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Synthesis of novel (NHC)Pd(acac)Cl complexes (acac = acetylacetonate) and their activity in cross-coupling reactions

Oscar Navarro,[a] Nicolas Marion,[a] Natalie M. Scott,[a] Juan González,[a] Dino Amoroso,[b] Andrew Bell[b] and Steven P. Nolan[a,*]

[a]*Department of Chemistry, University of New Orleans, 2000 Lakeshore Dr, New Orleans, LA 70148, USA*
[b]*Promerus LLC, 9921 Brecksville Rd, Brecksville, OH 44141-3289, USA*

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Abstract—The synthesis and characterization of two new complexes (IPr)Pd(acac)$_2$ (**1**) and (IPr)Pd(acac)Cl (**2**) (IPr = (*N*,*N*'-bis(2,6-diisopropylphenyl)imidazol)-2-ylidene, acac = acetylacetonate) are described. Complex **2** can be prepared in a one-pot protocol in high yield. A study detailing the versatility of **2** to effectively catalyze a series of cross-coupling reactions is discussed.

1. Introduction

Research focusing on palladium compounds and their use in catalysis at both industrial and laboratory scales has exponentially increased during the last 10 years.[1,2] Although, ligandless systems are also known,[2a] it is well understood that the ancillary ligation to the metal center plays a crucial role in dictating the efficiency of a catalytic system.[3] Bulky, electron-rich phosphines ligands such as P(*t*-Bu)$_3$ are now commonly used to stabilize the Pd(0) intermediates thereby avoiding the precipitation of the metal in homogeneous catalysis.[4] However, the most common phosphine ligands possess several drawbacks: (1) they often are prone to air oxidation and therefore, require air-free handling, (2) when these ligands are subjected to higher temperatures, significant P–C bond degradation occurs and require the use of an excess of the phosphine and (3) they often react with Pd precursors such as Pd(OAc)$_2$ in a reduction process forming Pd(0)P$_n$ and phosphine oxide.[5]

N-Heterocyclic carbenes (NHC)[6] have become increasingly popular in the last few years as they represent an attractive alternative to tertiary phosphines in homogeneous catalysis. The NHC exhibit reaction behavior different than phosphine especially displaying high thermal stability and tolerance to oxidation conditions. We have developed several systems based on the combination of imidazolium salts (air-stable precursors for NHC) and Pd(0) or Pd(II) sources to generate catalytically active species in situ and these mediate numerous organic reactions, principally cross-coupling reactions.[7] These preliminary systems by us and others[8] showed the importance of the NHC/Pd ratio on the efficiency of the reactions, pointing to an optimum 1:1 ligand to metal ratio in most cases. From there, we aimed our efforts on the development of monomeric NHC-bearing Pd(II) complexes and the study of their catalytic activity. Generally, shorter reaction times are observed in these well-defined systems, since the carbene is already coordinated to the palladium center. Also, the use of a well-defined pre-catalyst allows for a better knowledge of the amount of ligand-stabilized palladium species in solution, by reducing the possibility of side reactions leading to ligand or palladium precursor decomposition prior to the coordination of the ligand.

We have reported on the synthesis of monomeric (NHC)Pd(allyl)Cl complexes[7f,9] and (NHC)Pd(carboxylate) complexes[10] among many architectures,[11] and have studied activation mechanisms and catalytic activities. The synthesis of most of these complexes is directly related to successful in situ systems involving the use of NHC and the corresponding palladium source. We reported on a catalytic system for the Heck reaction involving the use of diazabutadiene ligands and Pd(OAc)$_2$, that also could use Pd(acac)$_2$ as palladium precursor.[12] Using the same approach as for (IPr)Pd(OAc)$_2$, we decided to test whether analogous species using Pd(acac)$_2$ as starting material was possible. We report here the synthesis of (IPr)Pd(acac)$_2$ (**1**) and (IPr)Pd(acac)Cl (**2**) (IPr = (*N*,*N*'-bis(2,6-diisopropylphenyl)imidazol)-2-ylidene) complexes and preliminary

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* Corresponding author. Tel.: +1 504 286 6311; fax: +1 504 280 6860; e-mail: snolan@uno.edu

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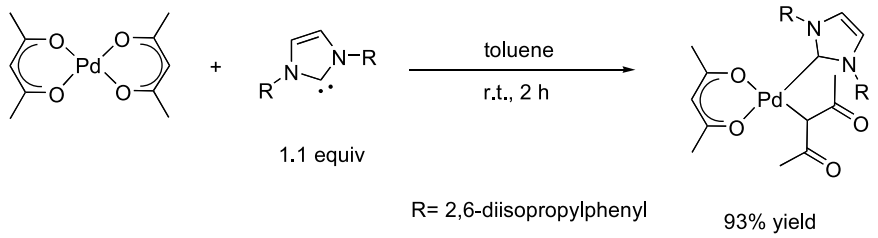


Scheme 1. Synthetic path leading to (IPr)Pd(acac)$_2$.

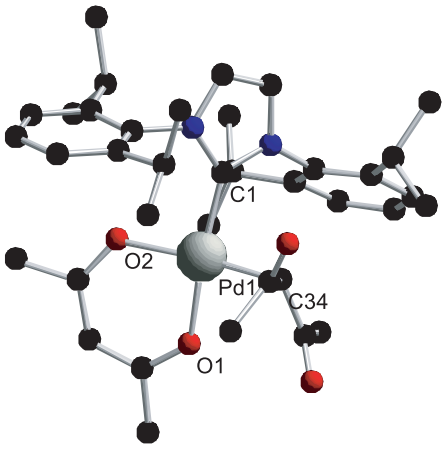


Figure 1. Ball and stick representation of (IPr)Pd(acac)$_2$ (hydrogens omitted for clarity). Selected bond distances (Å): Pd1–C1: 1.982(6), Pd1–C34: 2.073(6), Pd1–O1: 2.038(4), Pd1–O2: 2.081(4). Selected angles (deg): O2–Pd1–O1: 90.70(15), O1–Pd1–C34: 86.4(2), C34–Pd1–C1: 90.4(2), C1–Pd1–O2: 93.2(2).

studies on their catalytic activity in the Buchwald–Hartwig aryl amination reaction and the α-ketone arylation reaction.

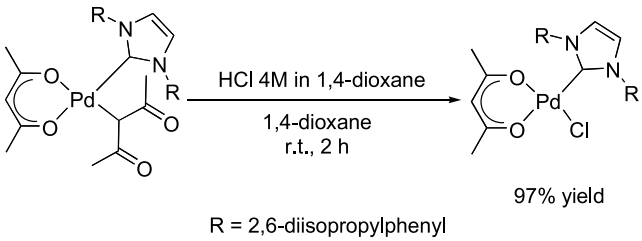
2. Results and discussion

2,4-Pentadione (acetylacetonate, acac) and other β-carbonyl compounds are very versatile and common ligands in transition metal chemistry.[13] 2,4-Pentadione typically binds metal ions in a η^2-*O*,*O* fashion, although some other coordination modes have been observed in platinum (II) and palladium(II) complexes.[14,15] Previous work by Kawaguchi and co-workers focused on the reactivity of palladium(II) acetylacetonate and related compounds with phosphines leading to new complexes, but no catalytic applications were reported.[16] Recently, Shmidt and co-workers have performed a very extensive research on the use of such type of complexes as hydrogenation catalysts.[17]

We have synthesized a NHC-bearing analogue to the reported (PPh$_3$)Pd(acac)$_2$[16a] following a similar procedure (Scheme 1). Direct reaction of the free carbene IPr with Pd(acac)$_2$ at room temperature in anhydrous toluene yielded (IPr)Pd(acac)$_2$ (**1**) in very high yield as a yellow powder. The presence of one oxygen-chelating ligand and one C-bound ligand in the complex was apparent by both ^{13}C and ^{1}H NMR. In the ^{13}C NMR spectrum, 6 different signals above 160 ppm: 207.5 (C-bound acac), 192.9, 188.1, 185.6, 183.3 (carbonyl carbons), and 161.2 (carbenic carbon) were observed. In the ^{1}H NMR spectrum, four methyl-proton singlet signals were observed each at 2.63, 2.01, 1.63, and 1.31, together with two signals at 5.90 and 4.78 ppm. The lowest-field methyl peaks are assigned to the carbon-bonded acac, together with the lowest-field methenic hydrogen, while the other three signals are assigned to the oxygen-chelating ligand. It is of note that the PPh$_3$ analogue showed only one peak for the methyls of the carbon bound ligand, due to free rotation.[18] Clearly, the sterically demanding IPr ligand inhibits this rotation. The disposition of the ligands was unequivocally assigned when the crystal structure was resolved by X-ray diffraction (Fig. 1). A square planar configuration around the palladium center can be observed, with nearly no distortion. As expected, the Pd–C$_{carbenic}$ distance is in the range of a single Pd–C bond. The Pd–O bond opposite to the NHC is elongated compared to the other Pd–O bond due to a strong trans effect.

Preliminary tests on the activity of **1** for the Buchwald–Hartwig reaction using KO*t*Bu as base and DME as solvent at 50 °C for the coupling of 4-chlorotoluene and morpholine showed a moderate activity (43% product in 1 h with 1 mol% catalyst loading). The same moderate activity was observed for the coupling of 4-chlorotoluene and propiophenone using NaO*t*Bu as base and toluene as solvent at 60 °C. The reaction required 2 h to reach completion using 1 mol% catalyst loading. We decided on modifying the complex with the idea of increasing the activity in catalysis.

Kawaguchi reported on the reaction of (PPh$_3$)Pd(acac)$_2$ with benzoyl chloride to yield the new species(PPh$_3$)Pd(acac)Cl, proposing a sequence of oxidative addition–reductive elimination reactions.[16a] In a similar way, compound **1** reacts with 1 equiv of HCl at room temperature to produce the new species (IPr)Pd(acac)Cl (**2**) as a yellow powder in nearly quantitative yield (Scheme 2). The loss of the C-bound ligand is again clearly evidenced by NMR. In ^{13}C NMR, only two carbonyl carbons (187.1, 184.1 ppm) and the carbenic carbon (156.4 ppm) appear, whereas in ^{1}H NMR, only one acac ligand can be assigned: singlet at 5.12 ppm, accounting for one hydrogen, and two methylic singlets (1.84, 1.82 ppm). Again, the structural features



Scheme 2. Synthetic path leading to (IPr)Pd(acac)Cl.

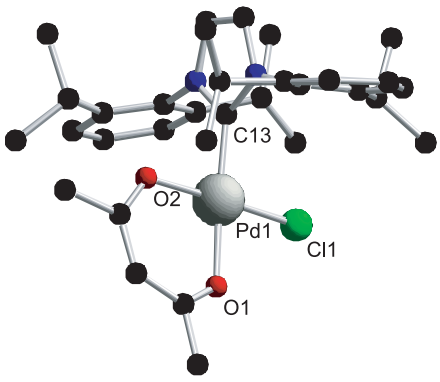
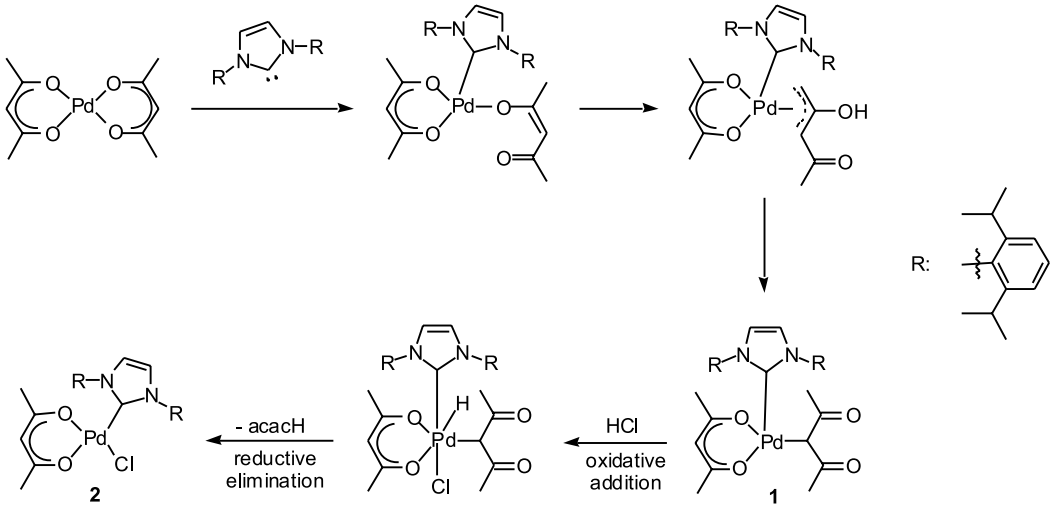


Figure 2. Ball and stick representation of (IPr)Pd(acac)Cl (hydrogens omitted for clarity). Selected bond distances (Å): C13–Pd1: 1.9694(17), Pd1–O2: 2.0362(15), Pd1–O1: 2.0439(14), Pd1–C13: 2.2820(6). Selected angles (deg): O2–Pd1–O1: 92.89(6), O1–Pd1–Cl1: 87.35(4), Cl1–Pd1–C13: 93.89(5), C13–Pd1–O2: 86.21(2).

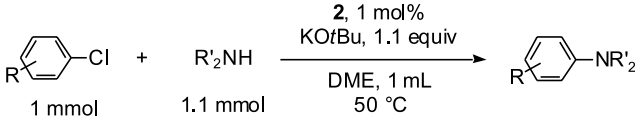
were unequivocally assigned when the structure was determined by single crystal X-ray diffraction (Fig. 2). For this complex, the Pd–O distances are more similar (2.036, 2.044 Å), whereas the square planar coordination around the palladium center becomes slightly more distorted.

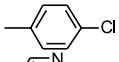
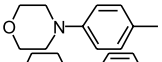
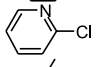
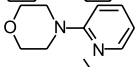
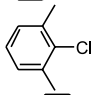
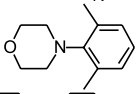
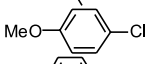
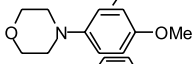
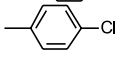
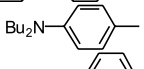
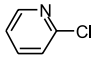
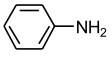
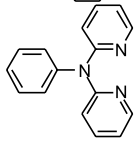
The formation of **1** and subsequently **2** can be postulated to occur by the pathway illustrated in Scheme 3. The coordination of the sterically demanding IPr by palladium is accompanied by the transition of one acac ligand from the η^2-*O*,*O*-chelate to the *O*-monodentate form, with subsequent transformation to the π-hydroxoallyl form and further to the C-bonded form. A similar pathway has been proposed by Shmidt for the phosphine analogues.[17b] Oxidative addition of HCl followed by reductive elimination of acacH yields **2**.



Scheme 3. Proposed mechanism for the formation of **1** and **2**.

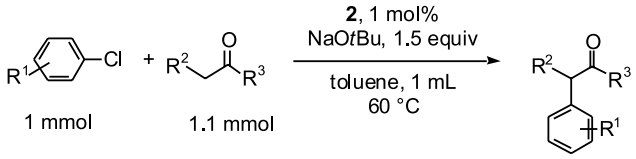
Table 1. Buchwald–Hartwig aryl amination of aryl chlorides using **2**

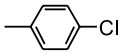
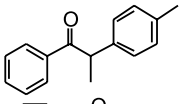
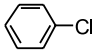
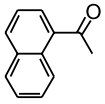
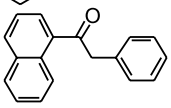
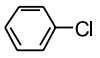
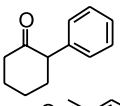
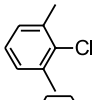
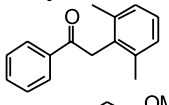
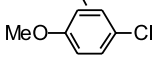
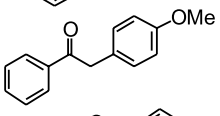
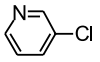
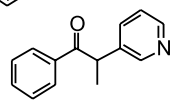


Entry	Aryl chloride	Amine	Product	Time (h)	Yield (%)[a]
1				0.5	97
2				0.5	98
3				1.5	90
4				4	99
5		Bu_2NH		6	95
6				10	93[b]

[a] Isolated yields, average of two runs.
[b] 2.1 equiv of aryl chloride were used.

Table 2. α-Ketone arylation with aryl chlorides using **2**



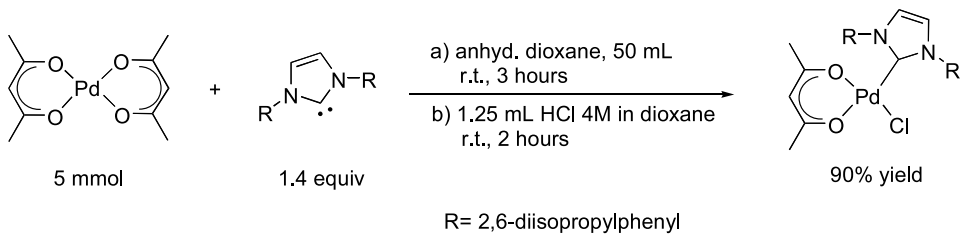
Entry	Aryl chloride	Ketone	Product	Time (h)	Yield (%)[a]
1				1	97
2				10	70
3				2	86
4				1	95
5				1.5	92
6				2	89

[a] Isolated yields, average of two runs.

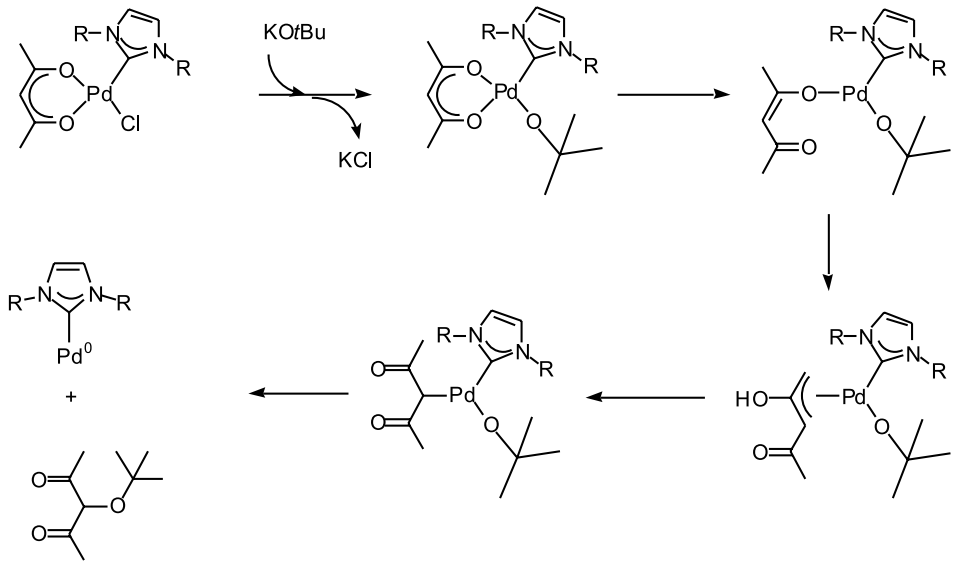
The activity of complex **2** for the Buchwald–Hartwig coupling reaction of morpholine and 4-chlorotoluene in the previously mentioned conditions was then tested. Using 1 mol% of **2**, the coupling occurred in 97% yield in only 30 min (entry 1, isolated yield). It is remarkable that the product could be obtained in good yield using low catalyst loading (0.1 mol%) or at room temperature if the reaction time was increased. Results for the amination of aryl chlorides using **2** as catalyst are shown in Table 1. Various substrates were examined: heteroaromatic (entry 2), sterically demanding (entry 3) and deactivated chlorides (entry 4). The coupling of the sterically demanding dibutylamine with 4-chlorotoluene required a longer time (entry 5), and was the only reaction, in which dehalogenation of the aryl chloride was observed (3% by GC). As the synthesis of unsymmetrical tertiary amines starting from primary amines remains a challenge,[19] we investigated the reaction between aniline and 2-chloropyridine. One-pot syntheses of *N*,*N*-bis(2-pyridyl)amino ligands, especially with aryl chlorides,[20] are attractive due to the number of applications in which these compounds can take part: C–C bond formation,[21] homogeneous and heterogeneous catalysis,[22] DNA binding[23] and nonlinear optical materials.[24] The formation of the double pyridilation product was observed in good yield when 2.1 equiv of the chloride were used (entry 6).

As for the Buchwald–Hartwig reaction, **2** performed more effectively than **1** for the α-ketone arylation reaction, requiring half the time in the coupling of propiophenone and 4-chlorotoluene (Table 2, entry 1). Using **2**, the system allowed for the coupling of aryl–aryl and aryl–alkyl ketones with a variety of aryl chlorides.

Since **2** displayed a higher activity than **1**, we realized the convenience of synthesizing **2** without the need of isolating the (IPr)Pd(acac)$_2$ intermediate. A one-pot multigram synthesis of **2** is summarized in Scheme 4. Reaction of the free carbene IPr with Pd(acac)$_2$ in anhydrous 1,4-dioxane at room temperature, followed by the addition of an equimolecular amount of HCl, leads to the formation of the desired product.



Scheme 4. One-pot protocol for the synthesis of (IPr)Pd(acac)Cl.



Scheme 5. Proposed mechanism for the activation of (IPr)Pd(acac)Cl.

A possible mechanism for the activation of **2** is depicted in Scheme 5.

The activation pathway involves the chloride/*tert*-butoxide anion exchange in a metathetical process followed by a rearrangement of the acac moiety prior to a reductive elimination step that yields the catalytically active [(IPr)Pd(0)] species. Recently, Hartwig reported that sterically demanding ancillary ligands promote the rearrangement of the κ^2-*O*,*O*-bound ligands to the C-tautomers in Pd(II) complexes with malonate or acetylacetonate anions.[25] It was also proposed that only complexes with these ligands in a C-bound mode are able to undergo reductive elimination in high yield. This fact not only supports the need of this rearrangement for the activation of **2**, but also for the formation of **1** and its later transformation into **2** by the addition of HCl (Scheme 3).

We have described the synthesis of two new NHC-bearing palladium complexes using $Pd(acac)_2$ as the Pd precursor. Complex **2** displays high activity for the Buchwald–Hartwig reaction and α-ketone arylation in short reaction times and very mild conditions. Both complexes are air- and moisture-stable and can be prepared on multigram scale in high yields. Studies focusing on the synthesis of related NHC-bearing complexes and their activity in homogeneous catalysis are currently ongoing in our laboratories.

3. Experimental

3.1. General remarks

^1H and ^{13}C nuclear magnetic resonance spectra were recorded on a Varian-300 or Varian-400 MHz spectrometer at ambient temperature in $CDCl_3$ (Cambridge Isotope Laboratories, Inc), unless otherwise noted. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., Madison, NJ. IPr·HCl was synthesized according to literature procedures but is also now commercially available from Strem Chemicals Inc or Sigma/Aldrich.[26]

3.2. Synthesis of complexes

3.2.1. (IPr)Pd(acac)$_2$ (1). In a glovebox, a Schlenk flask equipped with a magnetic bar was loaded with free carbene IPr (855 mg, 2.2 mmol), $Pd(acac)_2$ (609 mg, 2 mmol) and anhydrous toluene (30 mL), and sealed with a rubber cap. The mixture was stirred at room temperature for 2 h. The solvent was evaporated in vacuo and THF (25 mL) was added. The solution was filtered and the solid washed with THF (2×5 mL). The solvent was evaporated in vacuo; the complex was then triturated with cold pentane (25 mL) and the yellow precipitate was collected by filtration. Recrystallization from chloroform/pentane (25:75) yielded 1.28 g (93%) of the desired compound as a yellow microcrystalline material. ^1H NMR (400 MHz, C_6D_6): δ 7.28–7.24 (m, 2H), 7.18 (d, J=8.0 Hz, 4H), 6.47 (s, 2H), 5.90 (s, 1H), 4.78 (s, 1H), 2.88 (q, J=6.8 Hz, 4H), 2.63 (d, J=0.8 Hz, 3H), 2.01 (d, J=0.8 Hz, 3H), 1.63 (s, 3H), 1.35 (d, J=6.8 Hz, 12H), 1.31 (s, 3H), 0.97 (d, J=6.8 Hz, 12H). ^{13}C NMR (100 MHz, C_6D_6): 207.5, 192.9, 188.1, 185.6, 183.3, 161.2, 146.9, 135.9, 131.2, 130.4, 125.7, 125.2, 124.7, 124.5, 104.8, 100.3, 47.2, 31.9, 31.5, 29.3, 29.0, 28.9, 28.1, 27.0, 26.5, 26.2, 25.1, 24.0, 23.8, 23.4. Elemental analysis: Anal. Calcd: C, 64.11; H, 7.27; N, 4.04. Found: C, 63.89; H, 7.06; N: 3.86.

3.2.2. One-pot synthesis of (IPr)Pd(acac)Cl (2). In a glovebox, a Schlenk flask equipped with a magnetic bar was loaded with the free carbene IPr (2.73 g, 7 mmol), $Pd(acac)_2$ (1.53 g, 5 mmol) and anhydrous dioxane (50 mL), and sealed with a rubber cap. The mixture was stirred at room temperature for 2 h. After that time, 1.25 mL of HCl 4 M in dioxane was injected in the solution and the mixture allowed stirring at room temperature for another 2 h. The solvent was then evaporated in vacuo and diethyl ether was added until no more solid dissolved (20 mL). The solution was filtered and the solid washed with diethyl ether (2×10 mL). The solvent was evaporated in vacuo and the powder obtained dried under vacuum overnight to yield 2.85 g

(90%) of the desired product as a yellow microcrystalline material. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (t, J=7.6 Hz, 2H), 7.35 (d, J=8.0 Hz, 4H), 7.12 (s, 2H), 5.12 (s, 1H), 2.95 (q, J=6.4 Hz, 4H), 1.84 (s, 3H), 1.82 (s, 3H), 1.34 (d, J=6.4 Hz, 12H), 1.10 (d, J=6.4 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): 187.1, 184.1, 156.4, 147.0, 135.5, 134.8, 130.9, 125.7, 124.7, 124.6, 99.9, 29.1, 30.0, 27.6, 26.8, 23.7, 23.5. Elemental analysis: Anal. Calcd: C, 61.05; H, 6.88; N, 4.45. Found: C, 60.78; H, 7.15; N: 4.29.

3.3. Crystallographic data

3.3.1. (IPr)Pd(acac)$_2$ (1). Single crystals were grown by slow evaporation at room temperature of a concentrated methylene chloride/hexanes solution. $C_{37}H_{50}N_2O_4Pd$, M=693.2. Orthorhombic, space group $P2_12_12_1$, a=11.7529(6) Å, b=13.3836(7) Å, c=22.6493(12) Å, V=3562.6(3) Å^3; $D_c(Z=4)$=1.292 g cm^{-3}; μ_{Mo}=0.560 mm^{-1}; specimen: 0.6×0.5×0.3 mm; $T_{min/max}$=0.88; $2\theta_{max}$=40°; N_t=22450, N_o=3318; R=0.0340, R_w=0.0737.

3.3.2. (IPr)Pd(acac)Cl (2). Single crystals were grown by slow evaporation at room temperature of a concentrated methylene chloride/hexanes solution. $C_{32}H_{43}N_2O_2Pd$, M=629.53. Monoclinic, space group $P2_1/c$, a=10.957(2) Å, b=17.431(3) Å, c=16.814(3) Å, β=106.162(4) V=3084.4(10) Å^3; $D_c(Z=4)$=1.356 g cm^{-3}; μ_{Mo}=0.718 mm^{-1}; specimen: 0.6×0.6×0.4 mm; $T_{min/max}$=0.77; $2\theta_{max}$=45°; N_t=30901, N_o=4006; R=0.0259, R_w=0.0576.

CCDC reference numbers 263919-263920.

See http://www.rsc.org/suppdata/dt/b4/b4125540a/ for crystallographic data in CIF or other electronic format.

3.4. Cross-coupling reactions

3.4.1. Buchwald–Hartwig reaction of aryl chlorides with primary and secondary amines. *General procedure*: In a glovebox, **2** (1 mol%, 6 mg), potassium *tert*-butoxide (1.1 mmol, 124 mg) and DME (1 mL) were added in turn to a vial equipped with a magnetic bar, and sealed with a screw cap fitted with a septum. Outside the glovebox, the amine (1.1 mmol) and the aryl chloride (1 mmol) were injected in turn through the septum. The vial was then placed in an oil bath at 50 °C and the mixture stirred on a stirring plate. The reaction was monitored by gas chromatography. When the reaction reached completion, or no further conversion could be observed, the vial was allowed to cool down to room temperature. Water was added to the reaction mixture; the organic layer was extracted with diethyl ether and dried over magnesium sulfate. The solvent was then evaporated in vacuo. When necessary the product was purified by flash chromatography on silica gel (pentane/ethyl acetate: 9:1). Reported yields are the average of two runs:

3.4.1.1. 4-(4-Methylphenyl)morpholine (Table 1, entry 1).[27] The procedure afforded 171 mg (97%) of the title compound.

3.4.1.2. 4-(2-Pyridinyl)morpholine (Table 1, entry 2).[28] The procedure afforded 160 mg (98%) of the title compound.

3.4.1.3. 4-(2,6-Dimethylphenyl)morpholine (Table 1, entry 3).[29] The procedure afforded 170 mg (90%) of the title compound.

3.4.1.4. 4-(4-Methoxyphenyl)morpholine (Table 1, entry 4).[30] The procedure afforded 190 mg (99%) of the title compound.

3.4.1.5. *N*,*N*-Dibutyl-*p*-toluidine (Table 1, entry 5).[31] The procedure afforded 207 mg (95%) of the title compound.

3.4.1.6. *N*-Phenyl-*N*-(pyridin-2-yl)pyridin-2-amine (Table 1, entry 6).[32] The procedure with 2-chloropyridine (2.1 mmol, 200 μL), aniline (1.0 mmol, 93 μL), KO*t*Bu (2.2 mmol, 248 mg), (IPr)Pd(acac)Cl (1.0 mol%, 12.6 mg) and DME (2 mL) afforded 230 mg (93%) of the title compound as a white solid. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 8.22 (d, J=4 Hz, 2H), 7.61 (m, 2H), 7.38 (t, J=8.1 Hz, 2H), 7.24–7.16 (m, 3H), 7.00 (d, J=8.4 Hz, 2H), 6.97–6.94 (m, 2H). ^{13}C NMR (100 MHz, $((CD_3)_2CO)$): 159.5 (C), 149.4 (CH), 146.6 (C), 138.6 (CH), 130.7 (CH), 128.9 (CH), 126.6 (CH), 119.3 (CH), 118.0 (CH). Elemental analysis: Anal. Calcd for $C_{16}H_{13}N_3$ (M_W 247.29): C, 77.71; H, 5.30; N, 16.99. Found: C, 77.79; H, 5.57; N, 16.93.

3.4.2. α-Ketone arylation of alkyl or aryl ketones

General procedure: In a glovebox, **2** (1 mol%, 6 mg), sodium *tert*-butoxide (1.5 mmol, 144 mg) and toluene (1 mL) were added in turn to a vial equipped with a magnetic bar, and sealed with a screw cap fitted with a septum. Outside the glovebox, the ketone (1.1 mmol) and the aryl chloride (1.0 mmol) were injected in turn through the septum. The vial was then placed in an oil bath at 60 °C and the mixture stirred on a stirring plate. The reaction was monitored by gas chromatography. When reaction reached completion, or no further conversion could be observed, the vial was allowed to cool to room temperature. Water was added to the reaction mixture; the organic layer was extracted with diethyl ether and dried over magnesium sulfate. The solvent was then evaporated in vacuo. When necessary the product was purified by flash chromatography on silica gel (pentane/ethyl acetate: 9:1). The reported yields are the average of two runs:

3.4.2.1. 2-(4-Methylphenyl)-1-phenyl-1-propanone (Table 2, entry 1).[33] The procedure afforded 216 mg (97%) of the title compound.

3.4.2.2. 1-(Naphthyl)-2-phenylethanone (Table 2, entry 2).[34] The procedure afforded 173 mg (70%) of the title compound.

3.4.2.3. α-Phenylcyclohexanone (Table 2, entry 3).[35] The procedure afforded 150 mg (86%) of the title compound.

3.4.2.4. 2-(2,6-Dimethylphenyl)-1-phenylethanone (Table 2, entry 4). The procedure afforded 212 mg (95%) of the title compound as a white compound. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.09 (d, J=7.2 Hz, 2H), 7.64 (t, J=7.2 Hz, 1H), 7.54 (t, J=8.0 Hz, 2H), 7.14–7.06 (m, 3H), 4.40 (s, 2H), 2.21 (s, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2):

197.5 (C), 137.7 (C), 133.7 (CH), 133.4 (C), 129.2 (CH), 128.5 (CH), 128.3 (CH), 127.3 (CH), 114.0 (C), 40.2 (CH_2), 20.6 (CH_3). Elemental analysis: Anal. Calcd for $C_{16}H_{16}O$ (M_W 224.30): C, 85.68; H, 7.19. Found: C, 85.36; H, 7.23.

3.4.2.5. 2-(*p*-Methoxyphenyl)-acetophenone (Table 2, entry 5).[36] The procedure afforded 208 mg (92%) of the title compound.

3.4.2.6. 1-Phenyl-2-(3-pyridinyl)-1-propanone (Table 2, entry 6).[37] The procedure afforded 188 mg (89%) of the title compound.

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