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Synthesis, characterization and catalytic behaviour of a palladium complex bearing a hydroxyfunctionalized N-heterocyclic carbene ligand†‡

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The synthesis of a new stable palladium(III) complex (**3**) featuring an unsymmetrical substituted N-heterocyclic carbene (NHC) ligand with a pendant hydroxy-functionalized group was successfully accomplished *via* transmetalation of the corresponding bis-NHC silver(I) complex (**2**). Solid-state structures of both **2** and **3** were determined by single-crystal X-ray diffraction. The catalytic behaviour of **3** in the direct regioselective arylation of furan and thiophene derivatives by using challenging aryl halides was studied, revealing that **3** was capable of promoting these environmentally attractive coupling reactions to afford arylated heterocycles in moderate to good yields.

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Introduction

N-heterocyclic carbenes (NHCs) have become ubiquitous ligands in organometallic chemistry, thus proving to be more than just phosphine mimics.¹ Due to their strong electronic σ -donating properties combined with a shielding steric pattern, NHCs form stronger bonds with metal centers than phosphine ligands,² leading to more stable transition metal complexes with superior catalytic activities. The structural flexibility of NHCs renders this class of ligands exceptionally intriguing and versatile, as evidenced by numerous applications ranging from homogeneous catalysis to material and medicinal sciences.^{1,2}

In the last few decades, heteroatom-functionalized NHCs incorporating a pendant neutral or anionic functional group have received considerable attention in the organometallic chemistry due to their ability to act as chelating or pincer ligands. Indeed, they are expected to enhance catalyst stability and to offer a key structure for the construction of stereodirecting elements for asymmetric catalysis purposes. Moreover, the introduction of a functional group into the side chain of a NHC ligand offers the possibility of anchoring the catalyst to a solid support.^{3–7} As a result, a huge library of early^{4b,c,8} and late transition⁹ metal

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complexes containing mono- and poly-ligating NHCs, pincer-NHCs and mixed donor systems has been generated and extensively utilized in homogeneous catalysis.^{1d,10}

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Our contribution in this field is mainly related to the exploration of modified NHC ligands for ruthenium olefin metathesis catalysts.¹¹ Recently, some of us reported on novel zirconium–diamide complexes bearing alkoxide-functionalized N-heterocyclic carbenes [NHC–O] that, in combination with methylaluminoxane, are able to polymerize ethylene to linear polyethylene and propylene to highly isotactic polypropylene.¹² Following this study, we decided to extend our investigation on functionalized NHCs to other metal complexes.

In particular, we focused our efforts on the development of NHC bearing Pd(n) complexes and the study of their catalytic activity. This family of palladium complexes has received a lot of academic and industry attention during the last ten years, as a result of their ability to mediate numerous organic reactions, principally cross-coupling reactions, and of their remarkable stability, easy handling and robustness under harsh reaction conditions.^{10b,d,13} Herein, we describe the synthesis and characterization of a new palladium(n) complex incorporating an hydroxy-functionalized NHC [NHC–OH]. This complex was obtained through a synthetic strategy involving transmetalation of the corresponding NHC–silver complex, whose detailed structural analysis is also given for the first time.

The catalytic behavior of the novel palladium complex has been explored in the direct arylation of heteroaromatic derivatives by using challenging aryl halides. This coupling reaction is very attractive because arylated heterocycles represent essential structural units of biologically relevant natural products, drugs and agrochemicals.¹⁴ Moreover, the catalyzed regioselective

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coupling reactions of heterocycles with aryl-halides by direct conversion of a C–H bond in a C–C bond,¹⁵ instead of traditional methods involving the stoichiometric reaction of aryl halides with organometallic derivatives of heterocycles or the reaction of heteroaryl halides with aryl-metal derivatives,¹⁶ are economically and environmentally effective. So far, the efficiency of NHC–Pd complexes has been almost unexplored for these couplings, whereas the discovery of more efficient catalysts would provide environmentally attractive and industrially viable procedures.

Results and discussion

The synthetic plan to reach the novel palladium complex is depicted in Scheme 1. The hydroxy-functionalized imidazolium salt (1) was easily prepared by ring opening of cyclohexenoxide with imidazole and subsequent reaction in acetonitrile with iodomethane.¹⁷ For coordination of the imidazolium salt 1 as NHC to palladium, a transmetalation reaction of the corresponding NHC–Ag complex (2) with PdCl₂(CH₃CN)₂ was employed affording [NHC–OH]PdCl₂(CH₃CN) (3) in good yield (69%).

Synthesis and characterization of the [NHC-OH]Ag complex (2)

Transmetalation has proven to be a convenient and efficient approach to synthesise NHC–metal complexes, since NHC–Ag complexes are generally air- and moisture-stable, easy to synthesize and with a strong tendency to crystallize. The driving force for this reaction is the precipitation of silver halide salts.¹⁸ Thus, *N*-methyl,*N'*-[(2-hydroxy-cyclohexyl)]-imidazolium iodide **1** was treated with Ag₂O (1.5 : 1 molar ratio) in refluxing CH₂Cl₂ under exclusion of light. Ag₂O particularly serves as a mild base, reacting predominantly at the C2 position of the imidazolium salt without deprotonation of other acidic protons. The silver complex **2** was isolated as a white solid after filtration and removal of the solvent under reduced pressure (57%).

Initial structural analyses of the isolated product were conducted using ¹H and ¹³C NMR. The product appeared to be spectroscopically pure and, as expected, in the ¹H NMR spectrum the C2-H signal of the imidazole ring was absent, whereas in the ¹³C-NMR spectrum the characteristic coordinated carbene



Scheme 1 Synthesis of [NHC-OH]Pd(II) complex 3.

resonated at 184.2 ppm as a sharp singlet. The lack of carbene–C coupling to silver suggests a fluxional behaviour of the NHC–Ag complex 2.¹⁹ Although chemical shifts in the NMR spectra clearly indicated the formation of an NHC–Ag complex, they did not allow unambiguous distinction of whether a mono- or bis-NHC complex was formed.

Mass spectrometry (ESI-MS) provided fundamental data on the structure of compounds in the gas phase. In fact, the maximum peak at 467 Da, associated with M + 2 at 469 Da, is attributable to [(NHC-OH)₂Ag]⁺. On the other hand, the elemental analysis of 2 gives a molar ratio among silver, ligand and iodide of 1:1:1, therefore, taken together, the NMR, MS and elemental analyses suggest that complex 2 very likely consist of ionic structures based on [(NHC-OH)₂Ag]⁺ cations and $[AgI_2]^-$ anions.²⁰ As for NHC Ag(1) complexes reported up to now, complex superstructures are frequently observed in the solid state, especially when the NHC contains additional donor functionalities.^{9d,18} Usually, with coordinating anions (X = e.g.)halides) mono-NHC Ag(I) complexes of the formula $[(NHC)AgX]_n$ are formed, whereas bis-NHC Ag(I) complexes of the type [(NHC)₂Ag]X when X is a noncoordinating anion, such as NO3⁻, OTf⁻, BF4⁻, and PF6⁻, are obtained.¹⁸ In solution, mono-NHC Ag(1) complexes are typically in fast equilibrium with the respective homoleptic species, whereas bis-NHC Ag(1) complexes are static in coordination (Scheme 2).

Single crystals of 2 suitable for X-ray diffraction were grown by slow evaporation of a saturated CH_2Cl_2 solution. The asymmetric unit of the Ag compound is built up by four independent $[Ag(NHC)_2]^+$ cations, two independent $[Ag_2I_4]^{2-}$ anions and two molecules of acetonitrile.²¹ A selection of bond distances and angles is shown in Table 1. Each anion is "sandwiched" between two cationic complexes $[Ag(NHC)_2]^+$ by means of short $Ag \cdots Ag$ and $Ag \cdots C(carbene)$ interactions. The two "sandwiches" display some differences as far as the anion position is concerned. In the first arrangement, shown in Fig. 1, both the metallic centres of the anion are involved in $Ag \cdots Ag$ interactions with the cations as well as in $Ag \cdots C1(carbene)$ short contacts (Table 2).

The latter systems are slightly different from the previous one because the anion is not centered between the two cations and, accordingly, only one metallic center, Ag7, can interact with the cationic Ag atoms and with the carbene carbons C1G and C1H (Fig. 2).

This asymmetric arrangement produces a guest cavity which, in the crystal, contains two molecules of acetonitrile. In all the independent cationic Ag complexes the C1(carbene)–Ag–C1'(carbene) angles are slightly bent $[C-Ag–C angle of 157^{\circ}]$



Scheme 2 Solution structures of mono-NHC Ag(ı) complexes.

Table 1 Selected bond distances and angles (Å and degrees) for ${\bf 2}$

Distances			
Ag1-C1A	2.122(8)	Ag1-C1B	2.102(8)
Ag1-C1A	1.342(11)	CIB-N1B	1.339(11)
C1A-N2A	1.349(11)	C1B-N2B	1.358(11)
Ag2-C1C	2.083(8)	Ag2-C1D	2.132(8)
C1C-N1C	1.367(10)	CID-N1D	1.356(11)
C1C-N2C	1.361(11)	C1D-N2D	1.311(12)
Ag6-C1E	2.096(11)	Ag6–C1F	2.089(10)
C1E-N1E	1.356(12)	C1F-N1F	1.367(13)
C1E-N2E	1.344(13)	C1F–N2F	1.340(12)
Ag5–C1G	2.088(9)	Ag5–C1H	2.104(10)
C1G-N1G	1.359(13)	C1H-N1H	1.360(12)
C1G-N2G	1.362(12)	C1H-N2H	1.344(12)
Ag3–I1	2.711(1)	Ag4–I4	2.705(1)
Ag3-I2	2.864(1)	Ag4–I2	2.833(1)
Ag3-I3	2.861(1)	Ag4–I3	2.883(1)
Ag7-I5	2.720(1)	Ag8–I8	2.710(1)
Ag7–I6	2.806(1)	Ag8–I6	2.779(1)
Ag7–I7	2.839(1)	Ag8–I7	2.838(1)
Angles			
C1A-Ag1-C1B	155.5(3)	C1C-Ag2-C1D	155.0(3)
N1A-C1A-N2A	105.0(7)	N1C-C1C-N2C	104.4(7)
N1B-C1B-N2B	103.3(8)	N1D-C1D-N2D	106.6(8)
C1E-Ag6-C1F	158.9(4)	C1G–Ag5–C1H	157.8(4)
N1E-C1E-N2E	105.1(8)	N1G-C1G-N2G	103.4(8)
N1F-C1F-N2F	103.9(8)	N1H-C1H-N2H	104.7(8)
I1-Ag3-I2	116.56(4)	I5-Ag7-I6	131.53(4)
I1-Ag3-I3	134.36(4)	I5-Ag7-I7	120.53(4)
I2-Ag3-I3	108.97(4)	I6-Ag7-I7	107.94(7)
I4-Ag4-I2	125.04(4)	I8-Ag8-I6	122.46(5)
I4-Ag4-I3	125.04(4)	I8-Ag8-I7	128.59(5)
I2-Ag4-I3	109.21(4)	I6-Ag8-I7	108.73(4)
Ag3-I2-Ag4	71.07(3)	Ag7–I6–Ag8	71.61(3)
Ag3-I3-Ag4	70.40(3)	Ag7–I7–Ag8	70.29(4)



Fig. 1 ORTEP²² view of the first arrangement of **2** where a $[Ag_2I_4]^{2-}$ anion is "sandwiched" between two identical but crystallographic independent $[Ag(NHC)]^+$ cations. The thermal ellipsoids are at the 50% probability level.

(on average for the four cations)], with respect to the typical linear conformation of other similar structures, $^{23-26}$ in order to allow the formation of an intramolecular O-H···O hydrogen

 Table 2
 Intermolecular short interactions (Å) for 2

O1A···O1B	2.813(10)	Ag1···Ag3	3.252(1)
$O1A \cdots O1B(1 - x, -y, 1-z)$	2.971(11)	Ag1···Ag4	3.239(1)
01C···01D	2.774(11)	Ag2···Ag3	3.128(1)
O1C···O1E	2.751(11)	Ag2···Ag4	3.166(1)
O1D···O1F	2.871(13)	Ag5···Ag7	3.186(1)
O1E···O1F	2.788(10)	Ag6· · ·Ag7	3.276(1)
O1G···O1H	2.851(12)	Ag3···C1A	3.180(10)
$O1G \cdots O1H(-x,2-x,2-z)$	2.992(12)	Ag3· · ·C1C	3.212(9)
		Ag4···C1B	3.346(10)
		Ag4···C1D	3.074(10)
		Ag7···C1F	3.242(11)
		Ag7· · ·C1G	3.292(11)



Fig. 2 ORTEP²² view of the latter arrangement of **2** where a $[Ag_2I_4]^{2-}$ anion is asymmetrically "sandwiched" between two $[Ag(NHC)]^+$ cations. The thermal ellipsoids are at the 50% probability level.

bond between the hydroxo groups of cyclohexanol substituents. The hydrogens of hydroxo groups of structure 2 could not be localized. Beyond the intramolecular O–H···O hydrogen bonds the hydroxo groups are also involved in intermolecular hydrogen bonds between couples of cations which are, in such way, held together by a circular hydrogen bond system as shown in Scheme 1.

The crystal is characterized by infinite ribbons built up by couples of cations linked by O–H···O H-bonds and inter-connected to the anions by means of Ag···Ag and Ag···C(carbene) short interactions···[Ag(NHC)₂]₂⁺···[Ag₂I₄]^{2–}···[Ag(NHC)₂]⁺₂···[Ag₂I₄]^{2–}··· [Ag(NHC)₂]⁺₂··· (Fig. 3). The intra and intermolecular distances involving Ag metallic centres are in agreement with other carbene complexes displaying similar Ag(I)d¹⁰···Ag(I)d¹⁰ closed shell short interactions.^{23–26}

Synthesis and characterization of the [NHC-OH]Pd complex (3)

The so-generated NHC Ag(i) complex was afterwards employed in the reaction with $PdCl_2(CH_3CN)_2$ in CH_2Cl_2 at room temperature (1:1 molar ratio), following the synthetic procedure developed by Wang and Lin.¹⁹ Interestingly, although for NHC transfer reactions mono-NHC Ag(i) is by far the most frequently utilized, partially because the more stable bis-NHC Ag(i) complexes

Paper



Fig. 3 Infinite ribbons in the crystal of 2 built up by couples of cations linked by OH…O H-bonds and inter-connected to the anions by means of Aq···Aq and Aq···C(carbene) short interactions. (i): 1 - x, -y, 1 - z; (ii) -x, 2 - y, 2 - z.

are believed to be less active in these reactions,^{9d,27} we found that the bis-NHC Ag(I) complex 2 was capable of efficiently transferring one carbene ligand affording the mono-NHC Pd(II) complex 3. It is worth underlining that this synthetic approach allowed us to successfully achieve the desired palladium complex, whereas other methods of carbene introduction failed.²⁸ Notably, to the best of our knowledge compound 3 represents the first example of mono-NHC palladium complex featuring an hydroxyfunctionalized NHC ligand. Indeed, only bis-NHC Pd(II) complexes with similar modified NHC ligands have been reported so far.²⁹ Complex 3 was isolated as an air- and moisture-stable pale vellow solid and fully characterized by 1D and 2D NMR, mass spectrometry and elemental analyses.

The structural assignment of 3 was unambiguously established by X-ray diffraction. The ORTEP²² view of the Pd complex is shown in Fig. 4. A selection of bond distances and angles is given in Table 3.

The coordination geometry around the $Pd(\pi)$ centre is essentially square planar with one carbene, two chloride ligands and one acetonitrile ligand trans to the NHC (N-heterocyclic carbene). The coordination plane is almost perpendicular to the NHC ring, the dihedral angle between the two planes being $86.01(6)^\circ$. This conformation allows the formation of a O-H···Cl hydrogen bond, $O1 \cdots Cl1 = 3.263(3)$ Å, between the hydroxo group of the cyclohexanol substituent at the NHC ring and a coordinated Cl atom. Bond distances between Pd1 centre and the atoms of ligands are in perfect agreement with those observed in other very similar complexes.30-32

Catalytic activity

As a preliminary study on the catalytic behaviour of 3, we have chosen the direct regioselective coupling of heteroaromatics with aryl halides.

In recent years, numerous studies on the selective C2 or C5 arylation of heteroaromatics such as furans, thiophenes, thiazoles, oxazoles or indoles by means of palladium catalysed C-H bond activation have been reported.33 In most cases, the couplings were performed by using reactive aryl halides such as aryl iodides or electron-deficient aryl bromides. A limited number of coupling



Fig. 4 $ORTEP^{22}$ view of **3** showing the thermal ellipsoids at the 50% probability level.

reactions involving deactivated aryl halides have been described up to now,¹⁵ and the role of NHC ligands in these challenging transformations is almost unexplored.^{33g,34} Therefore, we decided to employ our Pd(II) complex to promote the direct C5 arylation of furans and thiophenes (see Scheme 3).

The coupling reactions were carried out by using 1 mol% of palladium and KOAc as base in DMF at 150 °C. The formation of the target arylated heterocycles was monitored by GC and ¹H NMR analyses over a period of 24 h, and the most relevant results are summarized in Scheme 3.

The reaction of deactivated aryl bromide 4-bromoanisole 4 with functionalized furan derivatives 5 and 7 proceeded to give, respectively, heterocoupled products 6 and 8 with moderate yields (34-40%) in 5 h. Prolonged reaction time (24 h) did not improve the yields, however, after this time, we observed the

Table 3 Selected bond distances and angles (Å and degrees) for 3



Scheme 3 Direct arylation of furan and thiophene derivatives with aryl halides promoted by 3. *Reaction conditions*: aryl halide (1 mmol), heteroaryl derivative (2 mmol), KOAc (2 mmol), 3 (0.01 mmol) and DMF (3 mL).

nearly complete conversion of 4-bromoanisole (80–100%) to undesired side-products. Symmetrical substituted mono-NHC palladium catalysts are reported to perform the same reactions

with slightly higher yields.^{33g} Only a few examples of the challenging direct coupling of arylchlorides to heteroaromatics with NHC-Pd complexes are known.^{33g} The reaction of 4-chloronitrobenzene 9 with furan derivative 5, promoted by catalyst 3, gave 10 in good yield (59%) within 3 h, whereas the reaction of 9 with furanic substrate 7 afforded 11 in lower yield (37%). Moreover, in the last case after 24 hours a decreased yield in the desired product was registered, as a consequence of undesired secondary reactions. It is worth to underline that for both reactions a complete conversion of 4-chloronitrobenzene to side-products is observed. We also examined the direct arylation of thiophenes with aryl halides. Also this coupling reaction has been scarcely investigated using NHC palladium catalysts up to now.^{33g} As for the reaction of the strongly deactivated arylbromide 4-bromo-N,Ndimethylaniline 12 with 2-methylthiophene 13, catalyst 3 revealed low efficiency, affording a very low yield (15%) of the arylated thiophene derivative 14 in 2 h. Prolonged reaction time (24 h) decreased the yield of 14, producing unidentified products and leading to full conversion of the arylbromide 12. A better result was obtained in the coupling of 4-chloronitrobenzene 9 with 2-methylthiophene 13, that proceeded to form the desired product 15 with 34% yield in 5 h, in line with the results obtained in analogous reactions promoted by similar mono-NHC palladium complexes.^{33g} In this case, conversion of the aryl chloride 9 is not complete (70%).

Conclusions

In summary, we have described an efficient synthetic route to mono-NHC Pd(II) complexes featuring a functionalized, unsymmetrical substituted NHC ligand. The presented complex 3, featuring both N-hydroxy functional group and N-methyl group on the NHC, was obtained for the first time through a transmetalation reaction of the corresponding bis-NHC silver compound 2. Both complexes 2 and 3 were fully characterized by NMR, MS and elemental analyses. The structures of 2 and 3 were confirmed by single-crystal X-ray diffraction studies. The catalytic behaviour of 3 was investigated in the attractive, direct regioselective C5 arylation of heteroaromatics by using challenging aryl halides, where only few NHC palladium complexes have been employed up to now. Catalyst 3 proved to be a suitable catalyst for these coupling reactions. Although no evidence for possible advantages of a pendant functional group on the NHC ligand is detected, our preliminary catalytic results encourage deeper investigation of the catalytic potential of this class of palladium complexes, also in other cross coupling reactions, to better recognize NHC modifications that could address further catalyst design. Moreover, the pendant hydroxyl group on the NHC ligand could be exploited as a good linker functionality for catalyst immobilization onto solid supports.

Experimental section

General information

All manipulations were performed under oxygen- and moisturefree atmosphere in an MBraun MB 200 glove-box. All of the

Paper

reagents were purchased from Sigma-Aldrich and were used as received. All the solvents were thoroughly deoxygenated and dehydrated under nitrogen by refluxing over suitable drying agents. Deuterated solvents (Euriso-Top products) were degassed under a nitrogen flow and stored over activated 4 molecular sieves. NMR spectra were recorded on a Bruker AM250 and a Bruker AM300 operating at 250 and 300 MHz for proton and 62.5 MHz and 75 MHz for carbon spectra, respectively. The ¹H and ¹³C NMR chemical shifts are referenced to SiMe₄ (d = 0 ppm) using the residual proton impurities of the deuterated solvents as internal standards. Spectra are reported as follows: chemical shift (ppm), multiplicity and integration. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (br). Elemental analyses for C, H, N were carried out on a ThermoFinnigan Flash EA 1112 and were performed according to standard microanalytical procedures. ESI-MS were performed on a Waters Quattro Micro triple quadrupole mass spectrometer equipped with an electrospray ion source.

Synthesis of complex 2

A 250 mL round-bottom flask was charged with molecular sieves, 0.5 g (16×10^{-4} mol) of **1**, 110 mL of CH₂Cl₂ and 0.244 g (10×10^{-4} mol) of Ag₂O. The mixture was protected from light and heated with vigorous stirring at 55 °C for 1.5 h. The resulting grey suspension was filtered through celite and the volatiles removed under reduced pressure to afford 0.380 g (57%) of the silver complex as a white solid. The crude product was crystallized from dichloromethane at room temperature.

¹H NMR (250 MHz, CD_2Cl_2): δ 7.04 (d, 2H), 4.43 (m, 1H), 3.87 (s, 3H), 3.79 (m, 1H), 2.94 (br, 1H), 2.12–1.27 (m, 8H). ¹³C NMR (62.5 MHz, CD_2Cl_2): δ 184.2 (*NCN*), 122.6, 118.8, 73.8, 67.5, 39.4, 35.2, 33.7, 25.5, 25.1. ESI-MS (CH₃CN, *m/z*): 467.36 [Ag(L)₂]⁺. Elem. Anal.: found (%): C 28.8, H 3.7, N 6.8. Calc. for $C_{10}H_{16}AgIN_2O$ (%): C 28.9, H 3.8, N 6.7.

Synthesis of complex 3

0.664 g of complex 2 (16×10^{-4} mol) and 0.414 g of PdCl₂-(CH₃CN)₂ (16×10^{-4} mol) were dissolved in CH₂Cl₂ (120 mL) and stirred at room temperature for 1.5 h. The reaction mixture was protected from light, and subsequently filtered through celite to afford a clear light yellow solution. The solvent was removed under reduced pressure to give 0.200 g (69%) of a light yellow solid. ¹H NMR (300 MHz, CDCl₃): δ 7.00 (s, 2H), 5.37 (br, 1H), 4.74 (br, 1H), 4.27 (s, 3H), 3.74 (br, 1H), 2.72 (bs, 2H), 2.26–1.62 (m, 9H). ¹³C NMR (75 MHz, CD₂Cl₂): δ 139.7 (*NCN*), 125.0, 120.1, 73.2, 67.6, 38.8, 35.6, 33.6, 25.6, 25, 1.4 (CH₃CN). ESI-MS (CH₃CN, *m*/*z*): 323.25 [Pd(NHC)Cl]⁺. Elem. Anal.: found (%): C 36.0, H 4.7, N 10.4. Calc. for C₁₂H₁₉PdCl₂IN₃O (%): C 36.1, H 4.8, N 10.6.

General procedure for direct arylations

In a typical experiment, the aryl halide (1 mmol), heteroaryl derivative (2 mmol), KOAc (2 mmol), the Pd complex **3** (0.01 mmol) and DMF (3 mL) were introduced into a vial, under nitrogen, equipped with a magnetic stirring bar. The vial was placed in a preheated oil bath at 150 $^{\circ}$ C, and the reactants were

stirred for 24 h. The reaction mixture was monitored by gas chromatography and ¹H NMR to determine the conversion of the aryl halide and the formation of the desired product.

Methyl 2-(4-methoxyphenyl)-5-methylfuran-3-carboxylate (6)

The reaction of 4-bromoanisole 4 (0.187 g, 1 mmol), methyl 2-methylfuran- 3-carboxylate 5 (0.280 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with Pd catalyst 3 (4 mg, 0.01 mmol) afforded the corresponding product 6 in 40% yield in 5 h.

[5-(4-Methoxyphenyl)furan-2-yl]methyl acetate (8)

The reaction of 4-bromoanisole **4** (0.187 g, 1 mmol), (furan-2-yl)methyl acetate 7 (0.280 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with Pd catalyst **3** (4 mg, 0.01 mmol) afforded the corresponding product **8** in 34% yield in 5 h.

Methyl 2-methyl-5-(4-nitrophenyl)furan-3-carboxylate (10)

The reaction of 1-chloro-4-nitrobenzene 9(0.157 g, 1 mmol) and methyl 2-methylfuran-3-carboxylate 5(0.280 g, 2 mmol) with Pd catalyst 3(4 mg, 0.01 mmol) afforded the corresponding product 10 in 59% yield in 5 h.

[5-(4-Nitrophenyl)furan-2-yl]methyl acetate (11)

The reaction of 1-chloro-4-nitrobenzene **9** (0.157 g, 1 mmol), (furan-2-yl)methyl acetate (0.280 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with Pd catalyst **3** (4 mg, 0.01 mmol) afforded the corresponding product **11** in 37% yield in 2 h.

2-Methyl-5-(4-methoxyphenyl)thiophene (14)

The reaction of 4-bromo-*N*,*N*-dimethylaniline (0.200 g, 1 mmol), 2-methylthiophene **13** (0.200 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with Pd catalyst **3** (4 mg, 0.01 mmol) afforded the corresponding product **14** in 15% yield in 3 h.

2-Methyl-5-(4-nitrophenyl)thiophene (15)

The reaction of 1-chloro-4-nitrobenzene (0.157 g, 1 mmol) and 2-methylthiophene (0.200 g, 2 mmol) with Pd catalyst 3 (4 mg, 0.01 mmol) afforded the corresponding product **15** in 34% yield in 5 h.

NMR spectra of new compounds and X-ray data for 2 (CCDC 948494) and 3 (CCDC 948493) are provided in the ESI.‡

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