil (R_f = 0.525). Isolated yield = 0.0300 g (28%). Compound **2** (R_f = 0.333) was isolated as a dark purple-red solid. Isolated yield = 0.0250 g (10.3%).

 (*N*-phenyl-4-amino-2-*tert*-butyl)phenanthridine (**3**): ^1H NMR (CDCl₃, 300 MHz, 22 °C): δ 9.15 (s, *H*C=N), 8.66 (d, 1H, J_{HH} = 9 Hz; Ar C*H*), 8.39 (br s, 1H; N*H*), 8.06 (dd, 1H, J_{HH} = 1.7 Hz, 6 Hz; Ar C*H*), 8.00 (d, 1H, J_{HH} = 1.8 Hz; Ar C*H*), 7.91-7.85 (m, 1H; Ar C*H*), 7.76 (d, 1H, J_{HH} = 1.8 Hz; Ar C*H*), 7.74-7.68 (m, 1H; Ar C*H*), 7.44-7.36 (m, 4H; Ar C*H*) 7.07-7.02 (ttt, 1H, J_{HH} = 1.8 Hz, 6.6 Hz; Ar C*H*), 1.48 ppm (s, 9H; (C*H₃*)₃). $^{13}C\{^1H\}$ NMR (CDCl₃, 75 MHz, 25 °C): δ 151.06, 149.57, 142.55, 140.31, 133.33, 131.89, 131.09, 129.53, 129.02, 127.42, 126.86,
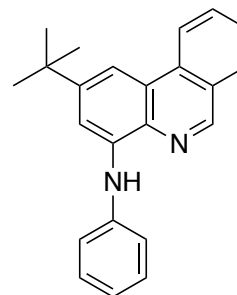
124.41, 122.50, 121.87, 119.65, 108.79, 107.71, 35.66, 31.62 ppm. HRMS (ESI-TOF/MS, m/z) calcd. for $C_{23}H_{22}N_2$ $[M+H]^+$, 327.1856; found 327.1853.

X-Ray Structure of 2 (CCDC 2081304): A crystal was grown by slow evaporation of fractions 8 and 9 from column chromatography. X-ray crystal structure data was using collected from a multi-faceted crystal of suitable size and quality selected from a representative sample of crystals of the same habit using an optical microscope. The crystal was mounted on a MiTiGen loop and data collection carried out in a cold stream of nitrogen (150 K; Bruker D8 QUEST ECO; Mo Kα radiation). All diffractometer manipulations were carried out using Bruker APEX3 software.[54] Structure solution and refinement was carried out using XS, XT and XL software.[55] The absence of additional symmetry was confirmed using ADDSYM incorporated in the PLATON program.[56] Purple blocks; $C_{35}H_{30}I_1N_2P_1Pd_1$ 742.88 g mol^{-1}, monoclinic, space group $P2_1/c$; a = 12.6156(7) Å, b = 13.6733(7) Å, c = 18.0793(10) Å, $\alpha = \gamma = 90°$, β = 107.258(3)°; V = 2978.2(3) $Å^3$, Z = 4, ρ_{calcd} = 1.657 g cm^{-3}; crystal dimensions 0.490 x 0.250 x 0.060 mm; $2\theta_{max}$ = 66.436°; 61181 reflections, 11384 independent (R_{int} = 0.0868), intrinsic phasing; μ = 1.741 mm^{-1}, absorption correction semi-empirical from equivalents (SADABS); refinement (against F_o^2) with SHELXTL V6.1, 364 parameters, 0 restraints, R_1 = 0.06232 (I > 2σ) and wR_2 = 0.1464 (all data), Goof = 1.020, residual electron density 2.175/−1.580 $Å^{-3}$.

ASSOCIATED CONTENT

Supporting Information. The following files are available free of charge:

Crystallographic information file (.cif) for **2** (CCDC Deposition Number 2081304)

PDF document containing copies of all UV-Vis, NMR and HRMS spectra

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