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Facile synthesis of Pd(II) and Ni(II) pincer carbene complexes by the double C–H bond activation of a new hexahydropyrimidine-based bis(phosphine): catalysis of C–N couplings†

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Hexahydropyrimidine-based bis(phosphine), a pro-NHC ligand, was synthesized in one step and excellent yield. It underwent spontaneous double C–H bond activation to give cationic pincer NHC complexes of the type [(PCP)MCl]X (M = Pd, Ni and X = Cl, BF_4) in the absence of any external reagents. Their structures were determined by X-ray diffraction methods and the mechanism of formation of palladium carbene complexes as analyzed by DFT calculations showed two transition states. The Pd(II) carbene complex effectively catalyzes a few C–N cross coupling reactions.

Introduction

The first pincer metal complex was synthesized by the chelate-assisted C–H activation reported by Moulton and Shaw in 1976.[1] Since then the chelate-assisted C–H activation in metal complex formation is a well-known method, and has been used most commonly for synthesizing PCP pincer complexes containing the M–C σ-bond.[2] Conversely, the double C–H bond activation of the methylene group, first reported by Shaw and co-workers in 1977,[3] has led to pincer carbene complexes containing the M–C double bond.[4] Alternatively, the central anchoring carbene carbon in pincer complexes has readily been installed using N-heterocycle carbene (NHC) precursors.[5]

Since the first report of the isolable stable NHC by Arduengo's group in 1991,[6] great progress has been made in NHC organometallic chemistry.[7] These NHC complexes have been shown to be excellent catalysts for numerous organic transformation reactions.[8] Among NHCs, the five-membered imidazolylidene-based NHCs are very common.[9] However, in recent years, a large number of metal complexes containing NHCs based on hexahydropyrimidine and dihydroperimidine, which are better σ-donors than the five-membered imidazolylidene NHCs,[10] have been reported.[11] These NHC carbene complex formations most often involve treatment of the cationic azolium salts with strong bases, reflux conditions or transmetalation reactions using a silver or mercury complex. In 2012, Hill and co-workers first reported the one-step synthesis of *N*,*N*-bis(phosphinomethyl)dihydroperimidines, and their Rh(I) and Ir(III) carbene complexes formed *via* facile double C–H bond activation in the absence of any base or heating.[12] In addition, the versatile nature of the ligand was shown by Ru(II),[13] Ni(0), Au(I)[11f] and Ir(I)[11j] complexes, in which it is coordinated as a neutral ligand. Following this, Gade and co-workers have reported diperimidine derivatives containing the perylene backbone and studied their Rh(I) complexes.[11i] To the best of our knowledge, there is no report of a spontaneous double CH activation without a base or heating to give a Pd(II) or Ni(II) complex containing the hexahydropyrimidine ring-based NHC ligand. Herein, we report the facile synthesis and structural characterization of Pd(II) and Ni(II) NHC complexes formed by the double C–H bond activation of the new pro-NHC ligand based on the hexahydropyrimidine ring along with DFT calculations and the catalysis of C–N cross couplings.

Results and discussion

Synthesis of the ligand and metalation

The one-pot reaction between 1,3-diaminopropane, diphenylphosphine and paraformaldehyde in a 1 : 2 : 3 ratio, respectively, under reflux conditions, readily afforded 1,3-bis(diphenylphosphanylmethyl)hexahydropyrimidine **1** as an oily compound in an excellent yield (91%) (Scheme 1). This method of synthesis is similar to that of *N*,*N*-bis(phosphinomethyl)dihy-

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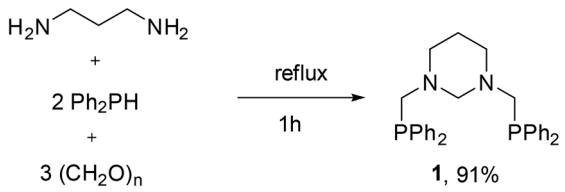
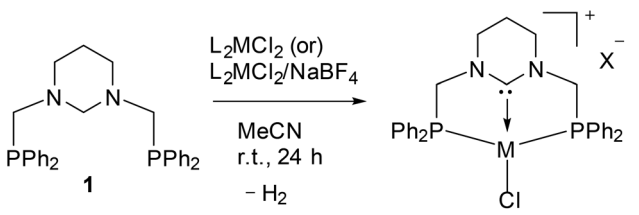
†Electronic supplementary information (ESI) available: NMR, IR, crystal structures, crystallographic data (CIF), optimized geometries with coordinates. CCDC 1862877–1862880 for **2a–3b**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8dt03413c



Scheme 1 Synthesis of *N,N′*-bis(diphenylphosphanylmethyl)hexahydropyrimidine **1**.

droperimidine.[12] **1** is air-sensitive and well soluble in common organic solvents. The ^{1}H NMR spectrum of **1** in $CDCl_3$ showed broad signals for all the hexahydropyrimidine methylene protons, indicating that the structure is in a dynamic process. However, the *P*-methylene protons showed a doublet owing to the proton–phosphorus coupling ^{2}J(P,H) = 4 Hz. The ^{31}P NMR spectrum of **1** in $CDCl_3$ featured a single resonance at δ = −26.3 ppm. This remains close to the chemical shift value of −26.0 ppm reported for 1,3-bis(diphenylphosphinomethyl)-2,3-dihydroperimidine,[12] indicating that both ligands have similar electronic environments. However, **1** possesses a flexible saturated hexahydropyrimidine ring and was synthesized from the cheap starting compound 1,3-diaminopropane.

Compound **1** could be the precursor of a new PCP pincer carbene ligand because of the presence of methylene protons flanked by two nitrogens. Hence, **1** was first treated with [$PdCl_2$(COD)] in CH_3CN at room temperature to give the cationic Pd(II) carbene complex **2a** containing the chloride counteranion. The same reaction in the presence of $NaBF_4$ afforded complex **2b** with the BF_4^- ion (Scheme 2). Both complexes are formed by the spontaneous double dehydrogenation of the NCH_2N methylene protons facilitated by two chelate rings formed around the palladium atom and are air stable. The presence of a Pd–C bond in the structure indirectly suggested by the number of methylene signals in their ^{1}H NMR spectra displayed three instead of four signals. Their ^{31}P NMR spectra showed singlets (δ = 26.3 ppm for **2a** and δ = 25.9 ppm for **2b**) and displayed a significant coordination-caused chemical shift change $\Delta\delta$ of ∼52 ppm with respect to the free ligand value. In addition, their ^{13}C NMR spectra displayed triplet patterns owing to the phosphorus coupling (δ = 189.9 ppm for **2a** and 186.7 ppm for **2b**) for the palladium-bound carbene carbon atoms.



Scheme 2 Synthesis of the NHC pincer Pd(II) and Ni(II) complexes **2** and **3**.

The structures of **2a** and **2b** were determined by single crystal X-ray diffraction studies. An ORTEP diagram of **2a** along with selected bond distances and angles is shown in Fig. 1. The structure of **2b** is provided in the ESI.† Complexes **2a** and **2b** crystallize in the monoclinic *C*2/*c* and the triclinic $P\bar{1}$ space groups, respectively, and their asymmetric units constitute the whole molecule together with the solvent of crystallization. The structure contains two fused five-membered rings around the palladium atom formed by the two diphenylphosphinomethyl arms. This results in the formation of *trans* disposition of the two phosphorus atoms, with the carbene carbon and chlorine atoms being *trans* to each other. The geometry around the palladium atom is distorted square planar, in which the fused ring angles (P–Pd–$C_{carbene}$ = 82.15(9)° and 80.67(9)°) are smaller than the other two angles (P–Pd–Cl = 95.97(3)° and 101.09(3)°). As a result, the palladium square plane and the mean plane formed by C18, N2, C17, N1 and C13 atoms are twisted. The twist angle is 19.6° for **2a** and 15.1° for **2b**. The Pd–$C_{carbene}$ distance of 2.011(3) Å in **2a** and 1.997(4) Å in **2b** is in the range reported for several palladium complexes containing the hexahydropyrimidine-based NHC ligands[14,11h] and others.[5c,h,15] The sum of the angles around the hexahydropyrimidine nitrogens in **2** is close to 360° (for example, 359.9(2)° and 359.4(2)° in **2a**), suggesting the planarity around these nitrogen atoms. The carbene carbon atoms in both the structures are completely planarized with the sum of the angles being equal to 360(2)° (**2a**).

In an analogous manner, the cationic nickel(II) complexes **3a** and **3b** were synthesized by treating **1** with [$NiCl_2$(DME)]/$NaBF_4$ in CH_3CN at room temperature. Like the palladium complexes, these complexes are also formed by facile double C–H bond activation. The ^{31}P NMR spectrum **3a** or **3b** displayed a singlet at δ = 24.8 ppm or δ = 25.4 ppm, respectively, which is close to the palladium complex signals, suggesting similar structures. Furthermore, the ^{13}C NMR spectrum of **3a** showed a broad singlet at δ = 186.7 ppm and **3b** displayed a triplet at δ = 190.0 ppm, supporting the carbene-bound nickel(II)

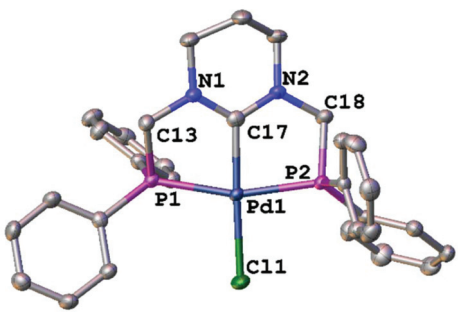


Fig. 1 Crystal structure of **2a** (50% displacement ellipsoids). Hydrogen atoms, Cl^- ion and solvent molecules are omitted for clarity. Selected bond lengths (Å) and bond angles (°): P1–Pd1 2.2912(8), P2–Pd1 2.2726(8), Cl1–Pd1 2.3415(8), C17–Pd1 2.011(3), N1–C17 1.334(4), N2–C17 1.338(4), C17–Pd1–P2 82.15(9), C17–Pd1–P1 80.67(9), P2–Pd1–P1 162.47(3), C17–Pd1–Cl1 177.49(9), P2–Pd1–Cl1 95.97(3), P1–Pd1–Cl1 101.09(3).

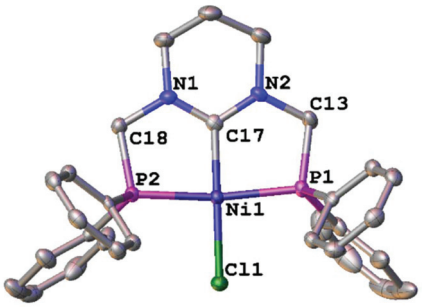
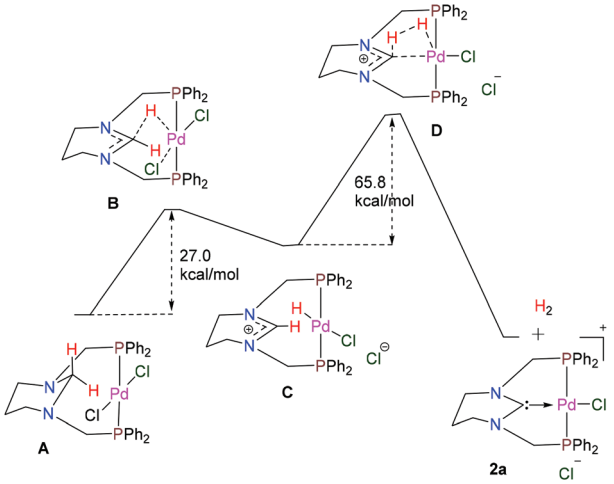


Fig. 2 Crystal structure of **3a** (50% displacement ellipsoids). Hydrogen atoms, Cl^- ion and solvent molecules are omitted for clarity. Selected bond lengths (Å) and bond angles (°): P1–Ni1 2.1638(7), P2–Ni1 2.1661 (7), Cl1–Ni1 2.1850(7), C17–Ni1 1.900(3), N2–C17 1.350(3), C17–Ni1–P2 86.29(8), C17–Ni1–P1 86.17(8), P2–Ni1–P1 170.13(3), C17–Ni1–Cl1 176.96(8), P2–Ni1–Cl1 93.78(3), P1–Ni1–Cl1 94.09(3).



Scheme 3 The proposed mechanism for the formation of pincer carbene complexes through the transition states **B** and **D** found in DFT calculations.

complexes. In addition, the carbon atom in the NCH_2P and hexahydropyrimidine ring N–CH_2 groups, and the phenyl *ipso*, *ortho* and *meta* carbons displayed triplets owing to the phosphorus coupling.

The X-ray structure of **3a** with selected bond distances and angles is shown in Fig. 2. The structure of **3b** is provided in the ESI.† While the chloride counteranion complex **3a** crystallizes in the monoclinic *C*2/*c* space group, the BF_4^- anion complex **3b** crystallizes in the triclinic $P\bar{1}$ space group. The geometry around the nickel atom in each complex is distorted square planar. As found in the palladium complexes, the P1–Ni–Cl and P2–Ni–Cl angles are larger than the P1–Ni–C and P2–Ni–C angles. The distance between the carbene carbon and nickel atoms is 1.900(3) Å in **3a** and 1.905(6) Å in **3b**, which are close to that found (1.911(2) Å) in the dichlorobis(1,3-dicyclohexylimidazol-2-ylidene) nickel(II) complex,[16] but are longer than that found in another nickel carbene complex, [(PCP)NiH]PF_6 (PCP = *o*-$C_6H_4(PPr^i_2)(NC_3H_5N)(PPr^i_2)$*o*-$C_6H_4$).[17] Furthermore, the Ni–P distances in **3a** or **3b** are slightly longer than those (2.1080(8) Å and 2.1129(9) Å) found in the reported complex, [(PCP)NiH]PF_6. The hexahydropyrimidine nitrogens and the carbene carbon are planar, indicating the donation of a lone pair of electrons from nitrogens to the carbon atom.

DFT calculations

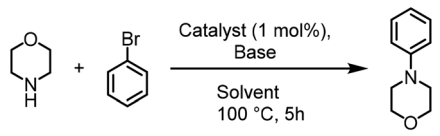
To understand the double C–H bond activation and the electronic structure of complexes **2** and **3**, DFT calculations were performed, which supported two transition states for the formation of the carbene complexes **2**, as shown in Scheme 3. The initial reaction between [$PdCl_2$(COD)] and **1** gives the chelate complex **A** in which the methylene protons are in close proximity to the palladium atom. As a result, the tetrahydropyrimidinium cationic palladium hydride intermediate **C** is formed *via* the transition state **B** which subsequently abstracts the remaining methylene hydrogen as a proton to give **2a** with H_2 formation through the transition state **D** showing the concerted fashion of proton abstraction.

As expected, the NBO analysis showed second-order perturbation stabilization energies of 131.05 and 136.42 kcal mol^{-1} for the N–$C_{carbene}$ π-interactions in **2a** and **2b**, respectively. Similar values were obtained for the nickel complexes **3a** and **3b** (132.35 and 130.91 kcal mol^{-1}, respectively). These values suggest that, in addition to the chelate effect imposed by the diphosphine, carbene formation by double C–H bond activation is driven by the π electron delocalization from the flanking nitrogens. As a result, the average carbene C–N bond length in **2a**, **2b**, **3a** and **3b** is 1.336, 1.341, 1.349 and 1.347 Å, respectively. The calculated average carbene C–N bond order in **2** or **3** is 1.31, which is higher than the calculated average carbene C–N bond order (1.27) with a distance of 1.375 Å found in the energy-minimized model complex [PdCl{C$(NCH_2PPh_2)_2C_{10}H_6$}]$^+$ containing the dihydroperimidine ring. This is attributed to the extent of π-interactions in the carbene C–N bonds which is higher when the ring is saturated in which the nitrogen lone pair is fully available to stabilize the carbene carbon, leading to shorter bonds. In the dihydroperimidine ring-based NHC complex, the nitrogen lone pairs are involved in extended conjugation with the naphthalene ring. This observation is in line with the reported palladium complexes containing the saturated and unsaturated NHCs.[18] While the saturated NHC palladium complex exhibits a slightly shorter average carbene C–N distance of 1.332(4) Å, the unsaturated one shows a slightly longer average distance of 1.345(4) Å. Furthermore, the NBO analysis showed a metal to carbene carbon back donation (M ⇒ $C_{carbene}$) energy of 16.85 kcal mol^{-1} in **2** and 12.23 kcal mol^{-1} in **3**. The Cl ⇒ **M** π-interaction energy of 8.08 kcal mol^{-1} in **2** and 11.12 kcal mol^{-1} in **3** was also estimated.

Catalysis of C–N couplings

The catalytic application of the palladium complexes **2a** and **2b** was examined with the Buchwald–Hartwig coupling. A

Table 1 The Buchwald–Hartwig coupling between bromobenzene and morpholine catalyzed by **2a** and **2b** in the presence of different bases and solvents[a]

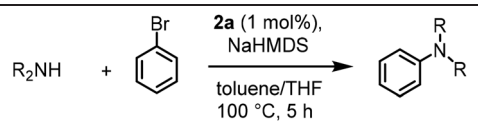


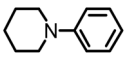
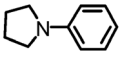
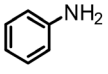
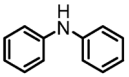
Entry	Catalyst	Base	Solvent	Yield[b], %
1	**2a**	$KOBu^t$	Toluene	81
2	**2a**	$KOBu^t$	DMF	69
3	**2a**	K_2CO_3	Toluene	0
4	**2a**	K_2CO_3	DMF	0
6	**2a**	Cs_2CO_3	Toluene	59
7	**2a**	Cs_2CO_3	DMF	18
8	**2a**	NaHMDS	DMF/THF	83
9	**2a**	NaHMDS	Toluene/THF	91(82)
10	**2b**	NaHMDS	Toluene/THF	89

[a] ArX (1.9 mmol), amine (2.28 mmol), base (2.9 mmol), **2a** or **2b** (1 mol%), solvent (5 mL), 100 °C, 5 h. [b] Estimated yields by GC (isolated yields are given in parenthesis).

variety of palladium metal complexes as precatalysts have been reported for this C–N bond formation reaction.[19] Using morpholine and bromobenzene, different bases and solvents were screened for the optimum conditions to obtain the product in a high yield (Table 1). While $KOBu^t$ gave a competitive yield of 81% in toluene, NaHMDS turned out to be the best base in toluene/THF yielding 91% of the product using 1 mol% of complex **2a**. A similar yield (89%) was also obtained with **2b**. Using these optimized conditions, other C–N couplings were carried out. The products were formed in excellent yields as estimated by GC using diphenylamine as an external standard, which are close to the isolated yields (Table 2).

Table 2 Buchwald–Hartwig couplings between bromobenzene and different amines catalyzed by **2a**[a]



Entry	Amine	Product	Yield[b], %
1			92 (85)
2			96 (89)
3			88 (80)

[a] ArX (1.9 mmol), amine (2.28 mmol), NaHMDS (2.9 mL, 1 M in THF), **2a** (1 mol%), toluene (5 mL), 100 °C, 5 h. [b] Estimated yields by GC (isolated yields are given in parenthesis).

Conclusions

The new pro-NHC pincer ligand was synthesized conveniently in a single step in an excellent yield. The NHC pincer palladium(II) and nickel(II) complexes were formed readily at room temperature without a base or transmetalation reaction, representing their facile formation *via* the double C–H bond activation of the hexahydropyrimidine-based NHC precursor **1**. The X-ray structures and DFT calculations showed the nitrogen π-electron delocalization over the carbene carbon atom, which makes it a better σ-donor. Furthermore, the DFT calculations showed that the double C–H bond activation occurred in a stepwise fashion. The palladium carbene complex is proposed to be formed *via* two intermediates and two transition states in which the methylene hydrogens are abstracted successively in a concerted fashion with the formation of H_2. Furthermore, the preliminary catalytic study using palladium complexes was demonstrated with Buchwald–Hartwig C–N couplings in which cross-coupled products were formed in very high yields, indicating that a highly active metal center is generated *in situ* during the catalysis processes with the support of the hexahydropyrimidine ring-based NHC ligand. Syntheses of other metal complexes and catalysis studies are ongoing research in our laboratory.

Experimental section

General

All reactions were carried out under a nitrogen atmosphere using standard Schlenk line techniques or a nitrogen-filled glove box. Petroleum ether (bp 40–60 °C) and other solvents were distilled under an N_2 atmosphere according to the standard procedures. $[PdCl_2(COD)]$[20], $[NiCl_2(DME)]$[21] and Ph_2PH[22] were synthesized according to the reported procedures. Other chemicals were obtained from commercial sources and used as received. ^1H NMR (200 or 400 MHz) and ^{13}C NMR (100.6 MHz) spectra were recorded at room temperature. For ^1H NMR spectra, chemical shifts are referenced with respect to the chemical shift of the residual protons present in the deuterated solvents and for ^{13}C NMR spectra, the $CDCl_3$ chemical shift was used as a reference. Chemical shifts are in parts per million, and coupling constants are in Hz. FTIR and ATR spectra were recorded using a PerkinElmer Spectrum Rx Spectrometer. Elemental analyses were carried out using a PerkinElmer 2400 CHN analyzer. A Thermo Scientific Trace 1310 GC chromatograph was used for detecting and calculating yields.

Synthesis of 1,3-bis(diphenylphosphanylmethyl) hexahydropyrimidine, 1

A mixture of 1,3-diaminopropane (0.97 mL, 11.621 mmol), diphenylphosphine (4.0 mL, 23.202 mmol) and paraformaldehyde (1.045 g, 34.798 mmol) was refluxed at 115 °C with stirring for 1 h. The reaction mixture was cooled to room temperature to give a colorless sticky precipitate, which was washed

with petroleum ether (2 × 10 mL) and dried under vacuum to give **1** as an oily compound (5.09 g, 10.548 mmol, 91%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43 (m, 10H, *Ph*), 7.30 (m, 10H, *Ph*), 3.66 (br s, 2H, NCH_2N), 3.27 (d, ^{2}J(P,H) = 4, 4H, PCH_2N), 2.82 (br s, 4H, pyrimidine CH_2), 1.68 (br s, 2H, pyrimidine CH_2). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 138.3 (d, ^{1}J(C,P) = 26.2), 132.7 (d, ^{2}J(C,P) = 36.2), 128.3, 128.1, 76.2, 57.0, 53.3 (d, ^{1}J(C,P) = 17.1), 21.4. ^{31}P{^{1}H} NMR ($CDCl_3$, 161.9 MHz): δ −26.3 (s). FT-IR (ATR, cm^{-1}): $\bar{\nu}$ = 3053 (w), 2937 (w), 2856 (w), 2791 (w), 1585 (w), 1481 (w), 1432 (m), 1381 (w), 1277 (w), 1244 (w), 1183 (w), 1098 (m), 1063 (m), 1027 (w), 1008 (w), 978 (w), 949 (w), 894 (w), 787 (w), 739 (s), 693 (vs), 628 (w), 644 (w), 502 (m).

Synthesis of [PdCl{C(NCH$_2$PPh$_2$)$_2$(CH$_2$)$_3$-κ^{3}P,C,P}]Cl, 2a

To a solution of [$PdCl_2$(COD)] (0.20 g, 0.70 mmol) in acetonitrile (20 mL) was added **1** (0.340 g, 0.704 mmol) and stirred at room temperature for 24 hours. The solvent was removed under vacuum and the residue was washed with petroleum ether (3 × 10 mL). The residue was dissolved in dichloromethane and layered with petroleum ether at room temperature. Orange crystals of complex **2a** were formed over a period of one week, which were separated and dried under vacuum (0.420 g, 0.565 mmol, 81%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.90 (m, 8H, *Ph*), 7.55 (m, 12H, *Ph*), 4.89 (t, ^{2}J(H,P) = 4, 4H, PCH_2N), 3.77 (t, ^{3}J(H,H) = 6, 4H, pyrimidine NCH_2), 2.20 (t, ^{3}J(H,H) = 6, 2H, pyrimidine CH_2). ^{13}C NMR (CD_3CN, 100.6 MHz): δ 189.9 (t, ^{2}J(C,P) = 17.6), 133.5 (t, ^{2}J(C,P) = 6), 132.2, 129.3 (t, ^{3}J(C,P) = 5), 126.9 (d, ^{1}J(C,P) = 25), 60.6, 45.4, 19.1. ^{31}P{^{1}H} NMR ($CDCl_3$, 161.9 MHz): δ 26.3 (s). FT-IR (ATR, cm^{-1}): $\bar{\nu}$ = 3365 (w, br), 3053 (w), 2959 (w), 2924 (w), 2865 (w), 1714 (w), 1662 (m), 1549 (w), 1437 (m), 1319 (w), 1248 (m), 1160 (m), 1118 (s), 1105 (s), 1017 (m), 998 (m), 839 (w), 732 (m), 693 (s), 638 (w), 651 (m), 605 (s).

Synthesis of [PdCl{C(NCH$_2$PPh$_2$)$_2$(CH$_2$)$_3$-κ^{3}P,C,P}]BF$_4$, 2b

To a solution of [$PdCl_2$(COD)] (0.050 g, 0.175 mmol) and $NaBF_4$ (0.019 g, 0.173 mmol) in acetonitrile (20 mL) was added **1** (0.085 g, 0.176 mmol). The solution was stirred at room temperature for 24 h and then the solvent was removed under vacuum. The resulting residue was washed with petroleum ether (3 × 10 mL), dissolved in chloroform and layered with petroleum ether at room temperature to give complex **2b** as orange crystals (0.110 g, 0.1585 mmol, 90%). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 7.90 (m, 8H, *Ph*), 7.60 (m, 12H, *Ph*), 4.98 (t, ^{2}J(H,P) = 6, 4H, NCH_2PPh$_2$), 3.47 (t, ^{3}J(H,H) = 12, 4H, pyrimidine NCH_2), 2.01 (br s, 2H, pyrimidine CH_2). ^{13}C NMR (DMSO-d_6, 100.6 MHz): δ 186.7 (t, ^{2}J(C,P) = 5), 133.0 (t, ^{2}J(C,P) = 14), 132.2, 129.4 (t, ^{3}J(C,P) = 11), 127.4 (t, ^{1}J(C,P) = 50), 60.3 (t, ^{1}J(C,P) = 34), 44.8 (t, ^{3}J(C,P) = 10), 18.9. ^{31}P {^{1}H} NMR (161.9 MHz, $CDCl_3$): δ = 25.9 (s). FT-IR (ATR, cm^{-1}): $\bar{\nu}$ = 3053 (w), 2930 (w), 2862 (w), 1675 (w), 1556 (m), 1481 (w), 1436 (m), 1355 (w), 1319 (w), 1215 (w), 1189 (w), 1050 (vs), 852 (w), 742 (s), 687 (s), 644 (w), 602 (s), 473 (m). Anal. calcd for $C_{30}H_{30}BClF_4N_2P_2Pd$: C, 50.81; H, 4.26; N, 3.95. Found = C, 50.84; H, 4.33; N, 3.77.

Synthesis of [NiCl{C(NCH$_2$PPh$_2$)$_2$(CH$_2$)$_3$-κ^{3}P,C,P}]Cl, 3a

To a solution of [$NiCl_2$(DME)] (0.10 g, 0.455 mmol) in acetonitrile (20 mL) was added **1** (0.20 g, 0.414 mmol). The solution was stirred at room temperature for 24 h and then the solvent was removed under vacuum. The resulting residue was washed with petroleum ether (3 × 10 mL), and dissolved in chloroform, which was allowed to evaporate slowly to give green crystals of **3a** (0.085 g, 0.1334 mmol, 29%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.92 (br, 8H, *Ph*), 7.57–7.47 (m, 12H, *Ph*), 4.66 (br s, 4H, NCH_2PPh$_2$), 3.58 (br s, 4H, pyrimidine NCH_2), 2.1 (br s, 2H, pyrimidine CH_2). ^{13}C NMR (DMSO-d_6, 100.6 MHz): δ 186.7, 131.3, 129.8, 129.1, 127.2, 125.4 (t, ^{1}J = 24), 57.6, 43.2, 17.1. ^{31}P {^{1}H} NMR ($CDCl_3$, 161.9 MHz): δ 24.8 (s). FT-IR (ATR, cm^{-1}): $\bar{\nu}$ = 3402 (br, s), 3051 (w), 2935 (w), 1637 (br, w), 1539 (s), 1483 (m), 1436 (s), 1354 (m), 1318 (m), 1263 (w), 1204 (w), 1187 (m), 1104 (s), 1026 (w), 998 (w), 942 (w), 867 (w), 748 (s), 712 (w), 696 (s), 592 (w), 548 (m), 524 (w), 501 (m), 483 (w), 458 (w). Anal. calcd for $C_{30}H_{30}Cl_2N_2P_2Ni{\cdot}3(H_2O)$: C, 54.25; H, 5.46; N, 4.22. Found = C, 54.52; H, 5.32; N, 4.31.

Synthesis of [NiCl{C(NCH$_2$PPh$_2$)$_2$(CH$_2$)$_3$-κ^{3}P,C,P}]BF$_4$, 3b

To a solution of [$NiCl_2$(DME)] (0.100 g, 0.455 mmol) and $NaBF_4$ (0.050 g, 0.455 mmol) in acetonitrile (20 mL) was added **1** (0.220 g, 0.455 mmol). The solution was stirred at room temperature for 24 h and then the solvent was removed under vacuum. The resulting residue was washed with petroleum ether (3 × 10 mL), dissolved in dichloromethane and then layered with petroleum ether at room temperature to give crystals of **3b** (0.20 g, 0.302 mmol, 66%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.84 (m, 8H, *Ph*), 7.63–7.49 (m, 12H, *Ph*), 4.55 (t, ^{2}J(H,P) = 4, 4H, NCH_2PPh$_2$), 3.49 (t, ^{3}J(H,H) = 6, 4H, pyrimidine NCH_2), 2.07 (m, 2H, pyrimidine CH_2). ^{13}C NMR (CD_3CN, 102.6 MHz): δ 190.0 (t, ^{2}J(C,P) = 19), 133.6 (t, ^{2}J(C,P) = 5 Hz), 132.3, 129.5 (t, ^{3}J(C,P) = 5), 127.0 (t, ^{1}J(C,P) = 25), 60.7 (t, ^{1}J(C,P) = 17), 45.5 (t, ^{3}J(C,P) = 5), 19.2. ^{31}P {^{1}H} NMR (161.9 MHz, $CDCl_3$): δ 25.4 (s). FT-IR (ATR, cm^{-1}): $\bar{\nu}$ = 3384 (w), 3060 (w), 2943 (w), 1650 (m), 1562 (w), 1539 (m), 1484 (w), 1436 (m), 1358 (w), 1319 (w), 1186 (w), 1157 (w), 1053 (s), 1021 (s), 859 (w), 816 (w), 739 (s), 693 (s), 547 (w), 518 (w), 499 (w), 482 (w). Anal. calcd for $C_{30}H_{30}BClF_4N_2P_2Ni$: C: 54.47 H: 4.57 N: 4.24. Found = C, 54.58; H, 4.42; N, 4.37.

General procedure for the Buchwald–Hartwig cross coupling of aryl halides with amines

An oven dried Schlenk flask was charged with morpholine (0.197 mL, 2.284 mmol) and complex **2a** (0.014 mg, 0.0188 mmol, 1 mol% with respect to bromobenzene) in 5 mL of dry toluene. The mixture was stirred at room temperature for 5 minutes under an argon atmosphere and then bromobenzene (0.2 mL, 1.911 mmol) and NaHMDS (2.9 mL, 2.9 mmol, 1 M in THF) were successively added. The reaction mixture was refluxed at 100 °C for 5 h. After cooling to room temperature, the reaction was quenched by adding 20 mL of distilled water and the reaction mixture was extracted with DCM (3 × 10 mL). The combined organic solution was dried

over anhydrous Na_2SO_4 and then filtered. 1 μL of this DCM solution was injected into GC to identify and calculate the yield of the coupled product against the external standard, diphenylamine. DCM was removed under vacuum and the resulting residue was loaded onto a silica gel column chromatography. Elution using petroleum ether/ethyl acetate (v/v = 10/1 mL) yielded 4-phenylmorpholine in a pure form after removing the solvents.

4-Phenylmorpholine. 0.257 g, 1.574 mmol, 82%. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.33–7.24 (m, 2H, *Ph*), 6.95–6.85 (m, 3H, *Ph*), 3.87 (t, ^3J(H,H) = 4.8, 4H, CH_2), 3.16 (t, ^3J(H,H) = 4.8, 4H, CH_2). These data match with the reported value.[23]

1-Phenylpiperidine. 0.263 g, 1.631 mmol, 85%. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.29–7.20 (m, 2H, *Ph*), 6.95 (d, ^3J(H,H) = 8, 2H, *Ph*), 6.82 (t, ^3J(H,H) = 7.2, 1H, *Ph*), 3.16 (t, ^3J(H,H) = 5.3, 4H, CH_2), 1.77–1.66 (m, 4H, CH_2), 1.62–1.52 (m, 2H, CH_2).[23]

1-Phenylpyrrolidine. 0.252 g, 1.711 mmol, 89%. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.28–7.17 (m, 2H, *Ph*), 6.71–6.57 (m, 3H, *Ph*), 3.30 (t, ^3J(H,H) = 6.6, 4H, CH_2), 2.05–1.98 (m, 4H, CH_2).[24]

Diphenylamine. 0.260 g, 1.536 mmol, 80%. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.32–7.24 (m, 4H, *Ph*), 7.09 (d, ^3J(H,H) = 8.6, 4H, *Ph*), 6.94 (t, ^3J(H,H) = 6.4, 2H, *Ph*), 5.71 (br s, 1H, N*H*).

X-ray crystallography

Suitable single crystals of **2a**, **2b**, **3a** and **3b** were grown from the solvents mentioned in their respective synthetic procedures. Single-crystal X-ray diffraction data collections were performed using a Bruker APEX-II or D8 Venture APEX3 CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were then solved using SHELXT-VERSION 2014/5,[25] which successfully located most of the nonhydrogen atoms. Subsequently, least-squares refinements were carried out on F^2 using SHELXL Version 2018/1 [26] to locate the remaining nonhydrogen atoms. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were fixed in calculated positions. The crystal structures were plotted with OLEX2 program version 1.2.10.[27] The hexahydropyrimidine methylene group in **3a** and **3b**, CH_2Cl_2 in **2a**, and BF_4^- anion in **2b** and **3b** were disordered over two positions and were handled with EADP refinement. The structure of **2b** was treated as it is co-crystallized with **2a**. Hence, the refinement was carried out with both the anions, BF_4^- and Cl^-. While all other atoms have full occupancy, only the anions were refined with partial occupancies (70% of BF_4^- and 30% of Cl^-).

Computational details

All DFT calculations were performed using the Gaussian 09 program[28] with the hybrid exchange-correlation functional proposed by Becke, Lee, Yang and Parr (B3LYP)[29] and the LANL2DZ[30] basis set. All optimizations were followed by frequency calculations to ascertain the nature of the stationary point. The Berny TS optimization method was used to obtain the optimized transition states from initial guess structures. The resulting transition state (TS) structures were confirmed by the frequency calculation method. In addition, these TS structures were subjected to IRC calculations to further confirm that they are in the desired reaction path. The optimized model structures were generated using Gaussview 5.0 program. Natural bond orbital (NBO) analysis was performed using the Gaussian NBO Version 3.1,[31] integrated into the Gaussian 09 program.

Conflicts of interest

There are no conflicts to declare.

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