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Reactivity of 6-(2-tolyl)- and 6-(2,6-xylyl)-2,2′-bipyridines with palladium(II) derivatives. Selective C(sp^3)–H vs. C(sp^2)–H activation

Sergio Stoccoro *, Barbara Soro, Giovanni Minghetti, Antonio Zucca, Maria A. Cinellu

Dipartimento di Chimica, Università di Sassari, via Vienna 2, I-07100 Sassari, Italy

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Abstract

Two new 6-substituted 2,2′-bipyridines, L, 6-(2-tolyl)bipy, L^1, and 6-(2,6-xylyl)bipy, L^2, have been synthesized. Their reactions with $Na_2[PdCl_4]$ or $\{Pd(OAc)_2\}$ afford either 1:1 adducts $[Pd(L)X_2]$ (X = Cl, OAc) or five-membered cyclometallated derivatives $[Pd(L^1\text{-}H)X]$ arising from C(sp^2)–H activation. From the chloro-alkyl intermediates [Pd(L)(Me)Cl], in the presence of $Na[BAr'_4]$ (Ar′ = 3,5-$(CF_3)_2C_6H_3$), cationic species $[Pd(L)(Me)(S)]^+$ (L = L^1, L^2; S = CH_3CN) can be obtained. At variance, in less coordinating solvents, e.g. dichloromethane, unexpected activation of a C(sp^3)–H bond occurs with loss of methane, to afford 6-membered cyclometallated derivatives. The latter species were isolated as $[Pd(L\text{-}H)(PPh_3)][BAr'_4]$.

Keywords: Cyclometallation; 2,2′-Bipyridine; Palladium

1. Introduction

Intramolecular C–H activation promoted by palladium derivatives has been a topic of interest for many years [1]. A number of N donors have been studied, as supporting ligands, including potentially bidentate heterocyclic molecules such as 2,2′-bipyridines and 1,10-phenanthrolines [1d,2]. Previously, we investigated the behaviour of several 6-substituted-2,2′-bipyridines with palladium(II) salts and isolated both adducts and cyclometallated derivatives with an N^N^C sequence of donor atoms [3]. The substituents were aryl, benzyl and alkyl groups and activation of both C(sp^2)–H and C(sp^3)–H bonds was achieved. The nature of the substituent was shown to be crucial in driving the reactivity of the ligand, often in unpredictable ways: even subtle differences can play a role in the outcome of the reaction. As part of an ongoing study into the effects of ligand variations, we have now synthesized two new ligands, namely 6-(2-tolyl)-2,2′-bipy and 6-(2,6-xylyl)-2,2′-bipy, which bear sterically demanding substituents. Their reactivity was explored at first with $Na_2[PdCl_4]$ and $\{Pd(OAc)_2\}$ and afterwards with palladium chloromethyl-derivatives. With the latter intermediates in the presence of $Na[BAr'_4]$ (Ar′ = 3,5-$(CF_3)_2C_6H_3$), in poorly coordinating solvents such as dichloromethane, metallation involving an unactivated methyl group vs. cleavage of an aromatic C–H bond was achieved.

Today the influence of the nature of the substituents on diimine ligands is of great interest particularly for d^8 complexes (Ni, Pd, Pt): species of this type are extensively investigated owing to their potential as catalytic precursors in processes of paramount importance such as polymerization of olefines (Ni, Pd) [4], copolymerization of CO/olefines (Pd) [5] and C–H intermolecular activation (Pt) [6].

* Corresponding author.
E-mail address: stoccoro@uniss.it (S. Stoccoro).

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Table 1
Proton and ^{31}P-NMR data[a]

Compound	CH_3	CH_2	H(6′)	Other aromatics	^{31}P
2-(2-tolyl)py[a]	2.35 [s, 3H]		8.67 [d, 1H]	7.16–7.71 [m, 7H]	
2-(2,6-xylyl)py[a]	2.04 [s, 6H]		8.72 [d, 1H]	7.25–8.49 [m, 6H]	
6-(2-tolyl)-2,2′-bipy (L^1)[a]	2.48 [s, 3H]		8.68 [d, 1H]	7.08–7.78 [m, 10H]	
6-(2,6-xylyl)-2,2′-bipy (L^2)[a]	2.12 [s, 6H]		8.70 [d, 1H]	7.13–8.42 [m, 9H]	
[Pd(L^1-H)Cl] (**1b**)[b]	2.63 [s, 3H]		8.89 [d, 1H]	6.89–8.06 [m, 9H]	
[Pd(L^1-H)I] (**1c**)[b]	2.66 [s, 3H]		9.31 [d, 1H]	6.86–8.33 [m, 9H]	
[Pd(L^1-H)(PPh_3)][BF_4] (**1d**)[b]	2.70 [s, 3H]			6.49–8.25 [m, 25H]	40.21
[Pd(L^1-H)(OAc)] (**1e**)[b]	2.17 [s, 3H]		8.61 [d, 1H]	6.91–8.04 [m, 9H]	
	2.61 [s, 3H]				
[Pd(L^1)($OAc)_2$] (**1f**)[b]	1.32 [s, 3H]				
	2.01 [s, 3H]				
	2.68 [s, 3H]			7.29–8.73 [m, 11H]	
[Pd(L^1)(Me)Cl] (**1g**)[a]	0.02 [s, 3H]		9.21 [d, 1H]	7.26–8.11 [m, 20H]	
	1.12 [s, 3H]		8.64 [d, 1H]		
	2.53 [s, 6H]				
[Pd(L^1)(Me)(MeCN)][BAr_4'] (**1h**)[a]	1.00 [s, 3H]		8.45 [d, 1H]	7.35–7.99 [m, 22H]	
	1.78 [s, 3H][c]				
	2.40 [s, 3H]				
[Pd(*L^1-H)(PPh_3)][BAr_4'] (**1j**)[a]		3.07 [s, 2H] {5.6}[e]		6.59–8.01 [m, 38H]	37.63
[Pd(L^2)Cl_2] (**2a**)[b]	2.34 [s, 6H]		9.39 [d, 1H]	7.12–8.18 [m, 9H]	
[Pd(L^2)($OAc)_2$] (**2f**)[b]	1.32 [s, 3H]		8.36 [d, 1H]	7.14–8.34 [m, 9H]	
	1.98 [s, 3H]				
	2.35 [s, 6H]				
[Pd(L^2)(Me)Cl] (**2g**)[a]	0.05 [s, 3H]		9.28 [d, 1H]	7.11–8.16 [m, 18H]	
	1.12 [s, 3H]		8.65 [d, 1H]		
	2.21 [s, 6H]				
	2.27 [s, 6H]				
[Pd(L^2)(Me)(MeCN)][BAr_4'] (**2h**)[a]	0.99 [s, 3H]		8.45 [d, 1H]	7.14–8.05 [m, 21H]	
	1.87 [s, 3H][c]				
	2.13 [s, 6H]				
[Pd(*L^2-H)(PPh_3)][BAr_4'] (**2j**)[a]	2.43 [s, 3H]	3.52 [br, 1H][d]		6.37–8.05 [m, 37H]	35.50
		2.45 [br, 1H][d]			

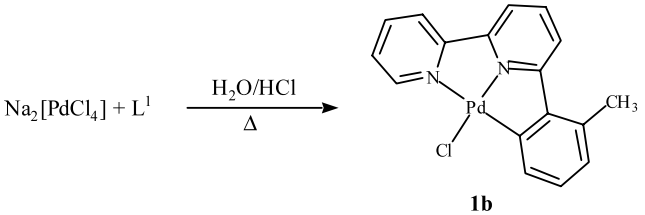
Spectra recorded at room temperature in $CDCl_3$ (a) or CD_2Cl_2 (b); chemical shifts in ppm from internal TMS (^{1}H) and external 85% H_3PO_4 (^{31}P); coupling constants are given in Hertz: J(P–H) in curly brackets; s = singlet, d = doublet, m = multiplet; (c) CH_3CN; (d) at −30 °C ABX system: X = ^{31}P; δ_A 3.44, $^3J_{P-H}$ = ca. 2 Hz; δ_B 2.36, $^3J_{P-H}$ = not resolved, J_{AB} = ca. 8 Hz; (e) $^{13}C\{^1H\}$-NMR in $CDCl_3$: δ 30.44 ($^2J_{C-P}$ = 3.0 Hz). *L^n-H: Pd–CH_2 bonded.

2. Results and discussion

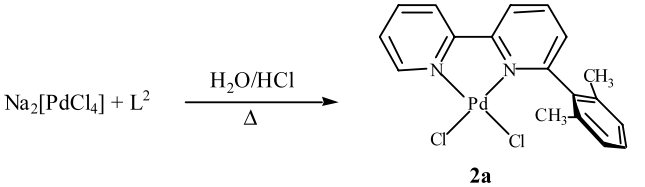
The two new ligands, 6-(2-tolyl)-bipy, L^1, and 6-(2,6-xylyl)-bipy, L^2, were prepared through a multistep reaction scheme according to literature procedures [7].

The intermediate pyridine 2-(2-tolyl)py was obtained in good yields, ca. 80%, whereas for 2-(2,6-xylyl)py the yield was low (ca. 25%). The ^{1}H-NMR data of L^1 and L^2 as well as of the corresponding pyridines are reported in Table 1.

With the aim of promoting metallation, the reaction of $Na_2[PdCl_4]$ with L^1 and L^2 was carried out in water in presence of HCl, heating the solution in a steam bath as previously described for similar 6-substituted-bipy [2a]. Under these conditions, the cyclometallated species **1b** and the adduct **2a** were obtained in good yields, according to reaction 1and 2:



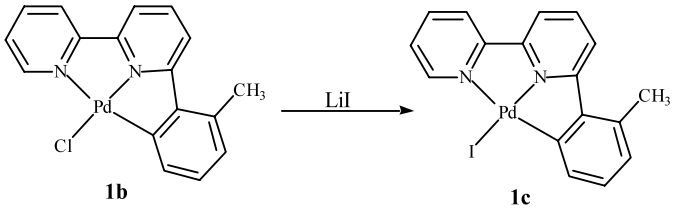
1b (1)



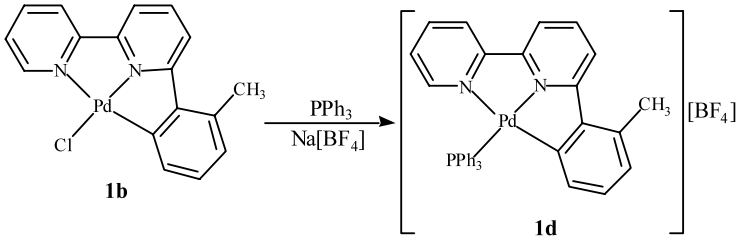
2a (2)

We were unable to isolate the adduct $[Pd(L^1)Cl_2]$ (**1a**), in pure form; however when the reaction is carried out at room temperature, the crude product is a mixture (ca. 1:1) of **1a** and **1b**. Their separation is hampered by the poor solubility of both species. Evidence for the presence of **1a** in the mixture is provided by the ^{1}H-NMR spectra: by comparison with similar species the two resonances at low field, δ 8.89 and 9.28 can be assigned to the H(6′) protons of **1b** and **1a**, respectively [3].

Complex **1b** belongs to a well known series of N^N^C(sp^2) cyclometallated derivatives 2a,b,c,8, and can easily be converted into other neutral, e.g. **1c**, or cationic, **1d**, complexes:



(3)



(4)

Under comparable conditions, substitution of CO for the chloride ligand does not occur.

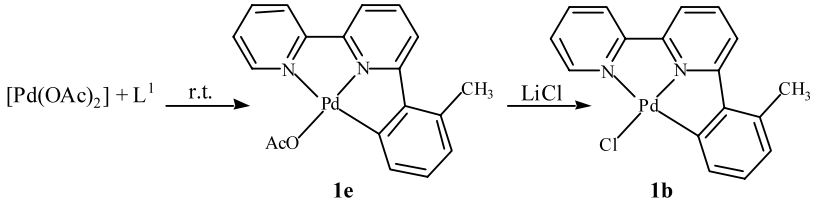
As expected the cyclometallation is easier and occurs under mild conditions if palladium acetate is used in place of the rather weak palladation agent $Na_2[PdCl_4]$ [1g].

The cyclometallated species **1e** is obtained by reaction of $\{Pd(OAc)_2\}$ with L^1 in methanol at room temperature (yield ca. 75%) or in refluxing acetic acid (ca. 55%). In methanol solution, in the presence of LiCl, the acetate **1e** is converted to **1b**, but yields are unsatisfactory, 20–25%.

Isolation of the adduct $[Pd(L^2)(OAc)_2]$ (**2f**), can be achieved directly from $\{Pd(OAc)_2\}$ in mild conditions, i.e. at room temperature in methanol, acetone or acetic acid. Addition of a few drops of acetic acid to the acetone solution of $\{Pd(OAc)_2\}$ to prevent the formation of dimers, improves the yields [9]. The latter expedient allowed us to isolate also the analogous adduct with L^1, $[Pd(L^1)(OAc)_2]$ (**1f**), in reasonable yields, ca. 65%.

It is worth noting that the ^{1}H-NMR spectra of the adducts **2a** and **2f**, at room temperature, show one resonance for the *ortho*-methyl protons, indicating either free rotation of the substituent or a xylyl group perpendicular to the coordination plane.

In conclusion, with both $Na_2[PdCl_4]$ and $\{Pd(OAc)_2\}$, metallation is achieved only in the case of L^1, and involves activation of a C(sp^2)–H bond of the aryl ring. No C–H cleavage of an alkyl group or a C(sp^2)–H bond of the heterocyclic ring is observed. On the whole, the behaviour of L^1 and L^2 is fully consistent with the



(5)

assumption that aromatic C–H activation is more facile than aliphatic C–H activation and five- vs. 6-membered rings are favoured [1].

Besides $Na_2[PdCl_4]$ and $\{Pd(OAc)_2\}$, we studied the behaviour of the two ligands L^1 and L^2 with the chloro-methyl intermediate [Pd(COD)(Me)Cl].

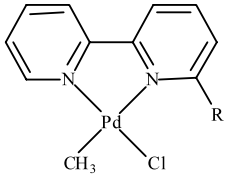
According to reaction (6)

$$[Pd(COD)(Me)Cl] + L \xrightarrow[r.t.]{C_6H_6} [Pd(L)(Me)Cl] + COD \quad (6)$$

$$L = L^1\mathbf{1g};\ \ L = L^2\mathbf{2g}$$

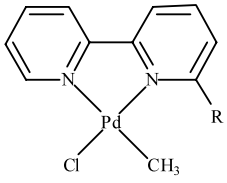
the adducts **1g** and **2g** are obtained in good yields by displacement of the coordinated 1,5-cyclooctadiene.

Complexes **1g** and **2g** were fully characterized by elemental analyses and ^{1}H-NMR spectroscopy. The ^{1}H-NMR spectra provide evidence for the presence in solution of two stereoisomers arising from the unsymmetrical nature of the ligands:



1g^t: R=2-tolyl ; **2g^t**: R=2,6-xylyl

1g^c/1g^t = 0.76/1



1g^c: R=2-tolyl ; **2g^c**: R=2,6-xylyl

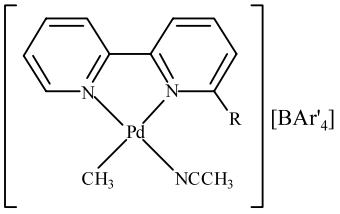
2g^c/2g^t= 1/1

(6)

There are two methyl signals Pd–Me, and two H(6′) resonances for both **1g** and **2g**. The upfield methyl signals, δ 0.02 and 0.05 can be assigned to **1g^c** and **2g^c**, respectively, taking into account the anisotropic shielding effect of the aryl substituent. The more deshielded H(6′) resonances, δ 9.21, **1g^c** and δ 9.28, **2g^c**, are related to the same isomers as previously observed for species having a chlorine in proximity of H(6′) [10]. To achieve further information a ^{1}H NOESY experiment on complex **1g** was carried out. The spectrum shows a selective NOE between the Pd–Me signal at δ 1.12 and the H(6′) resonance at δ 8.64 allowing their assignment to isomer **1g^t**. Phase sensitive NOESY spectra, having cross peaks with the same phase as the diagonal, indicative of exchange processes, are often reported as EXSY spectra. In our case the positive strong cross peaks between the Pd–Me of **1g^t** and the Pd–Me of **1g^c**, as well as between the H(6′) protons of both species, provide evidence for an equilibrium between the two isomers. It is worth recalling that two isomers were observed also for analogous platinum adducts when the 6-substituent was the phenyl group [11].

With the aim of promoting metallation, the ability of a non-coordinating anion such as $[BAr'_4]^-$ [Ar′ = 3,5-$(CF_3)_2C_6H_3$] to displace the coordinated chloride in complexes **1g** and **2g** was tested at first in presence of MeCN. Indeed, reaction (7) affords the cationic adducts **1h** ($L = L^1$) and **2h** ($L = L^2$).

$$[Pd(L)(Me)Cl] + Na[BA'_4] \xrightarrow[MeCN]{CH_2Cl_2} [Pd(L)(Me)(MeCN)][BA'_4] + NaCl \quad (7)$$

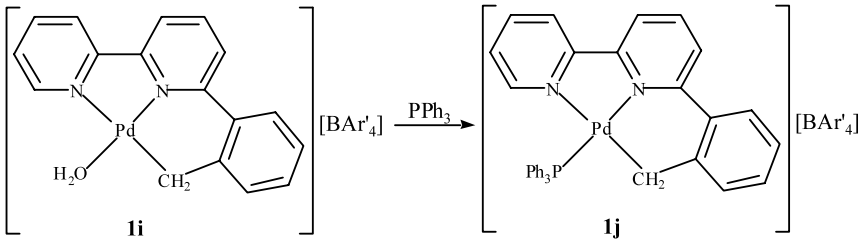


(7)

R: 2-tolyl **1h^t** ; 2,6-xylyl **2h^t**

The reaction is likely to be driven to completeness by the insolubility of NaCl in CH_2Cl_2. Complexes **1h** and **2h** were isolated and characterized: according to ^{1}H-NMR spectra, one isomer only is formed. The high-field resonance of the coordinated MeCN e.g. δ 1.78, **1h**, suggests an aryl ring in close proximity. Comparison of the H(6′) resonances with those of compounds **1g** and **2g** supports the isomers **1h^t** and **2h^t**.

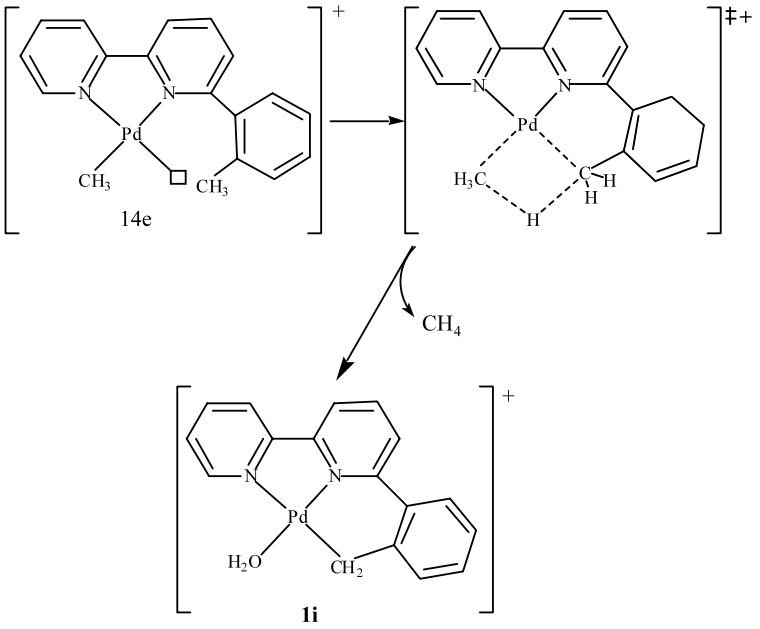
In the absence of MeCN, the reaction was monitored in an NMR tube. On addition of $Na[BAr'_4]$ to the suspension of the chloro-methyl derivative **1g** in CH_2Cl_2, evolution of gas is observed. The ^{1}H-NMR spectrum, besides a resonance at δ 0.20 probably due to dissolved methane, shows in the aliphatic region a resonance at δ 3.73 due to the CH_2 protons of a benzylic group. A broad resonance at δ ca. 2.2 shifts to



(8)

lower field by exchange with D_2O. These data suggest that, under these conditions, metallation occurs through activation of a C(sp^3)–H bond. The resulting species can be envisaged as the cationic six–membered cyclometallated species **1i**, where an adventitious water takes up the fourth coordination site around the palladium ion.

As expected, the coordinated water is rather labile and can be substituted by PPh_3:



(9)

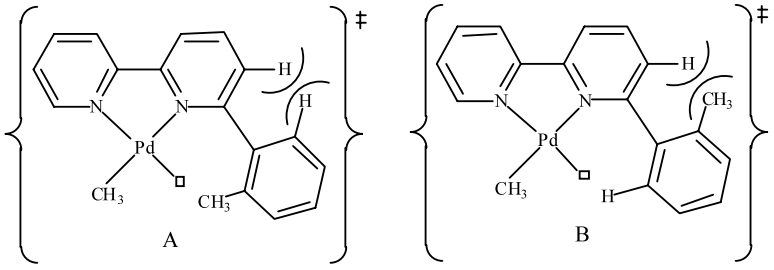
Complex **1j** can be obtained in good yields (ca. 80%) from [Pd(L^1)(Me)Cl] in a one-pot reaction:

$$[Pd(L^1)(Me)Cl] + Na[BAr'_4] + PPh_3 \xrightarrow{CH_2Cl_2} \underset{\mathbf{1j}}{[Pd(L^1\text{-}H)(PPh3)][BAr'_4]} + NaCl + CH_4 \quad (9)$$

The ^{1}H-NMR spectrum of complex **1j** shows a resonance at δ 3.07 due to the CH_2 group bonded to palladium: the value of $^3J_{P-H}$, ca. 6 Hz, fits a *cis* P–Pd–CH_2 arrangement. The $^{31}P\{^1H\}$-NMR spectrum provides evidence for one species only in solution. The $^{13}C\{^1H\}$ spectrum shows a resonance at δ 30.44 ($^2J_{C-P} = 3.0$ Hz), relative to a CH_2 group: the assignment was confirmed by a ^{13}C apt (attached proton test) experiment. The ^{1}H, ^{13}C and $^{31}P\{^1H\}$-NMR data are fully consistent with the values previously reported for complexes having an Ar–CH_2–Pd bond *cis* to a Ph_3P ligand in a six-membered cycle [12].

The selective metallation of L^1 to give **1i** and **1j** implies a six- vs. a five-membered C,N ring and activation of a C(sp^3)–H vs. a C(sp^2)–H bond. The result is quite unexpected: however, as previously observed [2], in palladium chemistry the behaviour of the 6-substituted 2,2′-bipy ligands is somewhat erratic and often hardly predictable.

In the case of Pd(II), metallation mostly entails an electrophilic attack of the metal to the C–H bond [1h]. In our case, however, the selective activation of a C(sp^3)–H vs. a C(sp^2)–H bond makes a straightforward electrophilic mechanism most unlikely. Abstraction of the chloride and substitution by a solvent such as H_2O (or CH_2Cl_2,), i.e. a very labile ligand, favours the

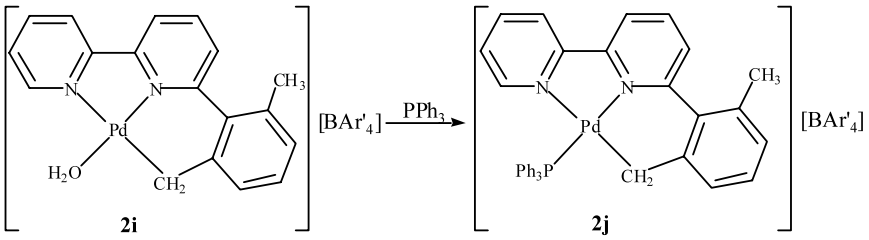


(10)

formation of a 14-electron intermediate. A plausible pathway for the metallation can be envisaged considering that rotation of the 6-substituent allows the localization of an aryl C–H bond or a methyl group in the palladium coordination plane. The C–H activation can occur through a four-centre ring, assisted by the methyl bonded to palladium acting as a base [1h].

Comparison of the two possible intermediates, A and B, shows thatthe first one, A, which implies a methyl pointing toward the metal and a C(sp^2)–H bond toward the H(5) atom of the substituted pyridine allows a C–H bond to be quite close to the metal. In addition, steric repulsion between the aryl 6-substituent and the H(5) atom should be lower than in B. Taken together, these factors are likely to be responsible for the activation of the aliphatic rather than the aromatic C–H bond.

Under the same conditions, the ligand L^2 gives the same kind of C–H activation:



(11)

The reaction however is much slower than for ligand L^1, probably owing to the enhanced repulsion between the 6-substituent and the pyridil ring.

The NMR spectra (^1H and ^{31}P, CD_2Cl_2 solution) show that complex **2j** is similar to **1j**. A difference in the ^1H spectrum is given by the CH_2 signal: at room temperature two broad signals (δ 3.52 and 2.45) are shown for complex **2j**, whereas a sharp doublet ($CDCl_3$, δ 3.07, d, $^3J_{P-H} = 5.6$ Hz) was detected for complex **1j**. On lowering the temperature the signals sharpen and at -30 °C an ABX system can be resolved (X = ^{31}P: δ_A 3.44, $^3J_{P-H}$ = ca. 2 Hz; δ_B 2.36, $^3J_{P-H}$ = not resolved; J_{AB} = ca. 8 Hz): the spectra indicate dynamic behaviour of the six-membered metallacycle which, in the case of **2j**, is relatively slow even at room temperature owing to hindrance of the methyl group.

In the chemistry of heterocyclic imine nitrogen donors, examples of intramolecular C–H bond activation of methyl groups promoted by palladium derivatives, are known [13]. Mostly they involve *tert*-butyl or neopentyl substituents as in the case of 6-substituted-2-2′-bipyridines previously reported by us [3,13d]. At variance with ligands where no competition with aryl C–H activation is possible, with the ligand L^1 both an arylic and an alkylic C–H bond can in principle be activated: it is remarkable that C(sp^3)–H cleavage occurs selectively, considering that this also implies a six- vs. a five-membered ring. Such a behaviour is still very rare: assuming in the present case the 14 electron species as the actual intermediate, the selectivity of the activation must be mainly dictated by the more or less close approach of the C–H bond to the metal centre. The role of this factor in driving the cyclopalladation toward C(sp^3)–H activation has been previously pointed out [14]: in our case it is noteworthy that the approach of the methyl to the metal centre in the coordination plane is not required by the geometry of the ligand as in the case e.g. of 8-methylquinoline [13a] and 7,8-benzoquinoline [15]. Steric repulsion does not hamper metallation of the 2,6-xylyl substituted ligand L^2 but considerably affects the rate of reaction.

3. Experimental

3.1. General procedures

The bipyridines L were prepared according to literature methods [7]. $Na_2[PdCl_4]$ (29.15% Pd) and $[Pd(OAc)_2]$ (47.4% Pd) were obtained from Enghelard. All the solvents were purified before use according to standard methods. Elemental analyses were performed with a Perkin–Elmer elemental analyser 240B by Mr A. Canu (Dipartimento di Chimica, Università di Sassari). Conductivities were measured with a Philips PW 9505 conductimeter. Infrared spectra were recorded with a Perkin–Elmer 983 using Nujol mulls. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$-NMR spectra were measured with a Varian VWR 300 spectrometer operating at 299.9, 75.4 and 121.4 MHz, respectively. Chemical shifts are given in parts per million relative to internal Me_4Si (^1H, ^{13}C) and external 85% H_3PO_4 (^{31}P). The 2D experiments were performed by means of standard pulse sequences. The

mass spectrometric measurements were performed on a VG7070EQ instrument, equipped with a PDP 11-250J data system and operating under positive ion fast atom bombardment (FAB) conditions with 3-nitrobenzyl alcohol as supporting matrix.

3.2. Preparations

3.2.1. Synthesis [Pd(L^1-H)Cl] (**1b**)

(a) To a solution of $Na_2[PdCl_4]\cdot 3H_2O$ (380.5 mg, 1.04 mmol) in water (40 cm^3) were added 1.04 mmol of L^1(258.6 mg) and 2 cm^3 of 2 M HCl. The mixture was heated in a water bath under stirring until the solution was colorless. The yellow precipitate formed was filtered off, washed with water, ethanol and diethyl ether to give the analytical sample as a yellow solid. Yield: 379.7 mg, 94%. M.p.: stable up to 290 °C. Anal. Found: C, 52.48; H, 3.41; N 7.35%. Calc. for $C_{17}H_{13}ClN_2Pd$: C, 52.68; H, 3.36; N, 7.23%. FAB mass spectrum, *m*/*z*: 386 [M^+], 351 [M–Cl].

(b) To a solution of [$Pd(OAc)_2$] (117.3 mg, 0.52 mmol) in methanol (50 cm^3) 127.0 mg of L^1 (0.52 mmol) were added. After stirring at room temperature (r.t.) for 2 days an excess of LiCl was added. The yellow precipitate was filtered off, washed with diethyl ether and recrystallized from CH_2Cl_2/Et_2O to give the analytical sample, as a solid yellow. Yield: 150.2 mg, 75%. M.p.: stable up to 290 °C.

3.2.2. [Pd(L^1-H)I] (**1c**)

To a suspension of **1b** (47.3 mg, 0.12 mmol) in acetone (15 cm^3) were added under stirring 40.8 mg of KI, (0.25 mmol). The mixture was stirred for 24 h at room temperature, then evaporated to dryness. The crude product obtained was crystallized from CH_2Cl_2/pentane to give **1c**. Yield: 35.3 mg, 61%. M.p.: stable up to 290 °C. Anal. Found: C, 42.79; H, 2.42; N 5.66%. Calc. for $C_{17}H_{13}IN_2Pd$: C, 42.62; H, 2.72; N, 5.85%.

3.2.3. [Pd(L^1-H)(PPh_3)][BF_4] (**1d**)

To a suspension of **1b** (50.8 mg, 0.13 mmol) in acetone (25 cm^3) were added under stirring 34.6 mg of PPh_3 (0.13 mmol) and 71.6 mg of Na[BF_4] (5:1 excess). The mixture was stirred for 1 h at room temperature, then evaporated to dryness. The crude material obtained was crystallized from CH_2Cl_2/Et_2O to give **1d**. Yield: 88.4 mg, 88%. M.p.: 267 °C. Anal. Found: C, 59.40; H, 3.71; N 4.36%. Calc. for $C_{35}H_{28}BF_4N_2PPd$: C, 59.93; H, 3.99; N, 3.99%. FAB mass spectrum, *m*/*z*: 613 [M^+], 351 [M–PPh_3]; Λ_M (5×10^{-4} M, acetone): 104.5 Ω^{-1} cm^2 mol^{-1}.

3.2.4. [Pd(L^1-H)(OAc)] (**1e**)

To a solution of [$Pd(OAc)_2$] (116.1 mg, 0.52 mmol) in methanol (50 cm^3) were added 127.8 mg of L^1 (0.52 mmol). The red solution was stirred at room temperature for 3 days, then evaporated to small volume. The precipitate formed, after addition of diethyl ether, was filtered off, washed with diethyl ether, and recrystallized from CH_2Cl_2/Et_2O to give the analytical sample as a yellow solid. Yield: 160.1 mg, 75%. M.p.: 243 °C. Anal. Found: C, 53.01; H, 4.21; N 6.75%. Calc. for $C_{19}H_{16}N_2O_2Pd\cdot H_2O$: C, 53.17; H, 4.21; N, 6.53%. FAB mass spectrum, *m*/*z*: 410 [M^+], 351 [M–CH_3COO]. Complex **1e** can also be obtained from [$Pd(OAc)_2$] in AcOH (105.3 mg, 57%) or in $(Me)_2CO$/AcOH (5:1) at room temperature (55.1 mg, 61%).

3.2.5. [Pd(L^1)($OAc)_2$] (**1f**)

[$Pd(OAc)_2$] (112.6 mg, 0.50 mmol) was dissolved at room temperature in acetone (10 cm^3). After 30 min the solution was filtered over fine paper and a few drops of glacial acetic acid were added to prevent formation of dimers. L^1 (147.7 mg, 0.60 mmol) was added as a solid to the red solution. In a few minutes a yellow product began to precipitate. After 30 min the precipitate was filtered off, washed with cold acetone and vacuum dried. Yield: 153.2 mg, 65%. M.p.: 144 °C. Anal. Found: C, 51.93; H, 4.18; N 6.00%. Calc. for $C_{21}H_{20}N_2O_4Pd\cdot H_2O$: C, 51.55; H, 4.50; N, 5.73%. FAB mass spectrum, *m*/*z*: 411 [M–CH_3COO], 352 [M–2CH_3COO].

3.2.6. [Pd(L^2)Cl_2] (**2a**)

Complex **2a** can be obtained according to the procedure (a) described for **1b**. Yield: 193.9 mg, 85%. M.p.: stable up to 290 °C. Anal. Found: C, 49.63; H, 3.74; N 6.32%, Calc. for $C_{18}H_{16}Cl_2N_2Pd$ requires C, 49.40; H, 3.68; N, 6.39%. FAB mass spectrum, *m*/*z*: 435 [M–H], 366 [M–2Cl], 351 [M–2Cl–Me], 336 [M–2Cl–2Me].

3.2.7. [Pd(L^2)($OAc)_2$] (**2f**)

To a solution of [$Pd(OAc)_2$] (113.7 mg, 0.51 mmol) in methanol (50 cm^3) was added 131.7 mg of L^2 (0.51 mmol). The red solution was stirred at room temperature for 3 h, then evaporated to small volume. The precipitate formed by addition of diethyl ether was filtered off, washed with diethyl ether, and recrystallized from CH_2Cl_2/Et_2O to give the analytical sample as a yellow solid. Yield: 162.6 mg, 65%. M.p.: 165 °C. {Compound **2f** can also be obtained from [$Pd(OAc)_2$] in CH_3COCH_3 (188.6 mg, 75%)}. Anal. Found: C, 52.11; H, 4.65; N 5.73%. Calc. for $C_{22}H_{22}N_2O_4Pd\cdot H_2O$: C, 52.50; H, 4.77; N, 5.57%. IR (Nujol) ν_{max}(cm^{-1}): 1642s, 1373s. FAB mass spectrum, *m*/*z*: 425 [M–CH_3COO], 366 [M–2CH_3COO].

3.2.8. [Pd(L)(Me)Cl] [L = L^1 **1g**, L = L^2 **2g**]

To a solution of [Pd(COD)(Me)Cl] (103.6 mg, 0.39 mmol) in benzene (3 cm^3) was added, under stirring, at room temperature 0.43 mmol of L (105.9, and 111.9 mg for L^1 and L^2, respectively) in 4 cm^3 of diethyl ether. In a

few minutes a yellow solid began to precipitate: after 1 h it was filtered off, washed with Et_2O, dried in vacuo, to give the analytical sample as a yellow solid. The product was obtained as a mixture of two isomers (**1g**^{t}/**1g**^{c} ca. 0.76/1; **2g**^{t}/**2g**^{c} ca. 1/1, NMR criterion).

3.2.9. ***1g***

Yield: 138.3 mg, 88%. M.p. (dec.): 175 °C. Anal. Found: C, 53.92; H, 4.40; N 6.73%. Calc. for $C_{18}H_{17}ClN_2Pd$: C, 53.57; H, 4.22; N, 6.94%. FAB mass spectrum, *m/z*: 401 [M–H$^+$], 351 [M–Cl–CH_3].

3.2.10. ***2g***

Yield: 141.6 mg, 87%. M.p. (dec.): 187 °C . Anal. Found: C, 54.71; H, 4.45; N 6.58%. Calc. for $C_{19}H_{19}ClN_2Pd$: C, 54.64; H, 4.55; N, 6.71%. FAB mass spectrum, *m/z*: 365 [M–Cl–CH_4].

3.2.11. [Pd(L)(Me)(MeCN)][BAr$'_4$] [L = L^1 ***1h****, L = L^2* ***2h****]*

To a solution of Na[BAr$'_4$] (113.9 mg, 0.13 mmol) in 0.25 cm^3 of MeCN, were added under stirring at room temperature 0.13 mmol of [Pd(L)(Me)Cl] (52.4, and 53.4 mg for L^1 and L^2, respectively) in 20 cm^3 of CH_2Cl_2. The yellow color of the solution immediately fades and a NaCl precipitate is formed. After stirring for **1h**, the solution was filtered and evaporated to dryness. The analytical samples of compounds **1h** and **2h** were obtained by crystallization from CH_2Cl_2/pentane.

3.2.12. ***1h***

Yield: 152.0 mg, 92%. M.p.: 113 °C. Anal. Found: C, 48.62; H, 2.46; N 3.32%. Calc. for $C_{52}H_{33}BF_{24}N_3Pd$: C, 49.09; H, 2.52; N, 3.30%. Λ_M (5×10^{-4} M, acetone): 58.0 Ω^{-1} cm^2 mol^{-1}.

3.2.13. ***2h***

Yield: 153.8 mg, 92%. M.p.: 103–104 °C. Anal. Found: C, 49.58; H, 2.64; N 3.33%. Calc. for $C_{53}H_{34}BF_{24}N_3Pd$: C, 49.48; H, 2.64; N, 3.27%. Λ_M (5×10^{-4} M, acetone): 60.0 Ω^{-1} cm^2 mol^{-1}.

3.2.14. [Pd(L-H)(PPh_3)][BAr$'_4$] [C(sp^3)-Pd] [L = L^1 ***1j****, L = L^2* ***2j****].*

To a suspension of [Pd(L)(Me)Cl] (0.20 mmol; 82.2, 83.9 mg for L^1 and L^2, respectively) in 15 cm^3 of CH_2Cl_2, were added 180.6 mg of Na[BAr$'_4$] (0.20 mmol). The suspension turned into a yellow solution with gas evolution and formation of NaCl precipitate. After addition of 53.0 mg of PPh_3 (0.20 mmol), the mixture was stirred for 1 h. The NaCl precipitate was filtered over fine paper and the yellow solution was evaporated to dryness. The crude product was crystallized from CH_2Cl_2/pentane to give **1j** and **2j**.

3.2.15. ***1j***

Yield: 239.7 mg, 81%. M.p.: 148–150 °C. Anal. Found: C, 54.91; H, 2.36; N 1.87%. Calc. for $C_{67}H_{40}BF_{24}N_2PPd$: C, 54.47; H, 2.71; N, 1.89%. FAB mass spectrum, *m/z*: 613 [M$^+$]. Λ_M (5×10^{-4} M, acetone): 44.1 Ω^{-1} cm^2 mol^{-1}.

3.2.16. ***2j***

Yield: 195.7 mg, 66%. M.p.: 130–132 °C. Anal. Found: C, 54.85; H, 2.64; N 1.92%. Calc. for $C_{68}H_{42}BF_{24}N_2PPd$: C, 54.76; H, 2.82; N, 1.87%. FAB mass spectrum, *m/z*: 627 [M$^+$]. Λ_M (5×10^{-4} M, acetone): 46.1 Ω^{-1} cm^2 mol^{-1}.

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