Available online at www.sciencedirect.com
ScienceDirect
Journal of Organometallic Chemistry 692 (2007) 3606–3613
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Pd(II) complexes of a sterically bulky, benzannulated *N*-heterocyclic carbene and their catalytic activities in the Mizoroki–Heck reaction

Yuan Han, Han Vinh Huynh *, Lip Lin Koh

Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore

Received 18 February 2007; received in revised form 16 April 2007; accepted 24 April 2007
Available online 1 May 2007

Abstract

The bis(*N*,*N*′-diisopropylbenzimidazolin-2-ylidene)Pd(II) complexes *trans*-[$PdBr_2(^iPr_2$-bimy$)_2$] (*trans*-**1**) and *trans*-[$PdI_2(^iPr_2$-bimy$)_2$] (*trans*-**2**) have been prepared in good yields by in situ deprotonation of the corresponding *N*,*N*′-diisopropylbenzimidazolium salt ($^iPr_2$-bimyH$^+$X$^-$) (**A**: X = Br, **B**: X = I) with $Pd(OAc)_2$ in DMSO at elevated temperature. Salt metathesis of *trans*-**1** or *trans*-**2** with AgO_2CCF_3 in refluxing CH_3CN afforded the novel mixed carbene–carboxylato complex *cis*-[$Pd(O_2CCF_3)_2(^iPr_2$-bimy$)_2$] (*cis*-**3**). This halo/trifluorocarboxylato ligand substitution can be regarded as a selective method for the synthesis of *cis*-configured bis(carbene) complexes. All compounds have been fully characterized by multinuclei NMR spectroscopies and ESI mass spectrometry. X-ray diffraction studies on single crystals of *trans*-**1**, *trans*-**2** and *cis*-**3** revealed a square planar geometry and a fixed orientation of the *N*-isopropyl substituents with the C–H protons pointing to the metal center to maximize rare C–H···Pd preagostic interactions. These interactions are also retained in solution as indicated by the large downfield shift of the isopropyl C–H protons in the ^{1}H NMR spectrum compared to those in precursor salts **A** or **B**. A preliminary catalytic study revealed that all complexes are highly active in the Mizoroki–Heck coupling of aryl bromides and chlorides. However, these complexes gave slower conversions as compared to catalysts with less bulky benzimidazolin-2-ylidenes. This is most likely due to the steric bulk of the ligands, which hamper a fast reductive formation of catalytically active Pd(0) species.

Keywords: *N*-Heterocyclic carbene; Palladium; C–C coupling; Homogeneous catalysis; Preagostic interaction

1. Introduction

N-Heterocyclic carbenes (NHCs) and their transition metal complexes are currently the focus of intense research in organometallic chemistry and homogeneous catalysis [1]. In particular, palladium(II) carbene complexes derived from imidazole and imidazoline precursors have been successfully developed as highly active precatalysts for a wide range of Heck-type C–C coupling reactions and CO-olefin co-polymerization. Such complexes offer the distinctive advantage of greater stability over the classical Pd/phosphine systems as the latter usually suffer from sensitivity to air and moisture [2]. Catalytic applications of carbenes derived from benzimidazole as a 3rd class of NHCs, on the other hand, have received less attention. This is in particular surprising, since benzannulated NHCs exhibit interesting properties due to their intermediate position between saturated and unsaturated analogues [3]. Only recently, we and others reported the catalytic activities of Pd(II) benzimidazolin-2-ylidene complexes [4]. Most of these examples contain non-bulky carbenes as ancillary ligands. As the steric bulk is believed to promote the reductive elimination step occurring in the catalytic cycle of Heck-type reactions, we became interested in benzimidazolin-2-ylidenes bearing bulky *N*-substituents. Recently, we reported the synthesis and catalytic activities of monocarbene–palladium(II) complexes with the bulky *N*,*N*′-diisopropylbenzimidazolin-2-ylidene ligand ($^iPr_2$-bimy), which also exhibited rare preagostic C–H···Pd and $C_{carbene}$–Br interactions [4b]. To

* Corresponding author. Tel.: +65 6516 2670; fax: +65 6779 1691.
E-mail address: chmhhv@nus.edu.sg (H.V. Huynh).

0022-328X/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2007.04.037

expand the scope of benzimidazolin-2-ylidene complexes in catalysis, we herein describe the synthesis and structural characterization of palladium(II) bis(carbene) complexes of this unique ligand as well as their catalytic activities in the Mizoroki–Heck reaction.

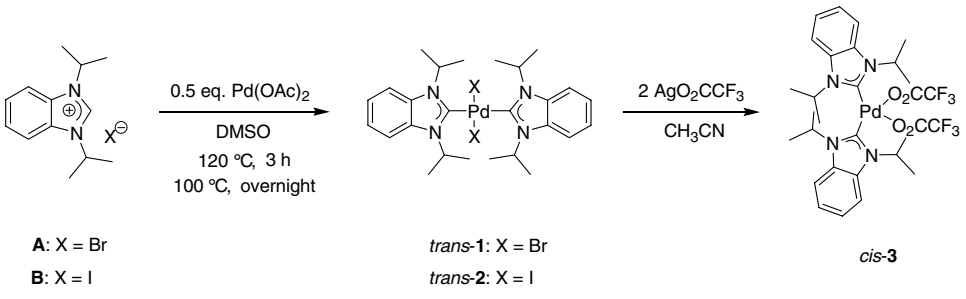
2. Results and discussion

2.1. Preparation and characterization of the complexes

In general, Pd(II) bis(carbene) complexes can be prepared by in situ deprotonation of azolium salts with $Pd(OAc)_2$ in a 2:1 ratio at moderate temperatures. As we reported recently, however, initial attempts to synthesize a bis(*N*,*N*′-diisopropylbenzimidazolin-2-ylidene)Pd(II) complex by reacting $Pd(OAc)_2$ with *N*,*N*′-diisopropylbenzimidazolium bromide (**A**) in various organic solvents (THF, CH_3CN and DMSO) and at various temperatures (30–90 °C) were unsuccessful. Instead, these reactions afforded complicated mixtures with the dimeric monocarbene complex $[PdBr_2(^iPr_2\text{-bimy})]_2$ as a major component [4b]. Similar binuclear complexes have been reported to be intermediate species to the formation of bis(carbene) complexes [5]. Apparently, the deprotonation of salt **A** proves more difficult and would require more drastic reaction conditions due to the +*I*-effect and the steric bulk of the *N*-isopropyl substituents as compared to benzimidazolium salts bearing *N*-methyl or *N*-methylene groups. Indeed, the targeted dicarbene complex *trans*-$[PdBr_2(^iPr_2\text{-bimy})_2]$ (*trans*-**1**) was obtained in 60% yield when the reaction was carried out in DMSO at 120 °C (Scheme 1). We have also observed traces of Pd black that forms due to the harsh reaction conditions. The choice of the solvent used is crucial for the isolation of complex *trans*-**1**, which is soluble in halogenated solvents, but only sparingly soluble in more polar solvents such as DMSO and DMF. Consequently, by employing DMSO as the reaction media pure *trans*-**1** precipitates from the initially clear yellow solution and can be isolated by a simple filtration-step. The filtrate, on the other hand, is a mixture as indicated by three major sets of signals in the ^1H NMR spectrum. These signals were assigned to the dimeric complex $[PdBr_2(^iPr_2\text{-bimy})]_2$ [4b], *trans*-**1** and its *cis*-isomer based on comparison with ^1H NMR spectra of the pure samples of the first two complexes. Upon prolonged standing of the filtrate, a second crop of precipitated *trans*-**1** can be isolated, which has most likely formed by isomerization of its *cis*-isomer. This observation is in agreement with our recent report on a solvent-controlled *cis–trans* isomerization equilibrium of related Pd(II) complexes [4d].

The formation of *trans*-**1** was confirmed by ^1H NMR spectroscopy, which shows the absence of the NCHN proton. In addition, the isopropyl C–H resonance is significantly shifted downfield upon coordination from 5.21 ppm in the precursor salt **A** to 6.25 ppm in *trans*-**1** ($\Delta\delta H = 1.04$ ppm). The large chemical shift of these protons is presumably caused by some type of C–H···Pd interactions. In literature, a few metal-hydrogen interactions (X–H···M, X = C, N) including agostic [6] and preagostic interactions [7] as well as hydrogen bonding [6c,8] have been described. Although there is no clear cut between these types of interactions, each of them has signature spectroscopic and geometric properties, which allow them to be generally distinguished from each other. Generally, an agostic interaction is described as 3-center-2-electron bond, which leads to a highfield shift of the corresponding hydrogen. Typical metal–hydrogen bonds on the other hand are linear 3-center-4-electron interactions leading to a downfield shift. In comparison, the significant downfield chemical shift of the isopropyl C–H protons together with the non-linear C–H···Pd geometry (vide infra) observed for complex *trans*-**1** best fit the definition of a C–H···Pd preagostic interaction. We have observed a similar, but slightly more pronounced downfield shift of the isopropyl C–H protons in Pd(II) monocarbene complexes of the same ligand [4b]. The smaller shift in bis(carbene) complex *trans*-**1** is most likely due to the competition of 4 compared to only 2 C–H protons in monocarbene complexes. Such an interaction has recently also been observed in Rh(I) complexes of NHC ligands [9]. However, the origin of such interactions is still under debate and may involve filled d_{z^2} or $d_{xz/yz}$ metal orbitals [6c,7c,7d,7e]. Finally, the ^{13}C NMR spectrum of *trans*-**1** shows the carbene carbon resonance at 180.0 ppm, which falls well within the reported range for *trans*-configured benzimidazolin-2-ylidene Pd(II) complexes [4c,10].

Single crystals of *trans*-**1** suitable for X-ray diffraction studies were obtained by evaporation of a $CHCl_3$ solution



Scheme 1. Synthesis of bis(carbene) Pd(II) complexes (*trans*-**1**, *trans*-**2**, *cis*-**3**).

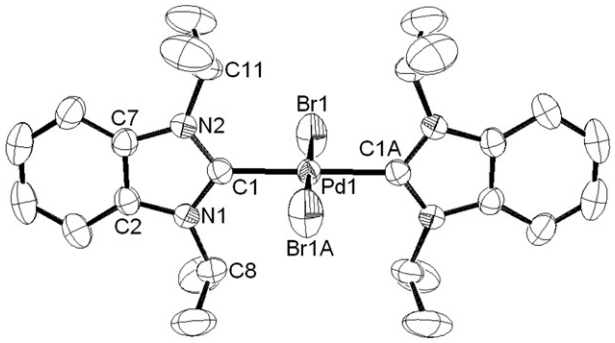


Fig. 1. Molecular structure of the complex *trans*-**1**.

at ambient temperature, and its molecular structure is shown in Fig. 1. Selected bond parameters are summarized in Table 1 and crystallographic data are listed in Table 2. The palladium center is coordinated by two carbene and two bromo ligands in a square-planar fashion. As found by ^{13}C NMR spectroscopy in solution, the two carbene ligands are arranged *trans* to each other with an ideal angle of 180° due to symmetry. Both carbene ring planes are oriented almost perpendicular to the PdC_2Br_2 plane with a torsion angle of 88.0°. More importantly, the Pd–C bonds in *trans*-**1** (2.017(2) Å) are longer than those (1.947(3) Å) in the dimeric $[PdBr_2(^iPr_2\text{-bimy})]_2$ complex. This is in line with the increasing steric bulk as well as the less Lewis acidic palladium center resulting from the coordination of an additional carbene ligand. It is also noteworthy, that the C–H protons of the isopropyl groups are all oriented towards the metal center resulting in relatively short C–H···Pd distances of 2.6856(1) and 2.7143(1) Å, respectively. These structural properties support the aforementioned C–H···Pd preagostic interactions as indicated by ^1H NMR spectroscopy. A comparison of structural and spectroscopic data supporting these interactions for all complexes discussed here is shown in Table 3.

In order to investigate the effects of different halo ligands on the Mizoroki–Heck coupling reaction as well as to have a more direct comparison of the catalytic activities with the previously reported complex *trans*-$[PdI_2(Me_2\text{-bimy})_2]$ [4d], we also prepared the iodo analogue *trans*-

Table 1
Selected bond lengths (Å) and angles (°) for *trans*-**1**, *trans*-**2** and *cis*-**3**

	trans-**1**	*trans*-**2**	*cis*-**3**
Pd1–C1	2.017(2)	2.018(3)	1.975(4)
Pd1–Br1	2.4260(3)	–	–
Pd1–I1	–	2.5906(3)	–
Pd1–O1	–	–	2.067(3)
N1–C1	1.344(3)	1.348(3)	1.352(5)
N1–C2	1.392(3)	1.400(3)	1.397(5)
N1–C8	1.477(3)	1.469(4)	1.481(5)
N2–C1	1.347(3)	1.350(3)	1.349(5)
N2–C7	1.395(3)	1.397(4)	1.392(5)
N2–C11	1.472(3)	1.480(3)	1.483(5)
C2–C7	1.392(3)	1.391(4)	1.391(6)
C1–Pd1–Br1	90.63(6)	–	–
C1–Pd1–Br1A	89.37(6)	–	–
C1–Pd1–I1	–	89.15(7)	–
C1–Pd1–I1A	–	90.85(7)	–
C1–Pd1–C1A	–	–	95.2(2)
O1–Pd1–O1A	–	–	82.1(2)
C1–Pd1–O1	–	–	91.4(1)
C1–Pd1–O1A	–	–	91.4(1)
C1–N1–C2	110.4(2)	110.1(2)	109.7(3)
C1–N2–C7	110.2(2)	110.0(2)	110.0(3)
N1–C1–N2	107.2(2)	107.4(2)	107.4(3)
PdC_2X_2/carbene dihedral angle (X = Br, I or O)	88.0°	89.3°	60.7°

Table 2
Selected crystallographic data for complexes *trans*-**1**,*trans*-**2** and *cis*-**3**

	trans-**1**	*trans*-**2**	*cis*-**3**
Formula	$C_{26}H_{36}Br_2N_4Pd$	$C_{26}H_{36}I_2N_4Pd$	$C_{30}H_{36}F_6N_4O_4Pd$
Formula weight	670.81	764.79	737.03
Color, habit	Pale yellow, block	Yellow, block	Colorless, block
Crystal size (mm)	0.50 × 0.40 × 0.34	0.34 × 0.30 × 0.16	0.20 × 0.06 × 0.06
Temperature (K)	295(2)	223(2)	223(2)
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	*Pbca*	*Pbca*	*C2/c*
a (Å)	17.2150(9)	17.774(2)	21.057(3)
b (Å)	9.4878(5)	9.402(1)	10.773(2)
c (Å)	17.8106(9)	18.014(2)	14.149(2)
α (°)	90	90	90
β (°)	90	90	101.415
γ (°)	90	90	90
V (Å^3)	2909.0(3)	3010.3(6)	3146.2(8)
Z	4	4	4
D_c (g cm^{-3})	1.532	1.687	1.556
Radiation used	Mo Kα	Mo Kα	Mo Kα
μ (mm^{-1})	3.405	2.687	0.667
θ Range (°)	2.29–27.50	2.26–27.50	1.97–27.49
Unique data	33420	19972	11028
Maximum, minimum transmission	0.3907, 0.2809	0.6731, 0.4619	0.9611, 0.8782
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0272$, $WR_2 = 0.0691$	$R_1 = 0.0297$, $WR_2 = 0.0719$	$R_1 = 0.0571$, $WR_2 = 0.1268$
R indices (all data)	$R_1 = 0.0344$, $WR_2 = 0.0729$	$R_1 = 0.0367$, $WR_2 = 0.0754$	R_1=0.0625, $WR_2 = 0.1293$
Goodness-of-fit on F^2	1.060	1.053	1.257
Largest difference in peak/hole [e Å^{-3}]	1.040/−0.800	1.210/−0.665	1.373/−2.080

Table 3
Comparison of selected structural and spectroscopic data for complexes *trans*-**1**, *trans*-**2** and *cis*-**3** supporting C–H···Pd preagostic interactions

Complex	*d*(C–H···Pd) (Å)	θ(C–H···Pd) (°)	δH (Δδ H)[a] (ppm)
trans-**1**	2.6856(1), 2.7143(1)	124.0(2), 124.1(2)	6.25 (1.04)
trans-**2**	2.6972(2), 2.7182(2)	123.1(2), 123.3(2)	6.00 (0.79)
cis-**3**	2.7112(4), 2.8355(4)	119.4(2), 120.0(2)	5.97 (0.76)

[a] $\Delta\delta H = \delta H$ ($CHMe_2$ in complex) − δH ($CHMe_2$ in salt **A**) measured in $CDCl_3$.

[PdI_2(^{i}Pr_2-bimy)$_2$] (*trans*-**2**) using $Pd(OAc)_2$ and two equivalents of salt **B** (Scheme 1). In contrast to the preparation of *trans*-**1** there is no evidence of Pd black formation in this reaction. We believe that this is due to the stabilizing effect of the softer iodo ligands. The replacement of bromo with iodo ligands does not affect the NMR spectra to a great extent. The only notable difference is an upfield shift of the isopropyl C–H resonance from 6.25 ppm in *trans*-**1** to 6.00 ppm in *trans*-**2**, which may be due to weaker C–H···Pd preagostic interactions caused by the bigger size of the iodo ligands. Finally, an X-ray diffraction study on single crystals confirmed that *trans*-**2** is isostructural to *trans*-**1** with bond parameters in the expected range (Table 1). Therefore, no further comments are required.

Complexes *trans*-**1** and *trans*-**2** offer a convenient entry to bis(carbene) complexes with more labile co-ligands. We anticipated that such catalyst precursors would offer the advantage of a faster activation step, since labile co-ligands can be more easily replaced by reducing agents to form catalytically active Pd(0) species. Therefore, *trans*-**1** (or *trans*-**2**) was reacted with two equivalents of AgO_2CCF_3 in refluxing CH_3CN (Scheme 1) according to a reported method [4c]. This reaction afforded the mixed di(trifluoroacetato)-bis(carbene) complex *cis*-[$Pd(O_2CCF_3)_2$(^{i}Pr_2-bimy)$_2$] (*cis*-**3**) in 75% yield. Complex *cis*-**3** is well soluble in halogenated solvents, acetone, CH_3CN, DMSO and DMF, but insoluble in nonpolar solvents such as diethyl ether, hexane and toluene. The ^{1}H NMR spectrum of *cis*-**3** in $CDCl_3$ shows two doublets of equal intensity at 1.72 and 1.33 ppm suggesting two inequivalent Me-groups. Correspondingly, two singlets at 21.4 and 20.3 ppm for the Me-groups are found in the ^{13}C NMR spectrum. These observations are in agreement with a sterically hindered rotation of the Pd–$C_{carbene}$ bond in the more congested *cis* configuration. The resonance for the isopropyl C–H protons are found at 5.97 ppm indicating slightly weaker C–H···Pd preagostic interactions in *cis*-**3** as compared to in *trans*-**1** again due to sterical reasons. Furthermore, the ^{13}C NMR spectrum shows a significant upfield shift of the carbene carbon resonance from 180.0 ppm in *trans*-**1** (or 177.9 ppm in *trans*-**2**) to 164.8 ppm in *cis*-**3** due to the shielding effect of fluorocarboxylato ligands [11]. The ^{13}C NMR signals for the CO groups (162.3 ppm, q, ^2J(C,F) = 36.0 Hz) and CF_3 groups (116.0, q, ^1J(C,F) = 289.1 Hz) of the trifluoroacetato ligands show the expected splitting pattern due to ^{13}C–^{19}F heteronuclear couplings, which fall in the range of ^2J(C,F) = 35–37 Hz and ^1J(C,F) = 264–290 Hz. The formation of *cis*-**3** was further confirmed by ESI mass spectrometry. The positive mode mass spectrum shows a base peak for the $[M-O_2CCF_3]^+$ fragment originating from loss of one trifluoroacetato ligand. In agreement with the previous results in our group [4c], it is noteworthy that the formation of *cis*-**3** from *trans*-**1** (or *trans*-**2**) supports the proposal, that the breaking of the Pd-halo bond and the subsequent coordination of the more labile trifluoroacetato ligand thermodynamically favor a *cis* arrangement due to the strong *trans* influence of the benzimidazolin-2-ylidene ligand. Therefore, this halo/trifluoroacetato ligand substitution can be regarded as a selective method for the synthesis of *cis*-configured bis(carbene) complexes.

Single crystals of *cis*-**3** suitable for X-ray diffraction studies were grown from a concentrated CH_3CN solution and its molecular structure is depicted in Fig. 2. As indicated by ^{1}H and ^{13}C NMR spectroscopy in solution, a *cis* configuration is revealed with the palladium center coordinated by two carbene and two trifluoroacetato ligands in a distorted square-planar geometry. The two trifluoroacetato ligands coordinate in a monodentate fashion with their pendent oxygen atoms found in *anti* conformation. More importantly, the Pd–C bonds in *cis*-**3** (1.975 Å) are shorter than those found in *trans*-configured analogues (~2.04 Å) [12], reflecting a strong *trans* influence of the carbene ligands and a preference for the *cis* arrangement. Remarkably, the dihedral angle between the carbene ring plane and the PdC_2O_2-coordination plane has significantly decreased from 88.0° in the precursor *trans*-**1** to 60.7° in *cis*-**3** in order to minimize ligand–ligand repulsion.

2.2. Catalytic studies

In a recent study, we have reported the catalytic activity of Pd(II) benzimidazolin-2-ylidene complexes with non-bulky *N*-methyl substituents in the Mizoroki–Heck reaction [4c,4d]. Similarly, the dicarbene complexes *trans*-**1**, *trans*-**2** and *cis*-**3** have been subjected to a catalytic investigation in order to determine the influence of more bulky *N*-substituents in benzimidazolin-2-ylidene supported catalysts. In addition, the previously reported mixed carbene–phosphine complex *cis*-[$PdBr_2$(^{i}Pr_2-bimy)(PPh_3)] (*cis*-**4**) [4b] was also included in this study for comparison. The coupling of aryl bromides and chlorides with *tert*-butyl acrylate in DMF under air with 1 mol% catalyst loading and a reaction time of 24 h was chosen as a standard test reaction and the results are summarized in Table 4. Entries 1–4 show that all four complexes can couple activated 4-bromobenzaldehyde in quantitative yield at 120 °C. However, the coupling reactions of deactivated 4-bromoanisole

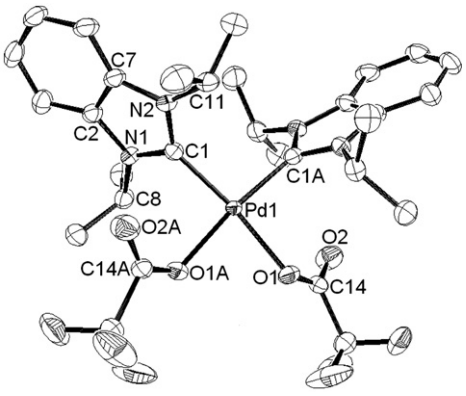
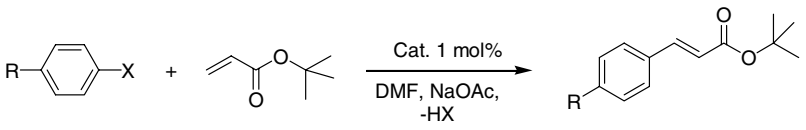


Fig. 2. Molecular structure of the complex *cis*-**3**.

Table 4
The Mizoroki–Heck reactions catalyzed by *trans*-**1**, *trans*-**2**, *cis*-**3** and *cis*-**4**[a]



X=Br,Cl
R=CHO,CH_3CO, OCH_3

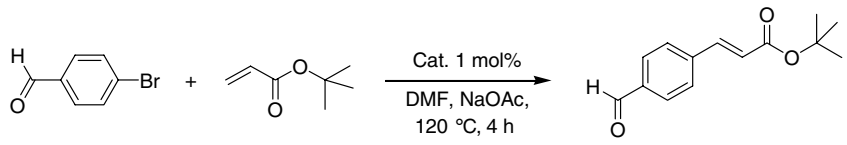
Entry	Catalyst	Aryl halide	Tempertaure (°C)	Yield (%)[b]
1	*trans*-**1**	4-Bromobenzaldehyde	120	100
2	*trans*-**2**	4-Bromobenzaldehyde	120	100
3	*cis*-**3**	4-Bromobenzaldehyde	120	100
4	*cis*-**4**	4-Bromobenzaldehyde	120	100
5[c]	*trans*-**1**	4-Bromoanisole	140	72
6[c]	*trans*-**2**	4-Bromoanisole	140	79
7[c]	*cis*-**3**	4-Bromoanisole	140	71
8[c]	*cis*-**4**	4-Bromoanisole	140	75
9[c]	*trans*-**1**	4-Chlorobenzaldehyde	140	90
10[c]	*trans*-**2**	4-Chlorobenzaldehyde	140	93
11[c]	*cis*-**3**	4-Chlorobenzaldehyde	140	91
12[c]	*cis*-**4**	4-Chlorobenzaldehyde	140	88
13[c]	*trans*-**1**	4-Chloroacetophenone	140	82
14[c]	*trans*-**2**	4-Chloroacetophenone	140	83
15[c]	*cis*-**3**	4-Chloroacetophenone	140	69
16[c]	*cis*-**4**	4-Chloroacetophenone	140	51

[a] Reaction conditions generally not optimized.
[b] Yields were determined by ^1H NMR spectroscopy for an average of at least two runs.
[c] With addition of 1.5 equivalents of $[N(n\text{-}C_4H_9)_4]Br$.

and activated aryl chlorides are more difficult and require the addition of $[N(n\text{-}C_4H_9)_4]Br$ and a higher temperature of 140 °C to afford moderate to very good conversions (Entries 5–16). Reactions catalyzed by complex *trans*-**2** showed overall the best yields. The slight superiority of *trans*-**2** over *trans*-**1** can be traced back to its higher stability (vide supra), which may lead to a higher concentration of active catalyst. Furthermore, it is noteworthy, that the mixed carbene–phosphine complex *cis*-**4**, in contrast to the results reported by Herrmann et al. on a imidazolin-2-ylidene analogue [13], did not exhibit a better catalytic activity than the dicarbene complexes *trans*-**1**, *trans*-**2** and *cis*-**3** under aerobic conditions. Instead, *cis*-**4** afforded the lowest yields in the coupling of aryl chlorides (Entries 9–16). This may be due to its lower stability compared to those of dicarbene complexes under the aerobic and relatively harsh reaction conditions, and thus leading to a more rapid decomposition of the catalyst or its precursor.

In an attempt to establish a reaction profile, the coupling of 4-bromobenzaldehyde with *tert*-butyl acrylate with 1 mol% *trans*-**2** has also been monitored. Surprisingly, this study revealed an unexpectedly slow conversion with only 6% yield after 4 h. This observation is in drastic contrast to the same reaction catalyzed by *trans*-$[PdI_2(Me_2\text{-bimy})_2]$, where a complete conversion was achieved within 90 min [4d]. The two complexes only differ in their *N*-substituents, which in general are believed to have a limited effect on the donor ability of NHCs derived from imidazole and imidazolines [14]. Electronic effects of *N*-substituents on benzimidazole-based NHCs, on the other hand, have not been investigated in detail yet. We have recently proposed that the formation of catalytically active Pd(0) species occurs more efficiently from *cis*-configured bis(carbene) complexes. This is because the strong *trans* effect of the NHC in such complexes facilitates dissociation of the halides, therefore allowing easier attack of the reducing agent. On the other hand, a Pd–halide bond cleavage is less favored in *trans*-bis(carbene) complexes and may account for an induction period in which *trans–cis* isomerization step might occur to facilitate the Pd–halide bond cleavage prior to the reduction step [4d]. Apparently, such a process is strongly hampered by the steric bulk of the isopropyl substituents in *trans*-**2** and may explain the observed slower conversion compared to that observed for reactions catalyzed by *trans*-$[PdI_2(Me_2\text{-bimy})_2]$. To find further support for this proposal, the behavior of *cis*-**4** was investigated under the same conditions. Here a higher, but yet low yield of 14% was obtained, indicating that the steric bulk around the metal center also makes the approach of the reducing agent difficult. With addition of sodium formate as reducing agent the reactions can be accelerated for all 4 complexes (Entries 3–6, Table 5). Overall, the results summarized in Table 5 show that the reactions catalyzed by *cis*-configured complexes (Entry 5/6) are generally faster than those catalyzed by *trans*-complexes (Entry 3/4).

Table 5
The effects of sodium formate addition and *trans*/*cis* configuration on the Mizoroki–Heck coupling reactions



Entry	Catalyst	Yield (%)[a]
1	*trans*-**1**	6
2	*cis*-**4**	14
3[b]	*trans*-**1**	18
4[b]	*trans*-**2**	16
5[b]	*cis*-**3**	58
6[b]	*cis*-**4**	50

[a] Yields were determined by ^{1}H NMR spectroscopy.
[b] With addition of 2 mol% of sodium formate.

This result is in line with the easier dissociation of the halo or carboxylato ligands in *cis*-configured complexes due to the strong *trans* effect of the carbene or phosphine ligand and therefore facilitating the reduction of Pd(II) to Pd(0) [4d].

3. Conclusion

In summary, we have synthesized and structurally characterized Pd(II) bis(carbene) complexes of the sterically bulky *N*,*N*′-diisoproylbenzimidazolin-2-ylidene ligand. The complexes show rare intramolecular C–H···Pd preagostic interactions as indicated by significant downfield shifts of the isopropyl C–H resonances and a common fixed orientation of the isopropyl substituents in their solid state structures. A preliminary catalytic study revealed that the complexes are highly active in the Mizoroki–Heck coupling of aryl bromides and chlorides. However, the steric bulk of the ligands is believed to hamper a fast reductive formation of catalytically active Pd(0) species and thus lead to a slower conversion as compared to catalysts with less bulky benzimidazolin-2-ylidenes. Electronic contributions originating from the +*I*-effect of the isopropyl groups resulting in a slower conversion are less likely, but cannot be fully excluded. Investigations are currently underway to gain a better understanding about electronic effects of *N*-substituents on catalytic activities.

4. Experimental

4.1. General considerations

Unless otherwise noted all operations were performed without taking precautions to exclude air and moisture. *N*,*N*-Dimethylformamide used for the Mizoroki–Heck reaction was purchased from J.T. Baker (“Baker analyzed” ACS reagent). All solvents were used as received. $Pd(OAc)_2$ was purchased from Alfa Aesar. Silver trifluoroacetate was obtained from Fluka. All chemicals were used as received without any further treatment if not noted otherwise. *N*,*N*′-diisopropylbenzimidazolium bromide **A** and *cis*-**4** were prepared according to a literature procedure [4b]. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker ACF 300 spectrometer and the chemical shifts (δ) were internally referenced by the residual solvent signals relative to tetramethylsilane (^{1}H, ^{13}C) or externally to CF_3CO_2H (^{19}F). Mass spectra were measured using a Finnigan MAT LCQ (ESI) spectrometer. Elemental analyses were performed on a Perkin–Elmer PE 2400 elemental analyzer at the Department of Chemistry, National University of Singapore.

4.2. Synthesis of *N*,*N*′-diisopropylbenzimidazolium iodide (*B*)

Salt **B** was prepared in analogy to a literature procedure [4b] from benzimidazole (354 mg, 3 mmol), K_2CO_3 (456 mg, 3.3 mmol) and isopropyl iodide (1.8 ml, 18 mmol). Yield: 894 mg, 2.7 mmol, 90%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 10.79$ (s, 1 H, NCHN), 7.83 (dd, 2 H, Ar–H), 7.64 (dd, 2 H, Ar–H), 5.21 (m, $^{3}J(H,H) = 6.7$ Hz, 2 H, NC*H*$(CH_3)_2$), 1.86 (d, $^{3}J(H,H) = 6.7$ Hz, 12 H, CH_3). $^{13}C\{^{1}H\}$ NMR (75.47 MHz, $CDCl_3$, 25 °C): $\delta = 139.5$ (s, NCHN), 130.9, 127.2, 114.1 (s, Ar–C), 52.5 (s, N*C*H$(CH_3)_2$), 22.3 (s, CH_3). Anal. Calc. for $C_{13}H_{19}IN_2$: C, 47.29; H, 5.80; N, 8.48. Found: C, 47.46; H, 6.02; N, 8.49%. MS (ESI): $m/z = 203$ $[M-I]^{+}$.

4.3. Synthesis of trans-dibromo-bis(*N*,*N*′-diisopropylbenzimidazolin-2-ylidene)palladium(II) (trans-*1*)

A mixture of **A** (283 mg, 1 mmol) and $Pd(OAc)_2$ (112 mg, 0.5 mmol) was dissolved in wet DMSO (6 ml) and stirred at 120 °C for 3 h and then at 100 °C overnight. The yellow precipitate obtained was filtered off and washed with small portions of DMSO and diethyl ether. It was then dried in vacuo to give the product as a yellow powder. Upon stirring the DMSO-filtrate at 100 °C overnight a second crop of the product can be obtained giving an overall

yield of 60% (200 mg, 0.30 mmol). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 7.59$ (dd, 4 H, Ar–H), 7.22 (dd, 4 H, Ar–H), 6.25 (m, ^3J(H,H) = 7.1 Hz, 4 H, NC*H*$(CH_3)_2$), 1.87 (d, ^3J(H,H) = 7.1 Hz, 24 H, CH_3). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$, 25 °C): $\delta = 180.0$ (s, NCN), 133.8, 122.1, 112.7 (s, Ar–C), 54.1 (s, N*C*H$(CH_3)_2$), 21.3 (s, CH_3). Anal. Calc. for $C_{26}H_{36}Br_2N_4Pd$: C, 46.55; H, 5.41; N, 8.35. Found: C, 46.63; H, 5.59; N, 8.32%. MS (ESI): $m/z = 591$ $[M-Br]^+$.

4.4. Synthesis of trans-diiodo-bis(N,N′-diisopropyl-benzimidazolin-2-ylidene)palladium(II) (trans-2)

Complex **2** was prepared in analogy to **1** from **B** (528 mg, 1.6 mmol) and $Pd(OAc)_2$ (180 mg, 0.8 mmol). Yield: 390 mg, 0.51 mmol, 64%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 7.57$ (dd, 4 H, Ar–H), 7.20 (dd, 4 H, Ar–H), 6.00 (m, ^3J(H,H) = 7.1 Hz, 4 H, NC*H*$(CH_3)_2$), 1.80 (d, ^3J(H,H) = 7.1 Hz, 24 H, CH_3). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$, 25 °C): $\delta = 177.9$ (s, NCN), 134.0, 122.0, 112.8 (s, Ar–C), 54.0 (s, N*C*H$(CH_3)_2$), 20.6 (s, CH3). Anal. Calc. for $C_{26}H_{36}I_2N_4Pd$: C, 40.83; H, 4.74; N, 7.33. Found: C, 40.74; H, 4.63; N, 7.20%. MS (ESI): $m/z = 637$ $[M-I]^+$.

4.5. Synthesis of cis-di(trifluoroacetato)-bis(N,N′-diisopropylbenzimidazolin-2-ylidene)palladium(II) (cis-3)

A mixture of complex **1** (112 mg, 0.17 mmol) and AgO_2CCF_3 (81 mg, 0.37 mmol) was suspended in acetonitrile (15 ml) and refluxed overnight shielded from light. The resulting suspension was filtered over celite and the solvent was removed in vacuo to give the crude product as yellowish powder. Slow evaporation at ambient temperature of a concentrated acetonitrile solution afforded the product as colorless crystals (94 mg, 0.128 mmol, 75%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 7.61$ (dd, 4 H, Ar–H), 7.28 (dd, 4 H, Ar–H), 5.97 (m, ^3J(H,H) = 7.0 Hz, 4 H, NC*H*$(CH_3)_2$), 1.72 (d, ^3J(H,H) = 7.0 Hz, 12 H, CH_3), 1.33 (d, ^3J(H,H) = 7.0 Hz, 12 H, CH_3). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$, 25 °C): $\delta = 164.8$ (s, NCN), 162.3 (q, ^2J(C,F) = 36.0 Hz, CF_3CO), 132.8, 123.5 (s, Ar–C), 116.0 (q, ^1J(C,F) = 289.1 Hz, CF_3), 113.5 (s, Ar–C), 54.6 (s, N*C*H$(CH_3)_2$), 21.4, 20.3 (s, CH_3). ^{19}F{^{1}H} NMR (282.38 MHz, $CDCl_3$, 25 °C): 1.83 (s, CF_3). Anal. Calc. for $C_{30}H_{36}F_6N_4O_4Pd$: C, 48.89; H, 4.92; N, 7.60. Found: C, 48.57; H, 5.16; N, 7.31%. MS (ESI): $m/z = 623$ $[M-O_2CCF_3]^+$.

4.6. General procedure for the Mizoroki–Heck coupling reaction

In a typical run, a reaction vessel was charged with a mixture of aryl halide (1.0 mmol), *tert*-butyl acrylate (1.5 mmol), anhydrous sodium acetate (1.5 mmol), catalyst (0.01 mmol) and [N(*n*-$C_4H_9)_4$]Br (1.5 mmol) (for Entries 5–16, Table 4). To the mixture was then added DMF (3 mL). The reaction mixture was vigorously stirred at the appropriate temperature. After the desired reaction time, the solution was allowed to cool. Ten milliliters of dichloromethane was added to the reaction mixture and the organic phase was extracted with water (6 × 5 ml) and dried over $MgSO_4$. The solvent was removed by evaporation to give a crude product, which was analyzed by ^{1}H NMR spectroscopy.

4.7. X-ray diffraction studies

Diffraction data for *trans*-**1**, *trans*-**2** and *cis*-**3** were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 223(2) or 296(2) K using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data were collected over the full sphere and were corrected for absorption. Structure solutions were found by the Patterson method. Structure refinement was carried out by full-matrix least squares on F^2 using SHELXL-97 [15] with first isotropic and later anisotropic displacement parameters for all non-hydrogen atoms. A summary of the most important crystallographic data is given in Table 2.

5. Supplementary material

CCDC 632107, 632108 and 632106 contain the supplementary crystallographic data for *trans*-**1**, *trans*-**2** and *cis*-**3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgement

We thank the National University of Singapore for financial support and technical assistance from our department.

References

[1] (a) F.E. Hahn, Angew. Chem., Int. Ed. 45 (2006) 1348;
(b) K.J. Cavell, D.S. McGuinness, Coord. Chem. Rev. 248 (2004) 671;
(c) V. César, S. Bellemin-Laponnaz, L.H. Gade, Chem. Soc. Rev. 33 (2004) 619;
(d) W.A. Herrmann, Angew. Chem., Int. Ed. 41 (2002) 1290;
(e) A.C. Hillier, G.A. Grasa, M.S. Viciu, H.M. Lee, C. Yang, S.P. Nolan, J. Organomet. Chem. 653 (2002) 69;
(f) D. Bourissou, O. Guerret, F.P. Gabbaï, G. Bertrand, Chem. Rev. 100 (2000) 39;
(g) M. Tamm, F.E. Hahn, Coord. Chem. Rev. 182 (1999) 175;
(h) W.A. Herrmann, C. Köcher, Angew. Chem., Int. Ed. Engl. 36 (1997) 2162.
[2] W.A. Herrmann, M. Elison, J. Fisher, C. Köcher, G.J. Artus, Angew. Chem., Int. Ed. Engl. 34 (1995) 2371.
[3] (a) F.E. Hahn, L. Wittenbecher, D. Le Van, R. Fröhlich, Angew. Chem., Int. Ed. 39 (2000) 541;
(b) F.E. Hahn, L. Wittenbecher, R. Boese, D. Bläser, Chem. Eur. J. 5 (1999) 1931.

[4] (a) F.E. Hahn, M.C. Jahnke, T. Pape, Organometallics 25 (2006) 5927;
(b) H.V. Huynh, Y. Han, J.H.H. Ho, G.K. Tan, Organometallics 25 (2006) 3267;
(c) H.V. Huynh, T.C. Neo, G.K. Tan, Organometallics 25 (2006) 1298;
(d) H.V. Huynh, J.H.H. Ho, T.C. Neo, L.L. Koh, J. Organomet. Chem. 690 (2005) 3854;
(e) F.E. Hahn, M.C. Jahnke, V. Gomez-Benitez, D. Morales-Morales, T. Pape, Organometallics 24 (2005) 6458;
(f) G. Zou, W. Huang, Y. Xiao, J. Tang, New J. Chem. 30 (2006) 803;
(g) C. Metallinos, F.B. Barret, J.L. Chaytor, M.E.A. Heska, Org. Lett. 6 (2004) 3641;
(h) R. Jackstell, A. Frisch, M. Beller, D. Röttger, M. Malaun, B. Bildstein, J. Mol. Cat. A: Chem. 185 (2002) 105;
(i) F.E. Hahn, M.C. Jahnke, T. Pape, Organometallics 26 (2007) 150.
[5] (a) L.J. Xu, W.P. Chen, J.L. Xiao, Organometallics 19 (2000) 1123;
(b) L.J. Xu, W.P. Chen, J.F. Bickley, A. Steiner, J.L. Xiao, J. Organomet. Chem. 598 (2000) 409.
[6] (a) M. Brookhart, M.L.H. Green, J. Organomet. Chem. 250 (1983) 395;
(b) R.H. Crabtree, Angew. Chem., Int. Ed. Engl. 32 (1993) 789;
(c) W. Yao, O. Eisenstein, R.H. Crabtree, Inorg. Chim. Acta 254 (1997) 105.
[7] (a) M. Bortolin, U. Bucher, H. Reugger, L.M. Venanzi, A. Albinati, F. Lianza, Organometallics 11 (1992) 2514;
(b) M. Cano, J.V. Heras, M. Maeso, M. Alvaro, R. Fernández, E. Pinilla, J.A. Campo, A. Monge, J. Organomet. Chem. 534 (1997) 159;
(c) Y. Zhang, J.C. Lewis, R.G. Bergman, J.A. Ellman, E. Oldfield, Organometallics 25 (2006) 3515;
(d) J.C. Lewis, J. Wu, R.G. Bergman, J. Ellman, Organometallics 24 (2005) 5737;
(e) L. Brammer, Dalton Trans. (2003) 3145.
[8] (a) L. Brammer, J.M. Charnock, P.L. Goggin, R.J. Goodfellow, T.F. Koetzle, A.J. Orpen, J. Chem. Soc., Chem. Commun. (1987) 443;
(b) J.C. Lee, A.L. Rheingold, B. Muller, P.S. Pregosin, R.H. Crabtree, J. Chem. Soc., Chem. Commun. (1994) 1021;
(c) L. Brammer, M.C. McCann, R.M. Bullock, R.K. McMullan, P. Sherwood, Organometallics 11 (1992) 2339;
(d) D. Braga, F. Grepioni, E. Tedesco, Organometallics 16 (1997) 1846.
[9] (a) P. Bazinet, G.P.A. Yap, D.S. Richeson, J. Am. Chem. Soc. 125 (2003) 13314;
(b) S. Gómez-Bujedo, M. Alcarazo, C. Pichon, E. Álvarez, R. Fernández, J.M. Lassaletta, Chem. Commun. (2007) 1180.
[10] H.M.J. Wang, I.J.B. Lin, Organometallics 17 (1998) 972.
[11] H.V. Huynh, D. Le Van, F.E. Hahn, T.S.A. Hor, J. Organomet. Chem. 689 (2004) 1766.
[12] (a) M.M. Konnick, I.A. Guzei, S.S. Stahl, J. Am. Chem. Soc. 126 (2004) 10212;
(b) N. Kuhn, C. Maichle-Möçmer, E. Niquet, I. Walker, Z. Naturforsch. 57b (2002) 47.
[13] W.A. Herrmann, V.P.W. Böhm, C.W.K. Gstöttmayr, M. Grosche, C.-P. Reisinger, T. Weskamp, J. Organomet. Chem. 617–618 (2001) 616.
[14] R. Dorta, E.D. Stevens, N.M. Scott, C. Costabile, L. Cavallo, C.D. Hoff, S.P. Nolan, J. Am. Chem. Soc. 127 (2005) 2485.
[15] G.M. Sheldrick, SHELXL-97, Universität Göttingen, Germany, 1997.